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OPPORTUNITIES IN HIGH-PRESSURE TECHNOLOGY

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OPPORTUNITIES IN
HIGH-PRESSURE TECHNOLOGY

REPORT OF THE
AD HOC COMMITTEE ON HIGH-PRESSURE TECHNOLOGY

NATIONAL MATERIALS ADVISORY BOARD
DIVISION OF ENGINEERING - NATIONAL RESEARCH COUNCIL

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13. ABSTRACT Potential applications of high-pressure technology, with particular reference to Department of Defense needs, were reviewed. The report consists of sections on science, synthesis, sintering and densification, devices, polymers, dynamic high-pressure processes, and high-pressure equipment, all of which evolved from committee discussion. This is followed by 13 appendixes on specific topics.		

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CONTENTS

<u>Chapter</u>		<u>Page</u>
I	INTRODUCTION	1
II	HIGH-PRESSURE SCIENCE	3
III	SYNTHESIS	6
IV	SINTERING AND DENSIFICATION	14
V	DEVICES	20
VI	POLYMER PROPERTIES AND MORPHOLOGY	22
VII	DYNAMIC HIGH-PRESSURE PROCESSES	24
VIII	DEVELOPMENT OF HIGH-PRESSURE EQUIPMENT	28
IX	CLOSING REMARKS	31

APPENDIXES

A	HIGH-PRESSURE SINTERING - G. A. Samara	35
B	POWDER CONSOLIDATION - S. H. Gelles	47
C	DYNAMIC HIGH-PRESSURE APPLICATIONS - G. A. Samara	57
D	HIGH-PRESSURE TECHNOLOGY - H. M. Strong	67
E	CALIBRATION OF THE SUPPORTED TAPER CELL FOR ELECTRICAL WORK - H. G. Drickamer	121
F	SOME KINETIC PROBLEMS IN VERY HIGH-PRESSURE RESEARCH - D. Turnbull	125
G	SUPERCONDUCTIVITY - C. W. Swenson	133
H	FERROMAGNETIC MATERIALS - G. A. Samara	141
I	DIELECTRIC AND FERROELECTRIC MATERIALS AND APPLICATIONS - G. A. Samara	149
J	HIGH-PRESSURE TECHNOLOGY AND MAGNETISM - John B. Goodenough	175

		<u>Page</u>
K	VERY HIGH PRESSURES USED IN POLYMER TECHNOLOGY - W. P. Slichter	195
L	HIGH-PRESSURE EQUATION OF STATE AND LATTICE DYNAMICS STUDIES - C. A. Swenson	199
M	ELECTRONIC PHENOMENA AT HIGH PRESSURE - H. G. Drickamer	203

I. INTRODUCTION

In this report those aspects of high-pressure technology likely to have expanding impact on materials research and development, and those aspects of high-pressure research most likely to lead to significant applications in the near future are discussed.

The original charge to the committee was to investigate the opportunities of "ultra-high-pressure technology," with some emphasis on the interests of the Department of Defense (DoD). In the early stages of consultation, certain modifications appeared necessary. It was found impossible to fit potentially fruitful areas into any satisfactory range of pressure clearly defined as "ultra high." The committee, therefore, proceeded to consider high-pressure technology in terms of work distinctly above one kilobar but extending to the highest available pressures. Major emphasis is placed on applications of static high pressure, although shock-wave work is discussed briefly. Contents of this report are largely limited to technology and to research directly applicable to current problems, as was indicated in the committee's charge. However, a brief discussion of the present situation in high-pressure science is included, and several of the appendixes focus on primarily scientific topics.

The report contains a short section on high-pressure science, longer sections on syntheses, sintering and densification, and shorter sections on devices, polymer properties and morphology, dynamic high-pressure processes, and development of high-pressure equipment. Metal forming and extrusion are

not discussed because it was explicitly excluded from the committee's charge; however, it is clear that significant developments in high-pressure technology will occur in this area. Also included are appendices, signed reports by individual members of the committee and by outside experts invited to present material, on specific topics.

The material and conclusions presented in the main body of the report have been reviewed and approved by the entire committee. Much of the material presented in the appendices is used in the main body of the report; however, the appendices have not been reviewed in their entirety by the whole committee and do not necessarily have the endorsement of the committee as a whole. Nevertheless, even though there may be individual differences of opinion about some aspects of the appendices, the latter, as personal reports, represent the opinions of individuals with considerable background and should be useful in planning high-pressure applied research and development.

II HIGH-PRESSURE SCIENCE

The theme of this report is potential high-pressure technology. However, a brief outline of the current situation in basic high-pressure research is not inappropriate in that this research ultimately forms the basis of future technology -- a technology, in most cases, farther in the future than that described in much of this report.

Most of the work done in high-pressure science falls in one of four categories: (1) studies of cohesive energy and the equation of state; (2) studies of structure and morphology, including phase diagrams and synthesis of new phases; (3) studies of atomic and ionic motion in solids (and liquids); and (4) studies of electronic phenomena, including cooperative effects.

While work in the first category has been done for many years, it is still very active. Developments of importance include: the introduction of new techniques (e.g., ultrasonic velocity and x-ray diffraction); extension of the low-temperature, high-pressure range to a few degrees Kelvin at pressures of over 50 kilobars; extension of the static-pressure range plus the refinement of shock measurements; and improvements in theoretical analysis of cohesive energy.

Between 1930 and 1945 Bridgman demonstrated that polymorphic transitions in solids were a common phenomenon. The measurement of equilibrium phase diagrams over an extended range of pressure and temperature has been and is an active field. The development of high-pressure x-ray crystallography has aided in identifying high-pressure phases. The "quenching in" of these phases is widely practiced for both scientific (e.g., geophysical) and practical purposes -- the synthesis

of diamond and cubic boron nitride (BN) being outstanding examples. Recent work by Phillips and Van Vechten raises the exciting possibility that one may be able to predict such transitions, at least for limited classes of materials. Research areas offering a high potential in terms of both basic interest and application include metastability, the rates of first order phase transitions, and the rates of crystal growth at high pressure.

The study of atomic and ionic motion by tracer methods has revealed important and useful information concerning the bonding in ionic and metallic crystals and the nature of impurity sites. The use of nuclear magnetic resonance (NMR) to study rotational as well as translational motion in solids, and also in liquids and polymers, is an important aspect of modern chemistry. The high-pressure applications have been impressive, and a significant increase in such applications is to be expected. The study of polymers, in particular, has important practical applications.

Pressure has been used to study electronic behavior in solids for about 25 years. Essentially all of the measurements of solid state physics can be carried out in the hydrostatic range to 12 kilobars. During the past 15 years it has been demonstrated that the quasistatic range to several hundred kilobars is of great importance. Techniques like optical absorption and emission, NMR, and Mössbauer resonance can be applied over an extended range of pressures.

High-pressure studies have been important in the delineation of the band structure of practical semiconductors like Si, Ge, and the III-V compounds, in providing an under-

standing of the electronic energy states of a variety of luminescent materials, and in the study of ferromagnetism and anti-ferromagnetism, ferroelectricity, and superconductivity. High-pressure research has been extensively used in the study of insulator-metal transitions. The practical aspects of a number of these studies are mentioned in other parts of the report.

From the viewpoint of electronic structure, the basic effect of pressure is to shift one type of orbital in energy with respect to another. A possible consequence of this shift is the establishment of a new ground state for a system, or a ground state greatly modified by configuration interaction. In the past decade it has been shown that these "electronic transitions" are common phenomena and that they have chemical as well as physical consequences. One of the more active branches of high-pressure science involves the prediction, discovery, and explanation of electronic transitions. Chemists have been relatively slow to use high pressure as a variable in studies of electronic behavior, but the next decade will probably see a large increase in such work in a chemical (and biochemical) framework.

Recently, scientific progress has been made in the understanding of deformation and the effect of defects on mechanical properties. One can expect considerable progress in this aspect of high-pressure research in the next decade.

III. SYNTHESIS

One of the most important applications of high-pressure technology is to the synthesis of new materials. Usually this has involved the establishment of a new crystal structure that possesses advantageous mechanical, electronic, magnetic, optical, etc., properties and can be retained stably or metastably at one atmosphere.

Hydrothermal syntheses typically are done at between 1 and 3 kilobars pressure and are used for a variety of practical materials. Diamond and cubic boron nitride are synthesized in the 50 to 100 kilobar range at elevated temperature. Considerable work is being done in solid-state synthesis in the U.S. and abroad, especially in France, Sweden, Japan, and the U.S.S.R. A great deal of new and exciting chemistry undoubtedly will result from these efforts. There are, however, severe boundary conditions on the syntheses of practically useful materials at very high pressure, the most general of these being that materials synthesized in the 50 to 100 kilobar region at elevated temperature cost several thousand dollars per pound. This limits practical materials to those that can be used in small quantities and offer considerable durability or a high unit value.

A number of the Appendices (including those by Goodenough, Swenson, Samara, Strong, Turnbull, and Drickamer) touch on various aspects of synthesis at high

pressure. Only those materials that may most profitably be synthesized at high pressure and the possibilities, limitations, and problems of each are discussed here. Also listed are some areas of study that could contribute significantly to more efficient and imaginative high-pressure synthesis for a broader range of materials.

"Electronic materials" constitute a class with potentially high value per unit mass. This definition encompasses not only devices for electronic circuits, but also magnetic, luminescent, and ferroelectric materials. Typical materials include hard magnets like CrO_2 and orthoferrites (LaFeO_3). One problem with electronic devices is that they usually must be single-crystal material with a minimum of strains and with carefully controlled impurity levels. These conditions can frequently be met in hydrothermal synthesis, and diamonds have been grown with controlled impurities. However, the technique of "quenching in" high-pressure phases has not been conducive to the growth of single crystals, strain-free material, or material of controlled impurity content in the parts-per-million range. An important aspect of further work would be to develop more general methods for growth of single crystals with controlled properties in the higher pressure range. (See Appendix F)

There has so far been very little work done on developing high-pressure luminescent or photochromic materials. These applications could involve small amounts

of high-unit-value materials. High-pressure phases of phosphors could involve higher luminescent efficiencies and different lifetimes, as well as more stable photochromic states, than the corresponding low-pressure phases. In this regard, more crystalline polymers, especially inorganic polymers, offer the possibility of luminescent material of stability over a large range of temperature.

High-pressure experiments have been important in understanding the phenomenon of superconductivity, and a number of high-pressure phases have proved to be superconducting where the low-pressure phases are not. Since, in a number of cases, superconductivity is associated with metastability, the possibility of quenching in high-temperature superconductors is intriguing. The economic potential of electrical transport by high-temperature superconductors is enormous. Much of the discussion has centered around the possibilities of the metallic phase of hydrogen, but it is difficult to give any prognosis which is more than a guess. According to various calculations, hydrogen will become metallic at a pressure which is variously estimated between 0.8 and 6 megabars--most calculations give a range of 1.5 to 3.0 megabars. A number of analyses indicate that the high-pressure phase would be a high-temperature superconductor (T_c 60-200°C), although this conclusion is by no means universally accepted. Grave doubts arise concerning the probability of retaining the high-pressure phase metastably. (See Appendix F) It would appear that even if

bulk metastability were a possibility, the material would decompose by surface instability. With the present state of knowledge it is difficult to offer even tentative conclusions, and a number of investigations would be helpful. One diatomic molecular crystal, iodine, has been shown to be metallic above the 130 to 170 kilobar range. An investigation of its superconducting properties would be very helpful. Also, aromatic hydrocarbons like pentacene and hexacene become metals or semi-metals above 200 kilobars. Investigation of the metallic transitions (and ultimately the superconducting properties) of solid Br_2 , Cl_2 , F_2 , and hydrogen-containing materials such as methane (CH_4) and ammonia (NH_3) would advance both the art and the understanding of high-temperature superconductivity. It is known that at moderate hydrogen pressures materials like palladium take up atomic hydrogen in a ratio of several atoms of hydrogen per palladium atom. It would be of interest to know the superconducting properties of these materials at sufficiently high pressure and hydrogen concentration.

The synthesis of diamond, and later of cubic boron nitride, has been a tremendous incentive to high-pressure work. Currently, much research is devoted to making diamond (or BN) with particular characteristics or to making it more cheaply. There have been, of course, strong incentives for making a harder material, but the possibilities (discussed in Appendix D) for such a material seem slight.

It is, however, possible that high-pressure phases which are not as strong as diamond may have either chemical or high-temperature properties of technological significance. It has not so far been possible to form solid solutions of diamond with BN, SiC, or other hard materials. At sufficiently high temperature and pressure it might be done, and the resulting materials could be of considerable interest. Strong discusses in some detail (Appendix D) the variety of new phases of inorganic solids that have been observed. The sintering of diamond and other materials is discussed elsewhere in the report.

A relatively uninvestigated field is that of using very high pressure to produce new catalysts. These materials satisfy the requirements of high value per unit mass and repetitive usage. It is clear that the form and structure of a material, as well as the chemical composition, is important in its catalytic activity; e.g., it has recently been demonstrated that 10 to 20 angstrom metallic alloy particles have very different catalytic (and electronic) properties than do larger particles. It would appear that high-pressure phases of many materials such as oxides could have different, and possibly better, catalytic properties than their low-pressure counterparts. It may be possible to produce materials with unusual oxidation states at high pressure, and these may have considerable potential as catalysts. Involving different stoichiometries and different degrees of doping in the high-pressure products

might also be feasible. People working in catalysis are generally unfamiliar with solid-state chemistry at high pressure, and vice versa. It would be desirable to encourage interaction.

The usual high-pressure polymerization from the gas phase or in solution occurs in a pressure range generally below that considered here. While the possibility of formation of polymers in the solid state at relative high pressure exists, the expense involved would eliminate these materials for most practical applications. However, as mentioned earlier, it may be possible to prepare polymers for special electronic or luminescent applications. In this regard, the field of inorganic polymerization appears to have special relevance.

Traditionally, solid-state synthesis at high pressure generally has meant the preparation at high pressure of a new crystal structure that can be retained metastably at one atmosphere. In general there are changes in chemical bonding, but the electronic effects usually have been subordinated to the structural effects. As discussed by Drickamer (Appendix M), pressure has a profound effect on electronic energy levels. Under many circumstances the relative shift in energy levels with pressure is sufficient to give a new ground state, or a ground state greatly modified by configuration interaction. It has recently been demonstrated that these new ground states may have very

different chemical as well as physical properties. The chemistry of these new ground states has been very little explored to date. It has, however, been shown that for many systems it is possible to estimate the possibility of a thermal electron transfer (an electronic transition) from the change of location and shape of appropriate optical absorption peaks. This area deserves further exploration and systemization for its potential practical applications.

Thus far in this report the synthesis of materials at high pressure for practical applications has been emphasized. There is, however, another aspect of high-pressure solid-state chemistry which has considerable practical potential: this lies in the area of the analogy between the effects of pressure and of composition changes on physical and electronic properties.

An interesting example of potentials in this area lies in the studies of metal-insulator transitions in solid solutions of $\text{Cr}_2\text{O}_3\text{-V}_2\text{O}_3$ conducted by McWhan and his colleagues at Bell Laboratories. They have demonstrated that changing the amount of Cr_2O_3 in the material is in many ways analogous to changing the pressure insofar as electronic properties are concerned. A second example involves studies of prototypes of hemoglobin such as hemin and hematin which demonstrated that the effects of pressure are in many ways closely analogous to the effects of adding electrophillic groups to the periphery of the molecule.

The study by Goodenough and his co-workers of the high-spin to low-spin transition in the MnAs-MnP system, where 1 kbar pressure was shown to be equivalent to 1 percent P is another striking example. However, there may also be important differences between pressure and composition effects, as has been emphasized by Goodenough and demonstrated by Kafalas, et al for the system $\text{Ca}_x\text{Sr}_{1-x}\text{MnO}_3$. For many systems, properties which could be practically advantageous but which cannot be quenched in may be observed at high pressure. If the analogy between pressure effects and composition effects for the type of system involved is clearly understood, it may be possible to prepare a material with the relevant properties at lower pressure, or even at one atmosphere.

The practical use of high-pressure synthesis would be greatly increased by more thorough understanding of a number of problems. These include the causes and control of metastability, the rates of first-order phase transitions, the rate of crystal growth, the probable pressure range of first-order phase transitions in various categories of materials, the probable pressure associated with electronic transitions of various types, and the relationships between various types of chemical doping and of pressure on various properties. In many of the above cases a significant start has been made on the solutions. An improvement in our predictive power could greatly reduce the time and expense involved in searching for practical materials.

IV. SINTERING AND DENSIFICATION

High pressure sintering and densification is an important aspect of high pressure technology, and one which will probably increase in significance in the immediate future. (Appendices A, B and D deal with various aspects of sintering.) Densification to theoretical or near theoretical density depends in part on the ability of particles to deform plastically by glide or creep to give more intimate contact between adjacent particles. The relevant operating variables are temperature, pressure, and time, with the first the most important and the last probably the least significant. The degree of success depends also on internal variables such as particle size and size distribution, purity of material, the initial stress condition of the particles, their surface condition (presence of surface impurities or absorbed gases), and the possible use of sintering aids or binders.

Most sintering to date has taken place at one atmosphere or under modest pressures, up to 1 to 2 kilobars. (See, however, the discussion of diamond below.)

Pressure may act to add to the interfacial energy as a driving force for densification and tend to induce plastic flow as a mechanism for densification. For relatively low pressures with specific materials in which diffusion provides the mechanism of densification it is probable that the diffusivities will be decreased by the applied pressure. However, this effect appears to be secondary.

The advantages of using pressure include:

1. The possibility of using lower temperature and thus preserving a finer grain sized microstructure,

e.g., preventing grain growth which is accelerated by temperature.

2. The ability to produce higher density materials with less binder.
3. The possibility of staying within the stability range of a high-pressure phase while sintering --e.g., diamond vs. graphite.
4. The possibility of achieving densification in single-phase covalent-bonded materials which do not undergo densification under pressureless sintering. Fine-grained high-density hot pressed shapes of SiC, Si₃N₄, and B₄C are commercially available.

There are, however, definite limitations to the use of pressure in the sintering process. Besides the expense of high-pressure equipment, there are limitations on the size and shape of pieces which can be sintered, especially at the higher pressures, as well as problems in pressure uniformity. High-pressure sintering is a batch process and is therefore more expensive than processes which can be operated continuously. Frequently the economics involve a trade-off between temperature and pressure.

We mention below a few of the types of material for which high-pressure sintering and compaction have proven to be practical.

Most metal powders can be consolidated at 1 to 5 kilobars pressure at temperatures less than $0.5T_m$. An example of this pressure-temperature trade-off is beryllium powder which may be consolidated at 900° C and 10,000 psi or 1100° C and 2000 psi. High pressure

is especially advantageous for very high melting materials which at the highest available temperatures still have considerable resistance to flow.

A second practical application involves dielectric materials where pressure consolidation can give materials with low dielectric loss, high dielectric strength, high dielectric constant, non-linear response, a stronger piezoelectric response, etc.

Fully dense optical quality ceramics have been made from a wide variety of substances. Such materials are used as optical windows, radiation detectors, laser hosts, and electro-optic devices. Materials which are sintered below 1 kilobar include MgO , Y_2O_3 , Al_2O_3 , $MgAl_2O_4$, and the family of ferroelectrics consisting of lanthanum-doped lead zirconate-titanate. These materials were all first made by pressure sintering and still are being made by this process, although pressureless processes have also been developed for all except Y_2O_3 . Y_2O_3 is an excellent host for rare earth ions and is transparent from 0.3 to 8 microns. Single crystals can only be grown in small sizes not suitable for applications. The sintered material can be made fully dense with transmission characteristics which closely resemble the single crystal in sizes up to approximately 1 inch in diameter.

It is possible to sinter electronic materials to give better mechanical properties as well as improved electrical and thermal properties which result in longer lifetimes. A recent development is the sintering of doped silicon-germanium alloys for thermoelectric applications. It is of interest that, for this material, a moderate increase in sintering pressure from 28,000 to 32,000 psi gives marked improvement in alloy homogeneity, mechanical strength, and electrical and thermal properties. It seems probable that there will be a variety of other thermoelectrics and semiconductors produced by similar processes.

Structure sensitive magnetic properties such as initial permeability, B-H characteristics, and lossiness are affected by grain size, grain boundaries, and inhomogeneities. Thus, pressure sintering offers a possible method of controlling density and texture, and therefore the magnetic properties of polycrystalline materials. The method has been applied commercially for ferrites ($\text{MeO} \cdot \text{Fe}_2\text{O}_3$) and garnets ($3\text{Me}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$). The fact that pressure sintering can reduce the required temperature is an important advantage here, as it is frequently necessary to control closely the valence state of the transition metal ions in ferrites and garnets, and this can best be done at lower temperatures.

The most significant development in sintering of useful materials in the higher pressure range (50 to 100 kilobars) is that of diamond (and possibly also cubic BN). There have been a number of reports of successful sintering

both in the U.S. and Russia. The details are only poorly known at present, but it apparently usually involves a binder in significant quantities. (Strong, in his chapter in the Appendix, discusses a sintered diamond-tungsten carbide product which appears very useful for machining.) H. T. Hall at Brigham Young University has prepared sintered diamond with a variety of binders. Some of these products have undergone fairly extensive tests in potentially practical service. Sintered diamond could have a wide variety of applications in machining, rock cutting, wire drawing, etc. There have been a number of reports that Vereschagin's group in the U.S.S.R. have developed sintered diamond cutting tools with impressive characteristics. The requirements for commercial application in competition with single-crystal diamond are rather severe in terms of friability, cutting ability, durability, etc. It would appear probable that techniques can be perfected to make sintered diamond competitive for many, if not all, such applications.

A possible application of interest is the manufacture of pistons and vessels for high-pressure work to extend the pressure range. This problem is discussed briefly in a later section.

Many of the problems encountered with diamond are also present with refractory materials and solutions of the diamond problem will be applicable in a high degree to oxides, carbides, borides, and nitrides.

It seems very probable that high-pressure compaction methods will be applicable in the growing field of composites which are finding an increasing variety of applications.

A process related to compaction and sintering is high-pressure bonding in metal-metal, metal-ceramic, and ceramic-ceramic systems. A good example is the bonding of fine-grain alumina discs to each other and to metals. The isostatic process has great potential in this operation.

The application of shock techniques to these processes is discussed briefly in a later section.

There are a number of aspects of sintering and densification where a better understanding of the variables would increase the practical possibilities. These include: the effect of surface morphology and surface cleanliness on bonding; the function of the bonding and/or binder (indeed different binders may have quite different functions), and a more quantitative understanding of the tradeoff between temperature, pressure, and time for various categories of materials.

V. DEVICES

In a previous section we discussed the high-pressure synthesis of materials that could be recovered for application at one atmosphere. Here we discuss materials with properties directly useful at high pressure. Perhaps the most obvious application is the pressure gauge. Techniques are well known for measuring static pressure at equilibrium. The usual standards are the resistance of manganin for hydrostatic pressures to 30 kilobars and electrical resistance discontinuities or maxima or changes in lattice parameter for higher pressures. While these techniques are not completely satisfactory we shall not concern ourselves with them here.

It is, in principle, possible to make use of phase transitions (e.g., insulator-metal transitions) or changes in energy of optical absorption or emission peaks to measure impact pressures on rapidly oscillating pressures. Optical transitions have the advantage of high speed (10^{-10} - 10^{-12} seconds) and require only small samples. The technological problems involved in development of truly practical devices are severe.

In several places in this report it has been mentioned that a general effect of pressure is to shift the energy of one type of electronic orbital with respect to another. This relative shift could have a number of applications besides pressure detection. One such possibility is the pressure tuning of lasers. A second application is the

change of the absorption edge of photocell detectors to shift the region of maximum sensitivity to lower or higher energy. The application of uniaxial stress might also be useful in these applications.

A different high-pressure application would involve the absorption of shock or impact. The obvious mechanism would be to make use of the latent heat and/or volume change at a first order transition. One would like transitions which occur at modest pressures if the idea is to protect a material from high-pressure shock. The rubidium halides have transitions near 4 or 5 kilobars with large volume changes, but small latent heats. They have low mechanical strength. Melting or vaporization at high pressure would supply large latent heat. The actual development of a practical device would require a detailed knowledge of the particular application.

VI. POLYMER PROPERTIES AND MORPHOLOGY

Moderate pressures have been widely used to synthesize polymers in the gaseous and liquid phases. We make no attempt to review this area in the report. Solid-state polymerizations at high pressure have been reported but they are without apparent direct application at this time. Pressure has, however, an important potential role in understanding better the structure and properties of commercially useful polymers. The situation is reviewed in the Appendix by W. P. Slichter. We summarize his comments briefly here. There are three categories of structural organization for bulk polymers: (1) crystalline regions; (2) rubbery structures, and (3) glassy arrays. The relative stability of these different arrays depends on the molecular structure, on the temperature, and on pressure. There are two temperatures which characterize the material, T_m , the melting temperature, and T_g , the glass point, which possibly is related to the point at which the free volume disappears. Measurements of the effect of pressure on T_g have been made. It would be most useful if these could be related to other pressure sensitive parameters such as heat capacity, thermal expansion coefficient, and molar volume.

Partially crystalline polymers have a morphology that is pressure dependent. Crystallization at pressures in the order of 10 kilobars leads to morphologies in which

the crystalline lamellae are 10^3 \AA thick or more and consist of chains in extended conformations. Crystallization at one atmosphere leads to lamellae of folded chains with a fold length of $\sim 100 \text{ \AA}$. The work to date has been largely on polyethylene; it is not entirely clear whether the modified forms have properties which would be commercially attractive.

An important aspect of high-pressure studies of polymers involves following the motion of molecular subgroups in all three regimes by nuclear magnetic resonance relaxation. Relative to the study of ordinary crystalline materials, high pressure studies on polymers are sparse, but they have yielded enough information to indicate that they should be pursued with some vigor.

The use of polymers in composites and the development of polymers capable of high-temperature, high-pressure applications (including inorganic polymers) make this an area of great potential importance.

VII. DYNAMIC HIGH-PRESSURE PROCESSES

In this report we have confined ourselves largely to static high-pressure processes for a number of reasons. However, it seems advisable to outline the potential impact of dynamic processes on technology. These matters are touched upon in a report by Samara in the Appendix, and also in the discussion of Gelles.

Shock measurements have long been important in high-pressure science in establishing equations of state over a very large range of compression and in locating phase transitions. Recent advances in shock-wave science in the understanding of dynamic yielding and elastic-plastic phenomena, in material strength and fracture, and in measuring the electrical and magnetic response in solids like quartz, germanium, and iron alloys have extended the usefulness of shock studies. These new developments are in their early stages and with proper support should add considerably to the possible usefulness of the technique.

There at present are a number of areas where dynamic techniques are commercially feasible or clearly potentially so. These include:

1. Explosives bonding,
2. Explosives forming,
3. Shockwave hardening,
4. Dynamic synthesis.

The first three techniques are primarily applied to metals and, although metal forming was specifically excluded from the committee's charge, a few sentences on these techniques would not be inappropriate. (See Appendix C for a more extensive discussion.)

Successful explosive welding and cladding has been performed on a number of combinations like bismuth-steel, aluminum-titanium, aluminum steel, and copper-molybdenum, where there are large differences in melting point so that conventional methods are unsuccessful. This can occur since melting is not necessary, and is in fact undesirable because of grain growth. Clean surfaces are essential. Explosive cladding is now used for material for coins. It holds promise for wear, erosion, and corrosion resistant applications and possibly for metal composites. Plates up to 300 ft² and cylindrical shapes of various sizes have been explosively clad. Explosive welding also has been used in joining dissimilar metals for marine applications and for welding tubes to plates in heat exchangers and boilers.

In the above processes, pressures of tens to hundreds of kilobars are required. In explosive forming, on the other hand, pressures of several kilobars are ample. The possible advantages of the technique include: meeting close tolerances on objects of all sizes; forming unsymmetrical and unusual shapes; forming large work pieces; utilizing cheap materials; utilizing a short response time; and forming metals difficult to form by conventional means.

Shock-wave hardening has been employed in the surface hardening of rails and crusher jaws. Pressures ranging from 10 to 100 kbars are used, and the hardness decreases with increasing depth. Both stress amplitude and duration of the shock wave affect the hardening -- a longer pulse of lower amplitude can be as effective as a short high-amplitude pulse. Recent studies on Hadfield steel over the range to 500 kbars indicate that it is the dislocation density and not the specific microstructure which controls the hardness of the steel. It is not yet clear whether this conclusion is general. An increase of hardness by a factor of four in 200 kbars has been observed. The field is not well developed, but holds considerable promise.

The field of shock synthesis is relatively new and comparatively unexplored. A number of groups have synthesized diamond by this technique. Du Pont has demonstrated the capability of applying high shock pressure to a relatively large volume with good product recovery. Information is not available to the committee on the properties of the recovered diamond or its usefulness on various applications. The economics compared with other processes are not known to this committee. It would appear that the technique would apply primarily to materials of high unit value.

Explosive compaction and sintering have received relatively little attention to date. It has attractive possibilities where very high pressure and temperature are involved. These variables can be controlled somewhat independently by changing the packing of the initial charge. There may be problems with stored strain and cracking of the resultant product. It is an area which deserves considerable further investigation.

A final application related to shock work involves the use of high-power lasers to generate an implosion. Investigations of this possibility are under way in several laboratories.

VIII. DEVELOPMENT OF HIGH-PRESSURE EQUIPMENT

A problem of at least potentially practical interest is the development of equipment to permit research at higher pressures. There is no agreement within the committee concerning the pressure limitations on existing equipment of various types. (See Appendix D for one set of opinions.) While there is a divergence of opinion, it appears that among techniques which have been in use for some time, it is certainly not possible to make any static measurements even on the smallest samples at pressures approaching the megabar region. For shock-wave work pressures of several megabars are not uncommon and 30 megabars has been reported in Russia. However, the temperatures in these experiments are too high and the times too short to permit many important experiments. Also, such pressures are obtained in only very stiff materials.

A significant extension of the pressure range could certainly yield important new scientific information and could influence technology, although the unit expense of the product would probably be very high. A number of laboratories are involved in efforts to extend the static pressure range. Two which have aroused considerable general interest are briefly mentioned here.

N. Kawai in Osaka, Japan, has developed and worked extensively with the "collapsing sphere" technique

first proposed by von Platen. He estimates that pressures of several megabars have been obtained. The data published in his papers do not permit an accurate evaluation of his estimates. The technique could, in principle, yield very high pressures if the problems of carbide deformation under these conditions are overcome. Further tests and much more detailed data would be of considerable interest.

At the Institute for High Pressure Physics of the Academy of Sciences of Moscow, under the leadership of L. Vereschagin, development of a device in which it is hoped to reach 2 megabars or higher has been underway for at least seven or eight years. The features of this development, as far as can be ascertained, include multiple staging, the employment of sintered diamond pistons and cylinders, and the use of a 50,000-ton press which has been the subject of considerable discussion.

The use of sintered diamond for high-pressure equipment has much to offer and has been discussed in various phases for a decade or more. There is no reason why it could not be tested in simpler smaller scale devices like the supported taper cell. Multiple staging or equivalent internal support in some form will almost certainly be essential in any extension of the pressure range. It would appear, however, that most forms of multiple staging as well as the use of new materials like sintered diamond could be tested in at least the initial stages without extraordinarily large presses.

Since one of the most important reasons, if not the prime objective, of the extension of the pressure range is to obtain metallic hydrogen and to test its properties, including superconductivity, operation at relatively low temperatures will be required. Thus, it would seem very desirable to keep the apparatus reasonably small in scale.

A development of particular interest is the high-pressure apparatus developed by R. S. Hawke and his colleagues at Livermore. Using magnetic flux compression, they have obtained pressures of one to several megabar in compressible materials like lucite. The compression is isentropic so that the temperatures, while elevated, are very much lower than those encountered in shock experiments at comparable compressions. The apparatus has very interesting possibilities. In particular, it may be possible, using this device, to establish relatively quickly, at least the dimensions and boundary conditions on the problem of making metallic hydrogen.

It would be useful to have materials such as sintered diamond and various support and multiple-staging devices tested in this country, preferably at a place (or at places) with appropriate experience in development. It would be important that the information be immediately accessible to the high-pressure community. In the opinion of the committee, pending further analysis, it is not clear that, at this stage, an effort built around a very large press is required.

IX. CLOSING REMARKS

Each section of the report contains suggestions and prognosis for future work, as do many of the individual reports in the Appendix. It would therefore be redundant and difficult to repeat recommendations about specific substances, techniques, or applications.

It may be worth emphasizing one general aspect, however. Both high-pressure technology and many aspects of high-pressure research have been very empirical to date-- more so perhaps than many other fields. Not only have new phenomena been uncovered largely by serendipity, but it has not generally been possible to predict from one example (or a few examples) of a new phenomenon under what conditions and for which substances one might observe related results.

There are distinct signs that in a number of areas (e.g., first-order phase transitions, electronic transitions, metastability) some rudimentary predictive capacity is developing. One can reasonably hope that similar developments in areas like sintering, rates of phase transitions, etc., will soon appear. The development of predictive capacity centers on the availability of a sufficient amount of the right kind of selective data plus some imaginative and broad-gauge analysis. The development of this predictive capacity constitutes a very "high leverage" situation in terms of introducing new applications. The strong support of interaction between experimentalists with a sound understanding of principles and theorists or analytical engineers with broad interests is a very wise and economical investment.

APPENDIXES

The following reports have been written by individual committee members and consultants. While they have not been reviewed by the committee as a whole, they contain information and opinions by experts in various aspects of high-pressure research and developments.

APPENDIX A
HIGH-PRESSURE SINTERING

by G. A. Samara
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1. INTRODUCTION

One area of high-pressure work that is becoming an important fabrication process for consolidated polycrystalline materials and ceramics and that is bound to be of added future importance in materials technology is high-pressure sintering or hot pressing. This process has been limited almost exclusively to rather low pressures (< 1-2 kbar), and the higher pressure potential remains largely unexplored. Although the pressure range currently used is so low as to be outside the present committee's charter, this area has been and undoubtedly will continue to be one of the most promising for the utilization of pressure in materials technology. In particular, pressure sintering techniques hold promise for solving some of DOD's pacing materials problems. Thus, it is worthwhile to comment briefly on this area. A description of early work and the current state-of-the-art can be found in the first two references cited.

Pressure sintering is not a cure for all material compaction and densification problems. Rather, while the process has both advantages and severe limitations, it is occasionally the only means available for producing certain properties and, in this situation, is most useful and advantageous. Among the strong advantages of pressure

sintering are its ability to: a. produce uniform high density (up to theoretical) materials, and b. control the microstructure (grain and pore size), thereby yielding high-strength materials often with improved mechanical and physical properties. Control of microstructure is achieved through the lowering of the sintering temperature and time at temperature over that needed in the conventional (pressureless) sintering process. The lower temperatures and times needed make it possible to sinter materials that cannot be sintered by conventional means (e.g., materials with high vapor pressures and low melting points and those that decompose at normal sintering temperatures).

The present limitations of the process are those imposed by apparatus and relate to the size and shape of sintered bodies that can be produced and to the pressure range that can be covered. The process also is largely a batch operation and, therefore, relatively costly. The added cost has to be justified by the nature of the application since pressure sintering is not merely a substitute for conventional methods. In fact, the use of pressure (other than in research efforts) will generally be avoided if desired properties can be achieved by other means such as the use of sintering aids when such aids can be tolerated.

2. THE PROCESS

Pressure sintering is commonly accomplished through the application of uniaxial pressure using a piston and cylinder (die) apparatus. The sample

(powder or powder compact) is sometimes encapsulated in a refractory material to prevent sample contamination. Heating is by electrical resistance or electrical induction means. The sintering can be done under vacuum or in a neutral or reactive (e.g., reducing or oxidizing) atmosphere. Graphite is the refractory material most commonly used at low pressures (< 1 kbar). Oxides such as ZrO_2 and carbides such as SiC have also been used at these and higher pressures. Metals such as TZM, a titanium-zirconium-molybdenum alloy, are also commonly used in vacuum pressure sintering. Pressures have been largely limited to less than 2 kbar, and temperatures as high as 2000 - 3000° C have been used. These high temperatures present severe, but not unsurmountable, apparatus limitations for extending the process to much higher pressures, especially for producing large bodies.

Another important variation of the process that allows unique fabrications features is hydrostatic- (or isostatic-) pressure sintering. In this method the powder is encapsulated in thin metal formed to the desired shape, evacuated and sealed, placed in a pressure vessel, and then pressurized by a fluid and heated. It is possible to produce shapes that clearly cannot be produced by the uniaxial process. Pressures as high as 3 kbar at temperatures to 2200° C have been employed by workers at Battelle while apparatus size and cost as well as safety present important process limitations, the process offers capabilities unique enough to justify it for certain applications.

3. MECHANISMS FOR PRESSURE SINTERING

Among the limitations of conventional sintering techniques are the difficulty in achieving full or sufficiently high density in some substances, and in restricting the grain growth that occurs at the high temperatures and the long times needed. Additives (aids) are sometimes used to help achieve densification and control grain growth. The additive often forms a liquid phase surrounding the grains and enhances diffusion during sintering. The control of grain size is important because it influences both the mechanical strength and the physical properties, (e.g., electrical and optical); generally the larger the grain size, the lower the strength.

Pressure affords an important variable for controlling the sintering process. By adjusting the pressure, temperature, time, and initial particle size, it is possible to control the final density and grain size to desirable levels. Fully dense, optically clear bodies have been produced from a wide range of different materials and often possess excellent mechanical and physical properties.

There has been considerable discussion of and speculation about the mechanisms involved in pressure sintering. It is doubtful that there is a single controlling mechanism. Rather, several phenomena come into play, including (a) diffusion, (b) plastic flow, and (c) atomic motion due to fracture and slip at grain boundaries. Particle rearrangement and packing is, of course, also

important in the initial stages.

It is generally agreed that diffusion is probably the controlling phenomenon at low pressures. Some diffusion is always necessary to achieve some grain growth and bonding for material strength, but a balance between strength and grain size is often sought. Plastic flow aids in densification by removing voids and creates new "clean" surfaces for better bonding between grains. It becomes important, however, only after a critical pressure (different for each material) is reached. Fracture and slip also aid in achieving densification and creating new surfaces.

None of the above phenomena or the interrelationships between the various process variables (pressure, temperature, time, particle size, etc.) are fully understood at present. Undoubtedly there will be differences between different classes of materials and the nature of the problem is such that many of these differences have to be sorted out experimentally.

4. APPLICATIONS

Present and potential applications of pressure sintering span a broad gamut of materials technology. Examples range from the familiar sintering of metal-metal carbides such as cobalt-bonded tungsten carbide to the more recent and much higher pressure sintering of diamonds. Some specific areas for which the potential of pressure sintering either has been demonstrated or appears promising are listed below.

a. Improved Dielectrics

These include materials with low dielectric loss, high dielectric strength, high dielectric constant, nonlinear response, stronger piezoelectric response, etc.

b. Optical Quality Ceramics

Fully dense, transparent ceramics have been made from a wide variety of substances. Such materials are finding applications as optical windows, radiation detectors, laser hosts, and electro-optic devices. Examples include MgO, Y₂O₃, CaF₂, Al₂O₃, MgAl₂O₄, and the more recently developed family of ferroelectrics consisting of lanthanum-doped lead zirconate-titanate (PLZT).³ All of these have been produced with sintering pressures < 1 kbar. Al₂O₃ (Lucalox), ThO₂-doped Y₂O₃ (Yttralox) and MgAl₂O₄ (Spinel) can also be produced by pressureless techniques. It now appears possible to make the PLZT's by conventional sintering also. These materials, however, were made first and are still being made by pressure sintering. Optical quality, undoped Y₂O₃ has been produced by pressure sintering only.⁴ It is an excellent host for rare earth

ions and is transparent from 0.3 to 8μ . Single crystals can be grown only in small sizes not suitable for many applications. The fully dense transparent material has transmission characteristics which closely resemble those for the single crystal and can be produced in relatively large (inch) sizes.

c. Electronic Materials

In addition to improving mechanical properties, pressure sintering can be utilized to improve electrical and thermal transport properties resulting in increased lifetimes. An important recent development is the pressure sintering of doped silicon-germanium alloys for thermoelectric applications. Particularly pertinent is the observation that a modest increase in the sintering pressure from 26000 psi to 28000 psi has resulted in marked improvements in alloy homogeneity, mechanical strength, and electrical and thermal properties.⁵ The process, which may also have important potential for other thermoelectrics and for semiconductors, serves to illustrate that higher pressures may be quite important for some materials.

d. Magnetic Materials

Structure-sensitive magnetic properties such as the initial permeability, B-H characteristics, and lossiness are affected by porosity, grain size, grain boundaries, and inhomogeneity. Pressure sintering offers a means of controlling the density and texture, and thereby the properties, of polycrystalline and ceramic magnetic materials. The process is particularly useful for $\text{MeO} \cdot \text{Fe}_2\text{O}_3$ (ferrites) and $3\text{Me}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$ (garnets), where Me = transition metal, and, in fact, hot pressed ferrites

have been produced commercially. Furthermore, the lowering of the sintering temperature in pressure sintering can also be used to great advantage. In ferrites and garnets it is sometimes necessary to control the valence state of the transition metal ion to obtain desired properties and for some oxides and reactions this can be done only at relatively low temperatures, hence the advantage of pressure sintering.

e. Diamonds and Other Hard Materials

Recent work in the United States and Russia indicates that diamond powders can be sintered at high pressures. The process requires pressures up to ~ 60 kbar and temperature up to 2000° C and, in addition, the use of a sintering aid or binder. Many of the details have not been published and the best binders are not known, although small amounts (~ 1 mole %) of silicon, beryllium, or boron are known to help. This development has great technological implications for the machining and grinding industries in the making of pistons, dies, and cutting tools, etc. It is most likely that cubic boron nitride and other future super-hard materials can be sintered in a similar manner.

f. Refractory Materials

Many substances including oxides, carbides, borides, and nitrides cannot be sintered by conventional means, presumably due to the low atomic mobilities for diffusion even at high temperatures. Pressure sintering techniques have, however, been successful in yielding high-density compacts. Here higher pressures are generally needed because of the higher intrinsic strength of these materials.

g. Pressure Bonding

Pressure sintering can be used to bond similar and dissimilar materials such as metal-metal, metal-ceramic, and ceramic-ceramic. The strength and microstructure of the bond can be made comparable to those of the parent material. The isostatic process has much potential in connection with bonding dissimilar materials and in cladding and forming structural shapes. A good example is the successful bonding of fine grain alumina discs and tubes to each other and to metal.

h. Composites

This is an area that can be expected to become increasingly more important. It is becoming possible to tailor-make fiber (wire) reinforced ceramic and metal composites to meet certain strength and thermal expansion requirements that cannot be met with the unreinforced materials. Present techniques employ very modest pressures (few thousand psi). Increasing the pressure range will undoubtedly open this area to a wider range of materials. Such composites have applications as structural elements, and as heat, radiation, and oxidation resistant materials.

5. IMPORTANT RESEARCH AREAS

Pressure sintering can benefit substantially from further scientific and technological advances in the following areas:

a. The Mechanisms for Sintering and Densification

Basic studies are needed, and emphasis should be given to the interrelationships among the process variables pressure, temperature, time, and particle size.

b. Processes of Plastic Deformation, Flow, and Diffusion Under Pressure in Particular Solids.

The elementary question of why pressure lowers the sintering temperature, involving these processes, has not been answered broadly, although diffusion models have been developed⁶ for surface energy and applied pressure as simultaneous driving forces. When diffusion transport is operative, these models can account for the lowering of the necessary processing temperature with applied pressure.

c. The Role of Inert Additives (Sintering Aids, Catalysts, etc.) and possibly Phase Transitions on Conventional and High-Pressure Sintering.

More work is needed to understand the mechanisms involved.

d. The Effects of Higher Pressure on the above Variables and Mechanisms.

The recent observation that raising the sintering pressure by < 10% greatly enhances the properties of thermoelectric silicon-germanium alloys strongly emphasizes the point. Extending the pressure range should open new possibilities for sintering heretofore untried and difficult materials. The recent successful sintering of diamond powders at pressures in the 50- to 60-kbar range illustrates the point.

e. The Scale-up Problems associated with going to Higher Pressures in both the Uniaxial and Isostatic Pressure Sintering Processes.

Emphasis should be placed on finding suitable refractory encapsulating materials and developing new and clever recovery techniques. Present very-high-pressure apparatus suffers from difficulty in recovering samples and the resulting sample damage in the form of cracks and laminations. Early results on materials sintered at very high pressures have

yielded low apparent mechanical strength, most likely resulting because of this damage. Thus, it is felt that the true strength has not been measured.

f. The Use of the Isostatic Process to Fabricate Structures, Parts, and Components of a Single Material or a Composite of Materials

This process offers much promise and more effort should be devoted to it and to extending its pressure range. The possibility of forming complicated shapes by this method also needs to be studied.

g. Automating or Semi-automating the Low-pressure Sintering Process

It is very doubtful that this could be done at very high pressures.

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APPENDIX B

POWDER CONSOLIDATION

by S. H. Gelles
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1. THE PROCESS

The consolidation of powder, whether metal or refractory compound, is usually accomplished in one of three basic ways. The first method is a cold-pressing operation usually involving a shaped die and high pressures (normally <100 ksi). This initial step is followed by a high-temperature sintering treatment which decreases the residual porosity in the compact and improves the mechanical and/or physical properties of the consolidated body. In the second method (hot pressing), pressure and heat are applied simultaneously to produce a body which usually has lower residual porosity than that from the cold-press sinter method. A combination of the two techniques (i.e., cold pressing followed by hot pressing) is also often used. The third technique, still in early stages of development, is that of explosive compaction. This process makes use of high explosives to produce the pressure for cold and, potentially for warm compaction.

The production of fully dense bodies from powders is dependent upon the ability of the powder particles to deform plastically by either glide or creep processes so that near intimate contact between adjacent particles is achieved. The degree of plastic deformation and, thus, the degree of interparticle contact is dependent on the powder particle-size distribution, purity, and the pressing

conditions of time, temperature, and pressure. Residual porosity is reduced or eliminated during heat treatment subsequent to cold pressing as a result of the operation of diffusion-controlled sintering processes. Such processes also occur during consolidation by hot pressing during which plastic deformation and sintering occur simultaneously.

Since it is thermally activated, the sintering operation depends on the time-temperature consolidation history with higher temperatures and longer times favoring the elimination of porosity and the strengthening of inter-particle bonds. The driving force for the sintering process is the reduction of surface energy and, therefore, is highly dependent on powder surface morphology, surface chemistry, and surface-defect structure. Certain impurities or additions to the powder surface sometimes contribute to enhanced or "activated" sintering (e.g., Ni or Pd additions to W) and provide fully dense bodies without pressure and at temperatures that are appreciably lower than those used in the hot-pressing process.

In conventional hot-pressing operations, pressure is generally not as sensitive a processing parameter as temperature with time at temperature and pressure being the least sensitive parameter. Hot-pressing pressures must be of about the same magnitude as the material-flow stresses at the processing temperature in order to produce the plastic deformation necessary for the intimate contact desired between powder particles. Pressure requirements can normally be reduced by increasing temperature. Thus, most metal powders

can be consolidated at pressures of about 1 to 5 kbars with temperatures $>0.5m$. There is an inherent trade-off between temperature and pressure with the usual result that it is more economical to increase temperature and thus reduce the flow stresses than it is to increase the pressure. Increasing temperature also has the advantage of promoting the sintering processes required for complete densification and increased interparticle bonding. As an example of the temperature-pressure trade-off, consolidation of beryllium powder may be accomplished at $1100^{\circ}C$ and 2000 psi or at $900^{\circ}C$ and 10,000 psi.

Increased processing pressures would have an advantage in the consolidation of very-high-melting-point compounds whose flow stresses are very high even at relatively high temperature. For these materials increases in both temperature and pressure may provide a practical solution to their processing. Explosive compaction coupled with moderate temperatures may also offer a reasonable alternative for the consolidation of hard refractory materials.

Very high pressures are necessary in the consolidation of materials such as diamond powder which is unstable at low pressures and elevated temperature. Even in this case it is usually possible to take advantage of the sluggishness of the decomposition which allows consolidation to be effected at pressures somewhat lower than the transformation pressure if processing is sufficiently rapid.

Cold consolidation of powders at very high pressures might also provide sufficient energy to the structure to produce recrystallization in the consolidated powder during a subsequent sintering operation. The resulting fine-grain size could lead to stronger more ductile products.

2. IMPORTANCE

Consolidation of powder materials into usable final shapes and into preforms for subsequent operations such as forging is steadily growing in importance. It has been found to be an economical process for producing complex small parts directly to final shape and dimensions. Gears, sprockets, etc., produced from iron and iron-alloy powders are examples of this type of part. More than 1,000 tons of iron powder are consumed per year in such applications. The number of parts from copper- and aluminum-base metals is also growing, and growth is expected in the processing of titanium alloy and superalloy powders.

When produced by consolidation from powders, certain materials such as beryllium and some types of tool steel have mechanical or physical properties which are superior to those produced by the more conventional cast and wrought route. Cylindrical pressings of these materials as large as a few feet have been produced.

For refractory materials such as high-melting-point metals, ceramics, and the so-called hard metal compounds such as the metallic carbides, nitrides, and borides, the most practical method of producing usable bodies is often through powder-consolidation techniques.

Processing of these materials requires relatively high temperatures because of their high melting points and relatively low diffusion coefficients and, in the case of the compounds, their lack of adequate low-temperature deformation systems. In spite of the high temperatures used, full density often is not achieved in these high melting materials. Application of higher pressure to this problem may achieve noteworthy results.

3. STATUS AND LIMITATIONS OF PROCESSES AND EQUIPMENT

The techniques and equipment used in the consolidation of powders by cold pressing and sintering or by hot-pressing operations have developed rapidly during the past few years. For example, manufacturing presses used in the cold compaction of powders have grown in capacity from the 100-ton to the 1500-ton range. The size and complexity of parts have also increased.

The cold-isostatic-pressing technique in which powder is packed into an elastomer container, sealed, and subjected to a fluid pressure has also developed significantly. Batch processes are conducted in autoclaves as large as 5 ft in diameter by ten ft long. Blocks of ceramic 17-in by 23-in x 116-in have been pressed in such equipment. Other cold isostatic equipment 2 ft in diameter by 8-ft long exists and is capable of pressures to 80,000 psi. This unit has been used for the green pressing of large beryllium bodies in preparation for hot-isostatic pressing. Research is now underway in automating such equipment so that it may be used for large production items. Experimental equipment

is also available (approximately 6" in diameter and 6" long) for cold isostatic pressing of powders in the 10 to 15 kbar range. Insufficient work has been done, however, to determine whether cold pressing with this apparatus at these pressure levels offers meaningful advantages. Theoretically, more intimate interparticle contact would be possible and would be accompanied by larger amounts of plastic deformation. The resulting increase in internal energy would enhance the sintering process and promote recrystallization during the post-pressing heat treatment thus leading to a fine-grain product.

Conventional hot pressing, usually carried out with graphite tooling, has been used to consolidate various intermetallics, refractory carbides, oxides, and metals. The technique is limited in operating pressure range to 2000 to 12,000 psi depending on the hot pressing size, by the tooling material, and it is often difficult to achieve full density under these conditions.

Hot-isostatic-pressing techniques in which a cold consolidated mass of powder is sheathed in a metallic container and subjected to a high gas pressure and elevated temperature have rapidly developed in the last few years. The process has produced large and complex shapes up to 2 ft in diameter and 5 ft long. The largest autoclave unit presently in operation has a 3-ft inside diameter and 9-ft inside length and can operate at pressures up to 15,000 psi. An autoclave 5 ft in diameter and 15 ft long operating in the same pressure range is now on the drawing board. Smaller autoclaves operating at higher pressures

(up to 150,000 psi) are available but only limited work has been performed especially at the higher pressures. The application of higher pressures in the consolidation of refractory compounds and metals would offer some advantages, but temperature limitations are presently imposed by the requirement for a ductile nonreactive sheathing material. Very little work has been performed on extending the pressure and temperature range of this process to consolidate refractory compounds to full density.

Some work has been conducted in the 20-to-70-kbar pressure range, and refractory borides, SmCO_5 and diamond powder are examples of the powders consolidated. Powder compaction at these very high pressures is still experimental and the amount of material that can be processed at a given time is very limited. Because of limited experience in this area, evaluation of the properties of the consolidated material has been largely neglected to date.

Explosive compaction of powders is another area that has received only limited attention in spite of the potentials of the process in regard to size and economy. The major problem area is the cracked compacts that often result from the process. Research efforts in sample design and in charge fixturing and detonation configuration coupled with the application of elevated temperature processing should lead to progress in the development of the process. The sintering of explosively compacted powder should be accelerated due to the relatively high energy imparted to the powder particles during compaction. Once again recrystallization could lead to a fine-grain structure having superior properties.

Finally it should be noted that relatively little work has been done in the area of surface morphology and chemistry and their effects on consolidation of powder. This is a very important field since these surface characteristics sensitively affect interparticle bonding and sintering processes. They are especially important in closed systems at high pressure where gas evolution as a result of adsorbed layers or impurity reactions involving gaseous products lead to high interparticle gas pressure and prevent full compaction. The problem can often be solved by hot outgassing and sealing in a closed container. Efforts to consolidate powders at high pressure must be concerned with these effects. Similarly, sintering aids (alloying elements added to the powder) can activate powder surfaces so that sintering reactions that occur after cold pressing or during hot-pressing operations would take place at lower temperatures. The reactions involved, however, are not too well understood.

4. RESEARCH RECOMMENDATIONS

Listed below are areas relating to the application of high-pressure technology to powder consolidation and visa versa that show promise of leading to scientific or technological advances in both areas.

a. Explosive Compaction of Powders

This area of our technology has not received much support although the potential benefits include economical powder compaction and consolidation of powders heretofore difficult or impossible to compact by other means. Exploration of warm or hot explosive compaction or cold compaction

followed by hot pressing or sintering are some of the areas that appear fruitful.

b. Diamond and Hard Refractory Compound Powder Consolidation

The successful consolidation of diamond powder and other refractory and wear-resistant materials could contribute significantly to technology. These materials could be used effectively in grinding or drilling tools and in dies such as those used in the drawing of fine wire. Diamond powder consolidation and fabrication into ultra-high-pressure (megabar range) chambers would allow the exploration of new forms of matter such as metallic hydrogen. Here again the use of explosive compaction might be of benefit although other techniques such as the use of sintering aids or special powder-surface preparations may help in the consolidation and powder-bonding processes.

c. Intermediate Pressure Consolidation

It is within the present state-of-the-art to build relatively large hydrostatic equipment (1 ft. in diameter and several feet long) capable of operating in the 10- to 15-kbar pressure range. Such equipment would greatly extend the present usual range of operating pressures for powder compaction and would be useful in the consolidation of refractory metals and ceramic materials. The higher pressure levels should allow compaction at lower temperatures and should produce materials with higher densities and improved properties. The materials thus produced would be of practical size and could in some cases be pressed to near-finished shape and dimensions. Solid-state bonding of

difficult-to-join materials may also be feasible by the application of the increased pressure. Research efforts in this area should be fruitful.

d. Material Deformation at High Pressure

Studies of the deformation of materials under high pressure would be helpful in determining the desired temperature and pressure conditions for powder compaction. Information on the temperature and pressure dependencies of flow characteristics and their variation with crystal structure is the type of information that would be useful.

APPENDIX C

DYNAMIC HIGH-PRESSURE APPLICATIONS

by George A. Samara
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A great deal of progress has been made during the past 20 years in studying the response of solids (and some fluids) to shock-wave compression. Much of the work has been motivated by military needs, but the results have been of scientific as well as applied interest. The shock method has many unique capabilities, very important among which are the ability to attain very high-pressure high-temperature states of matter not possible by present static high pressure means and the ability to study the elastic properties of solids over a large range of strain. For example, germanium has a Hugoniot elastic limit of over 40 kbar and that of sapphire can be over 200 kbar along certain crystallographic orientations.

Shock-wave research has made important contributions, particularly noteworthy are those in areas of high-pressure equation of state and polymorphism of solids. In addition, advances have been made in a number of other areas: including (1) dynamic yielding and the interpretation of elastic-plastic phenomena in terms of dislocation dynamics, (2) material strength and fracture (spallation), and (3) the electrical and magnetic response of certain classes of solids (e.g., quartz, germanium, and iron alloys). In most of the above areas results of carefully planned and detailed experiments are just beginning to appear and

much more work needs to be done before sufficiently quantitative models of the phenomena can be devised.

The objective of this brief appendix is not to deal with the above aspects of shock-wave (or dynamic) high-pressure research but rather to focus on a few specific applied areas.

Certain aspects of dynamic high-pressure work are finding important applications in and hold substantial further potential for metals and metals fabrication technologies. These are explosives operations and can be divided into (1) explosives bonding, (2) explosives forming, and (3) shock-wave hardening.

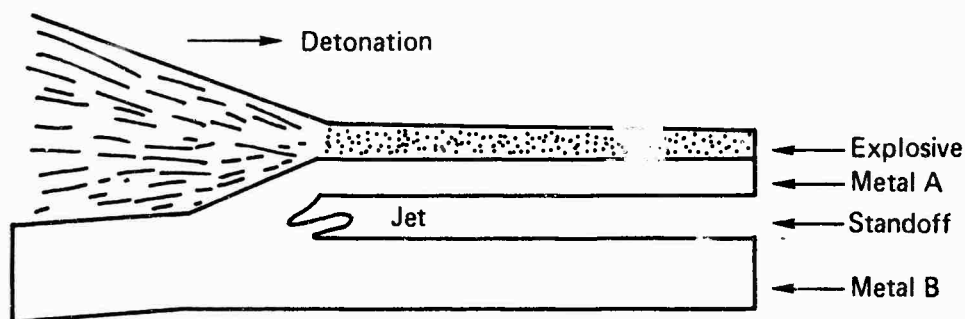
These operations have proven to be useful in metals work, and in some instances, for example the bonding of incompatible metals, they are the only means feasible for performing the job. This is not to say, however, that these are a cure for all difficult metals operations; rather, they complement and/or compete with existing fabrication methods. Such operations are most advantageously exploited in applications not economical using conventional means and in applications requiring the production of limited quantities.

A body of information on these operations exists in the literature and a fairly up-to-date review of the field can be found in the references cited at the conclusion of this appendix. Only general remarks on these operations, their potential, and problem areas that need further investigation will be made here.

1. EXPLOSIVE BONDING: WELDING AND CLADDING

These are commercial operations used to bond metals together. Many different combinations of metals such as bismuth-steel, aluminum-titanium, aluminum-steel, copper-molybdenum, and zinc-zinc have been successfully bonded with this technique and it should be applicable to most combinations of metals. By conventional methods it is often difficult or impossible to bond dissimilar metals, such as metals with widely different melting points (e.g., bismuth-steel and lead-tungsten). In explosive bonding melting is not a requirement, and furthermore, the process does not appear to be strongly influenced by large differences in the elastic and plastic properties of the metals. In fact, melting is not desirable since recrystallization and the possibility of formation of compounds and alloys at the interface between the two metals can lead to a weaker bond. Clearly then, explosive bonding is an important process. It generally has been applied for bonding simple geometrical shapes such as flat plates and cylindrical surfaces; more complicated shapes are more difficult but may be possible.

The process is illustrated schematically as shown:



The two metals to be bonded are placed a small stand-off distance apart. On detonating the explosive charge the upper metal plate is driven downward at high velocity to collide with the lower plate at a small angle. An explosive is usually selected that detonates at a velocity which is lower than the sound velocities in the metals. The collision point will then traverse the metal surface at a subsonic speed and permit jet formation upon collision. The colliding surfaces contain oxide layers and other contaminants which are peeled off by the jet which scours and exposes clean metal surfaces as it moves forward. The clean surfaces behind the jet are then forced together by explosive pressures in the tens to hundreds of kilobars forming a bond (or weld). The formation of clean surfaces is an essential step in the bonding process. If properly done, the resulting bond is mechanically stronger than the weaker of the two metals. The strength of the bond depends on a number of factors such as the pressure and temperature conditions, crystallographic misorientation, and the possible occurrence of melting at the interface. Desirable conditions have to be determined for different combinations of metals.

The mechanism by which explosive bonding is achieved is not fully understood. Most hypotheses to date are based on results of post-mortem analyses with no in-situ data. Some of the mechanisms that have been postulated include (a) fusion bonding, (b) cold pressure friction bonding resulting from the relative sliding motion of the two interfaces, and (c) bonding due to the jetting action that occurs under oblique high velocity impact. Most workers in the field favor the latter and this is

supported by post-mortem metallurgical examinations of interfaces which often reveal strong evidence for jetting. The two types of interfaces observed are (a) a straight interface resulting from the direct bonding of the two clean surfaces produced by collisions at large angles of incidence, and (b) a wavy interface resulting from oscillation in the jet flow and produced by collisions at small angles of incidence. The details of the wave formation are also not understood, but a qualitative explanation has been advanced by Crossland and co-workers. It is speculated that after detonation of the explosive the metal in contact with the explosive moves ahead of the other and a metal "tongue" from it penetrates the slower metal. This raises a tongue in the second metal ahead of the collision point and this tongue penetrates the first metal and the process continues. In the absence of any direct in-situ observations it is difficult to be sure how closely this description reflects the actual phenomenon. Evidence for small pockets of melting and solidification near the vortices of the waves has been noted. Under conditions of very-high-pressure collisions, these pockets coalesce to form a continuous cast interface -- often an undesirable situation resulting in a weaker bond.

Explosive cladding has been used to bond metals to make coins and holds considerable promise for forming speciality composites for wear-, erosion-, and corrosion-resistant applications and, possibly, metal composites suitable for high-temperature applications. Plates up to $\sim 300 \text{ ft}^2$ and cylindrical shapes of various sizes have been successfully clad. The welding process has been used for joining difficult dissimilar metals such

as aluminum-steel for marine applications and for welding tubes to tube plates in heat exchangers, condensers, and boilers, particularly in nuclear power generators. It has been speculated that the latter process may replace the conventional tube-expansion methods.

2. EXPLOSIVE FORMING

As opposed to explosive bonding in which dynamic pressures of tens to hundreds of kbar are needed, explosive forming is a relatively low-pressure process requiring pressures on the order of only several thousand psi. The pressure is generated by an explosive charge set off some distance away from the metal-form die combination and transmitted to the metal via an inert medium, generally water. The metal flows (stretches) to the desired form.

Explosive forming has proven to be economically sound and competitive for certain metal fabrications and, in some instances, is superior to conventional processes. Among its strong features are its ability:

- a. To meet close dimensional tolerance requirements on both small and large objects;
- b. To form nonsymmetric and unusual shapes (such shapes are often very difficult to produce by conventional means, but become easy by the explosive method after a form die is made);
- c. To form large workpieces;
- d. To utilize dies of low-cost materials when production quantities will be small;
- e. To allow quick response time; and
- f. To form metals that are difficult to form by conventional means.

The formability (ultimate elongation) of most metals is not

markedly changed by the high strain rates involved in explosive working, and the residual metallurgical properties usually are comparable to those following cold working to a similar level of deformation.

3. SHOCK-WAVE HARDENING

This has long been recognized as a useful metal-working process and has been employed in the surface hardening of rails and crusher jaws. Conventional processes require large plastic deformations to achieve needed hardness, while, on the other hand, the same results can be achieved with very little deformation under the very-high-strain-rate conditions of the dynamic process. Pressures in the 10 to 100-kbar range are involved and the hardness decreases with increasing depth into the object. The process does not appear to be widely used at present but it may have potential applications in wear-resistant and structural materials.

Both the shock-wave-stress amplitude and duration affect the residual hardness and microstructure of the material. A low-amplitude pulse of long duration can be as effective as a higher-amplitude pulse of shorter duration. The hardness of metal is thought to be determined by such factors as the density of dislocations, stacking faults, and deformation twinning. Recent investigations of the shock hardening of Hadfield steel from 0 to 500 kbar have indicated that it is the dislocation density and not the specific microstructure that controls the hardness of this material.⁴ Detailed studies of other materials are needed to establish if this is a general conclusion. Hadfield

steel, an austenitic manganese steel, exhibits an unusually large shock hardening effect. An increase in its hardness by as much as a factor of four in 200 kbar has been noted.

4. CONCLUSIONS AND RECOMMENDATIONS

Much technological progress has been made in recent years in explosive operations described above, and they are now recognized as competitive or unique metalworking processes. However, the mechanisms and nature of the phenomena involved are not sufficiently well understood. The energetics of explosive detonation and energy transfer to metal are reasonably well understood for high-density military explosives, but solution of such problems requires utilization of complex computer codes. Few industrial firms actively using explosive metalworking have the capability to perform such computations and, in fact, there has been no clear demonstration that such codes can indeed solve the design problems involved. Furthermore, performance data required by the codes are not available on the low-density, commercial explosive formulations most commonly used in metalworking applications. The rates, pressures, and temperatures achieved are important process parameters. All present knowledge about explosive bonding is based on post-mortem analyses. Direct observations and measurements are very difficult but sorely needed. Other important areas in need of research include those of metal plasticity and dislocation mechanics (as they affect flow and hardening) under conditions of very high strain rates. Some progress in these latter areas has been achieved in recent years but more remains to be done.

ACKNOWLEDGEMENT

I wish to thank J. E. Kennedy and R. A. Graham for helpful references and comments.

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APPENDIX D
HIGH-PRESSURE TECHNOLOGY

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1. INTRODUCTION

Since 1955, pressure has become a readily available and powerful thermodynamic variable in the hands of possibly 2,000 to 3,000 workers throughout the world. That so many should be thus engaged when so few profitable products, only two in fact, have been discovered may seem surprising until one realizes that an incentive even more powerful than product is curiosity. High pressure has served well in this respect; as a newly available thermodynamic variable it has offered many answers, many surprises, and many new questions. In addition, it has resulted in some metal working at 10 to 20 kbar, some sintered things, a couple of hard abrasives and interesting organic reactions, but no polymer products. At 60 kbar, the volume available is still much too small for superalloy or polymer parts.

Not many technologically important products can be expected in view of the present state of the art. The volume is too small, and only a few pressure-generated materials have any permanence after pressure is removed. Thus, what can be made or modified and does have permanence must find its place in technology in the form of small pieces--a few cubic centimeters. For the rest, pressure remains a pry for opening mysteries, such far-off mysteries perhaps as where lies metallic carbon, metallic hydrogen,

and metallic some other things. These are problems of the greatest technical difficulty and may demand static pressures of 1 to 6 megabars which severely strains pressure capabilities.

In this appendix an attempt is made to illustrate how pressure is achieved and to describe its principle effects on matter. To enumerate all its effects is an impossible undertaking; however, it is possible that from the vast literature on the subject, an imaginative person might find a few resources for generating novel solutions to specific problems. Most of the work accomplished to date seems to have been an effort to add to the expanding list of new forms of matter, new phase lines, new resistance phenomena, new curie points, new superconductors, etc. There might be virtue now in trying to discover whether there are useful properties for specific needs among all these stored treasures. The sort key may be an imaginative theoretical scan of what already exists.

2. APPARATUS

The real-life facts about high-pressure apparatuses are that they are expensive, their useful lives are relatively short, and their reaction volume is small. All of these factors become exponentially more unfavorable to man's purposes as the pressure demand increases. For this reason, any technologically useful product of high pressure made at 50 kbar, for example, must have an economic value of \$4,000 to \$5,000 per lb. This economic limit will go up or down as the pressure required increases or decreases.

All apparatuses for pressures exceeding about 40 kbar require massive support for the regions of most intense stress. Consequently, the machinery for applying the force must have capability for generating both the supporting forces as well as the compressive force. The ratio of total force to compressive force increases from approximately 2.0 at 40 kbar to 10 at 100 kbar for apparatuses capable of many excursions to high pressure.

While the designs and adaptations of high-pressure apparatuses differ in many details, the basic principles of design do not. All have evolved from the Bridgman piston and cylinder or anvil apparatuses through the Drickamer anvil, GE belt, or VonPlatten sphere into a proliferation of styles that employ Bridgman's principle of "massive support" to the regions of greatest stress.

It is comparatively easy to build an apparatus to perform a few laboratory experiments and quite another to build one with such exquisite perfection that it becomes a production machine. Thus, one is likely to read of performance claims that have not been tested thoroughly in everyday work.

The useful reaction volume at 20 kbar may be several cubic centimeters, but at 50 kbar the volume drops to around 1 or 2 cm³. At 150 kbar, one may be limited to match-head-size experiments, about 15 mm³. Naturally, the volume available is dependent also on the temperature that must be applied, and the volumes quoted above apply when temperatures over about 1000° C are used. At low

temperatures, the space needed for internal thermal insulation can be reduced and the working volume increased.

The illustrations (Figures 1 - 10) and descriptions of apparatuses that follow are intended to give a picture of the several types now said to be in use throughout the world.

The basic construction materials of high pressure equipment are high-grade steels for supporting rings and massive backup blocks, and cemented tungsten carbide with 1 to 6% cobalt for pistons and chambers. The strengths of several types of construction materials are given in Table 1 below.

TABLE I
Properties of Materials Useful in High-Pressure Construction

Material	Avg. Strength (kb)		Avg. Young's Modulus (kb)
	Compression	Tension	
Steel, 18-8 stainless	5-10	5-10	2000
Steel, 4340 or maraging	15-25	15-20	2000
Cobalt-cemented Tungsten carbide			
3% Co	60	11	6500
6% Co	45	14	5600
13% Co	40	22	5300
Beryllium copper	12	12	1200
Glass fibers, laid parallel in resin	6	10	380
Boron fibers, laid parallel in resin	10	20	4000
Single graphite fibers	-	25	4500
Sapphire	40	-	3500
Diamond	120+	-	13000
Pyrophyllite	1	0.1	800
NaCl	0.3	-	400

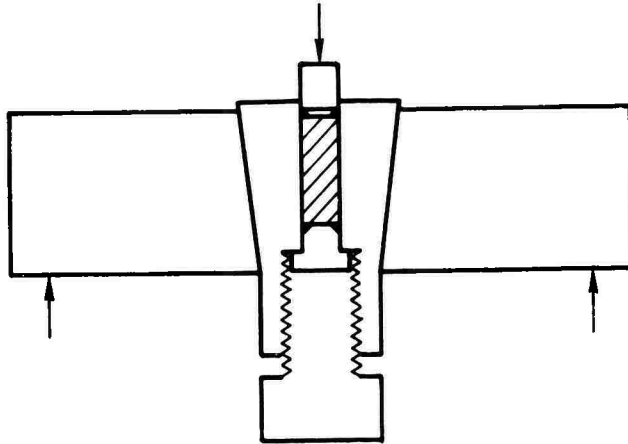


FIGURE 1 Progressive internal and external loading of pressure cylinder.

Pressure limit: about 40 kbar--for 1-5 excursions

Piston diameter: about 1/2 inch maximum

Piston material: tungsten carbide

Reproduced from: P. W. Bridgman, "The Physics of High Pressure," (London: G. Bell and Sons, Ltd., 1958).

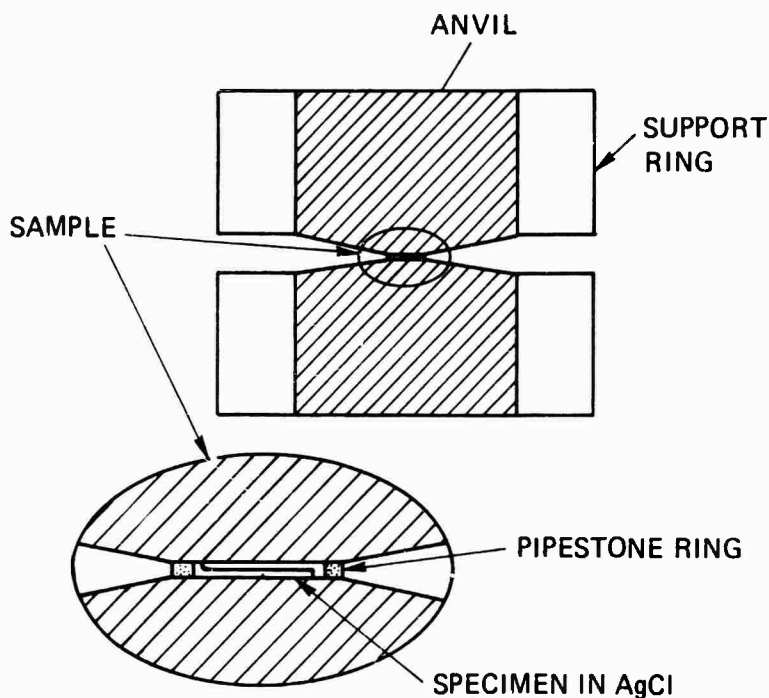
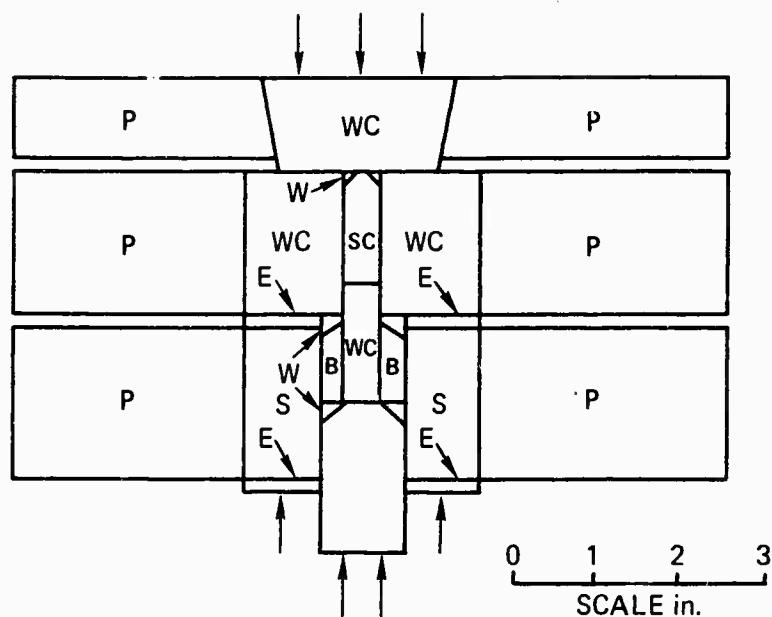


FIGURE 2. Opposed anvil apparatus of P. W. Bridgman

Pressure limit: about 100 kbar for a few excursions
Anvil material: tungsten carbide
Anvil diameter: about 1/2 inch, thickness, 0.010 in.

Reproduced from: P. W. Bridgman, Proc. Am. Acad. Arts and Sciences, 74, 425 (1942).



- P = HIGH PRESSURE "PLATE" OR SHRINK-FIT CONTAINING RING
- WC = TUNGSTEN CARBIDE
- S = STEEL
- E = STEEL END-LOAD RING
- SC = SAMPLE CHAMBER
- B = BISMUTH METAL
- W = STAINLESS STEEL WASHER

FIGURE 3. Double-staged piston-cylinder apparatus.

Piston has flank support through pressurized Bi

Pressure limit: 60 kbar

Piston diameter: 1/2 inch

Reproduced from: A. Jayaraman, W. Klement, Jr., R. C. Newton, and G. C. Kennedy, "Fusion Curves and Polymorphic Transitions of Group III Elements - Aluminum, Gallium, Indium, and Thallium - at High Pressures," J. Phy. & Chem. Solids, 24, 7 (1963).

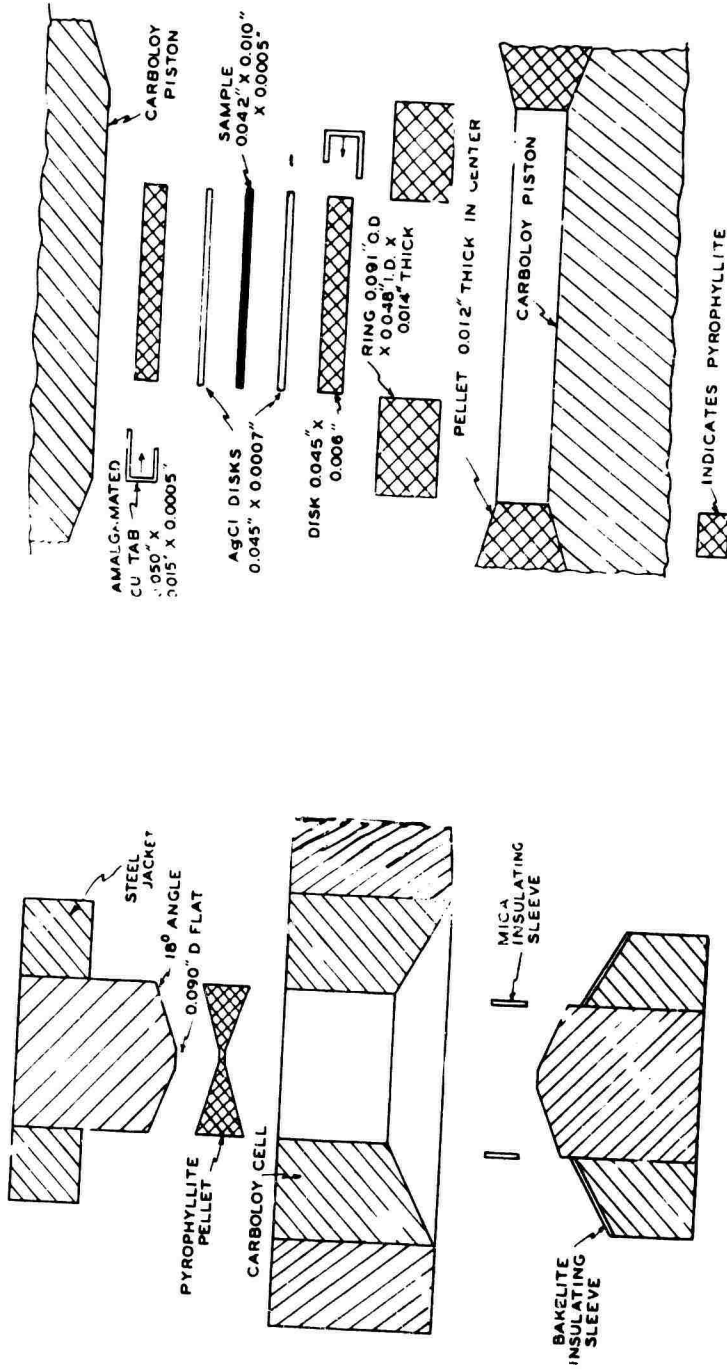


FIGURE 4 (a) Very high-pressure anvil apparatus of H. G. Drickamer

FIGURE 4 (b) Central high-pressure region of Drickamer anvils.

Pressure limit: about 300 kbar, 1-3 excursions

Reproduced from: A. S. Balchan and H. G. Drickamer, "High-Pressure Electrical Resistance Cell, and Calibration Points above 100 Kilobars," Rev. Sci. Instru., 32, 308 (1961).

* See Appendix E for evidence that pressures to 450 kbar have been reached.

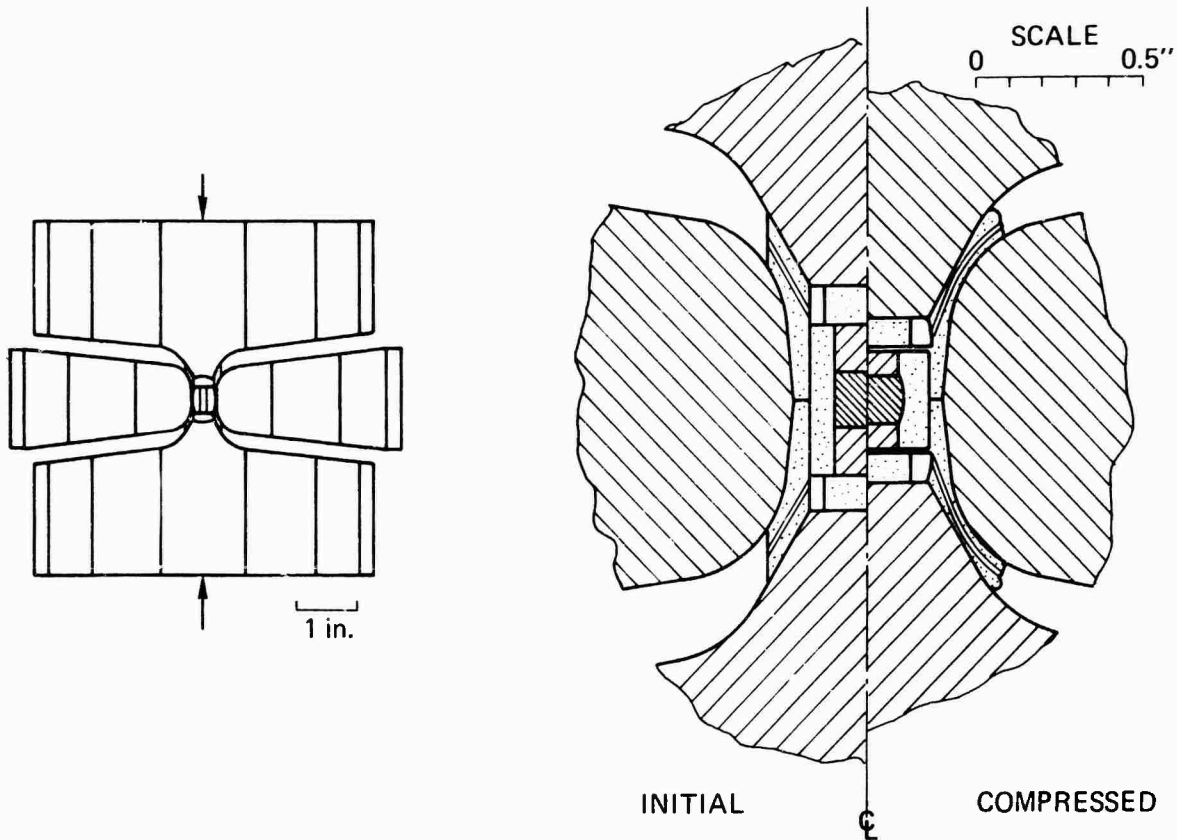


FIGURE 5(a) Belt apparatus of H. T. Hall

FIGURE 5(b) One side shown before compression: the other side shown at about 60 kbar.

Pressure limit, about 60-70 kbar;
10 to 400 excursions,
depending on pressure applied.

Reproduced from: H. T. Hall, Rev. Sci. Instru., 31, 125 (1960).

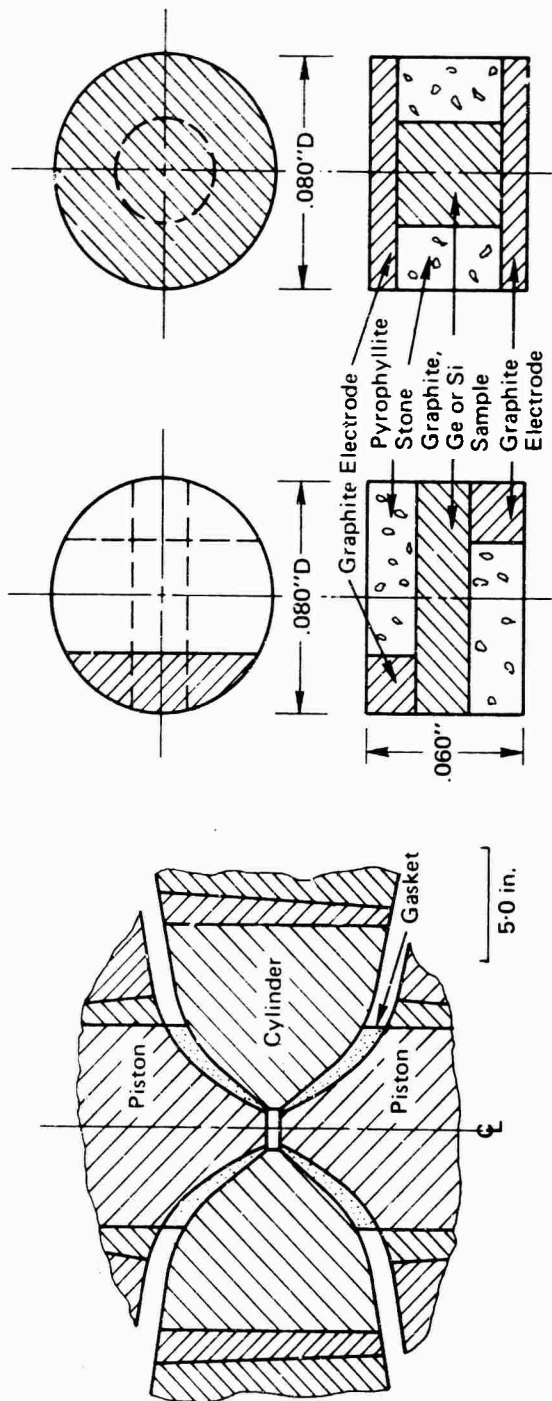


FIGURE 6 (a) High-compression "belt" apparatus of F. P. Bundy

FIGURE 6 (b) "Bar" samples and "spool" samples used in the high-compression "belt" apparatus.

Pressure limit: about 200 kbar

Heated volume: 15 mm^3

Total volume: 150 mm^3

Many excursions to high pressure possible.

Reproduced from: F. P. Bundy, J. Chem. Phys., 38, 631 (1963).

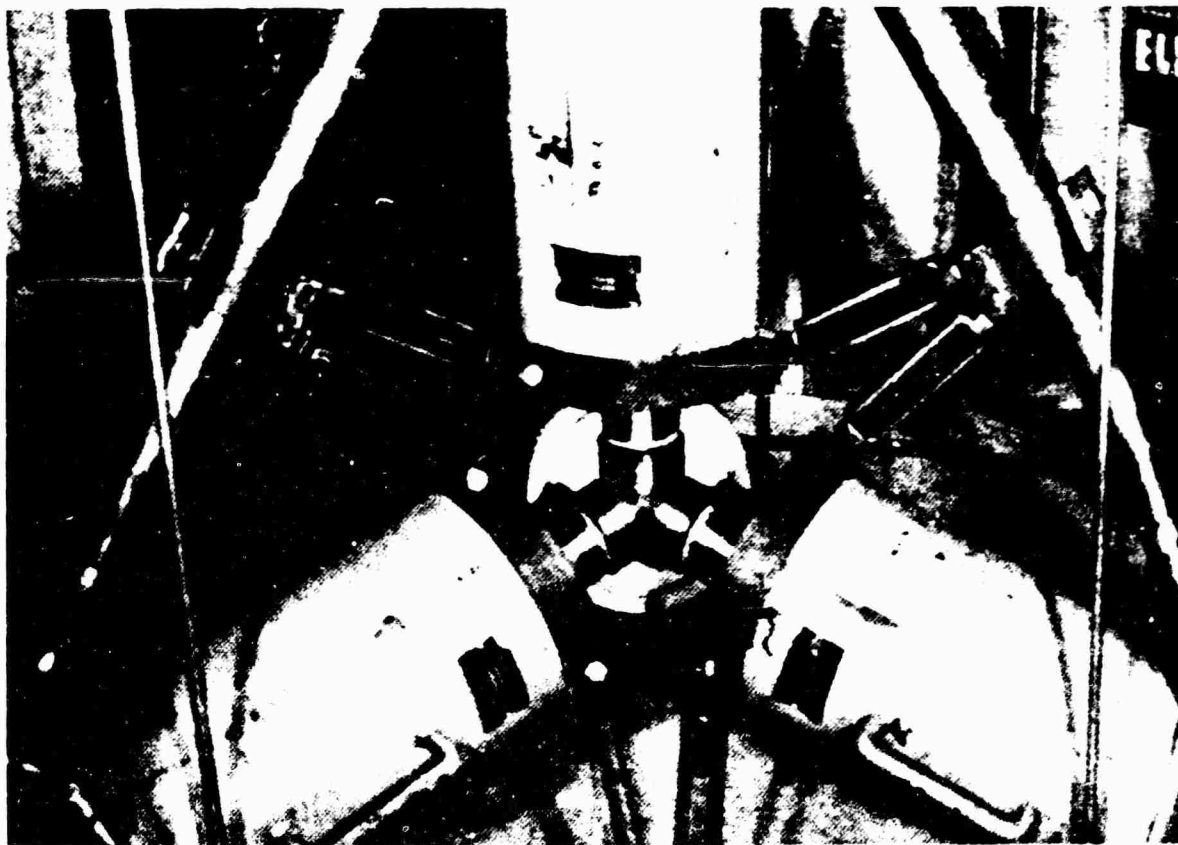


FIGURE 7(a) Tetrahedral apparatus of H. T. Hall

Pressure limit: about 60-70 kbars;
10 to 400 excursions,
depending on pressure applied.

Anvil face: $\sim 1/2$ - 1 inch

Reproduced from: H. T. Hall, Rev. Sci. Instru., 29, 267 (1958)
" " " 33, 1278 (1962)

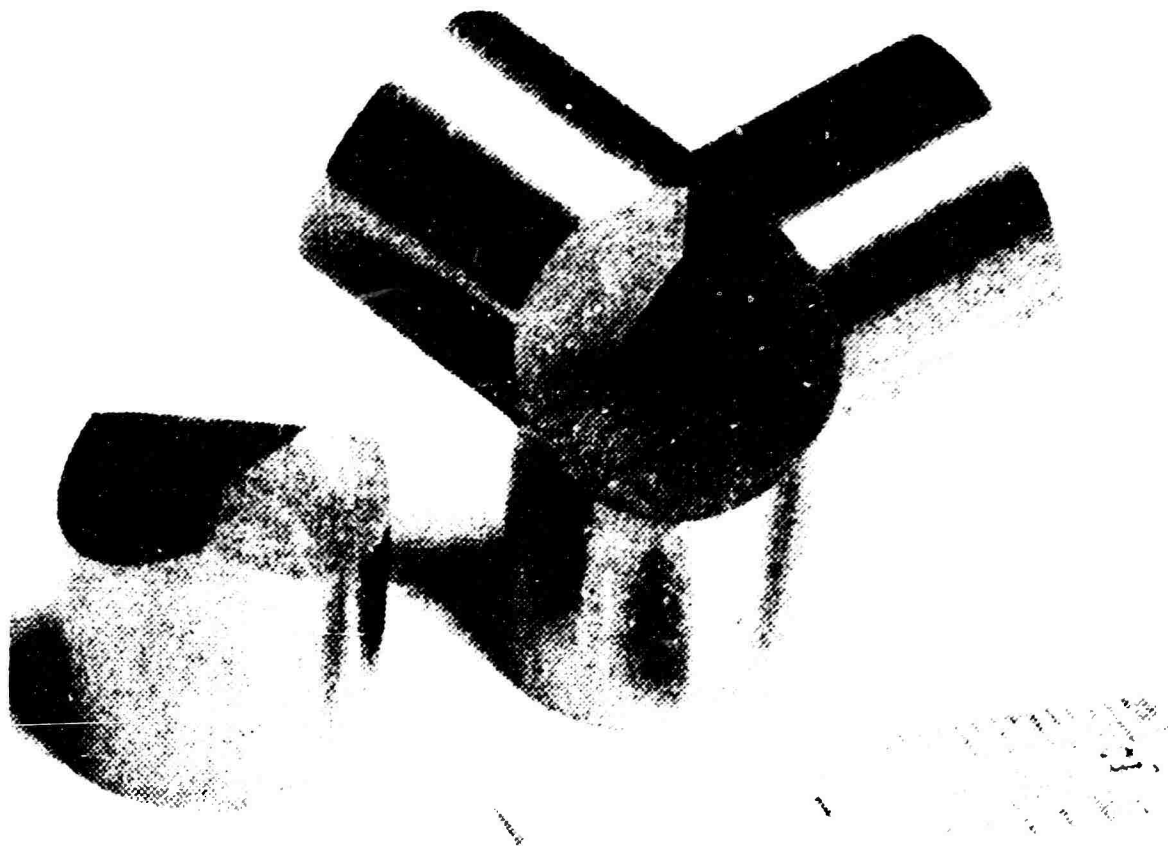


FIGURE 7(b) Nest of tetrahedral pistons.

Pressure limit: about 60-70 kbar;
10 to 400 excursions,
depending on pressure applied.

Anvil face: $\sim 1/2$ - 1 inch

Reproduced from: H. T. Hall, Rev. Sci. Instru., 29, 267 (1958).
" " " 33, 1278 (1962).

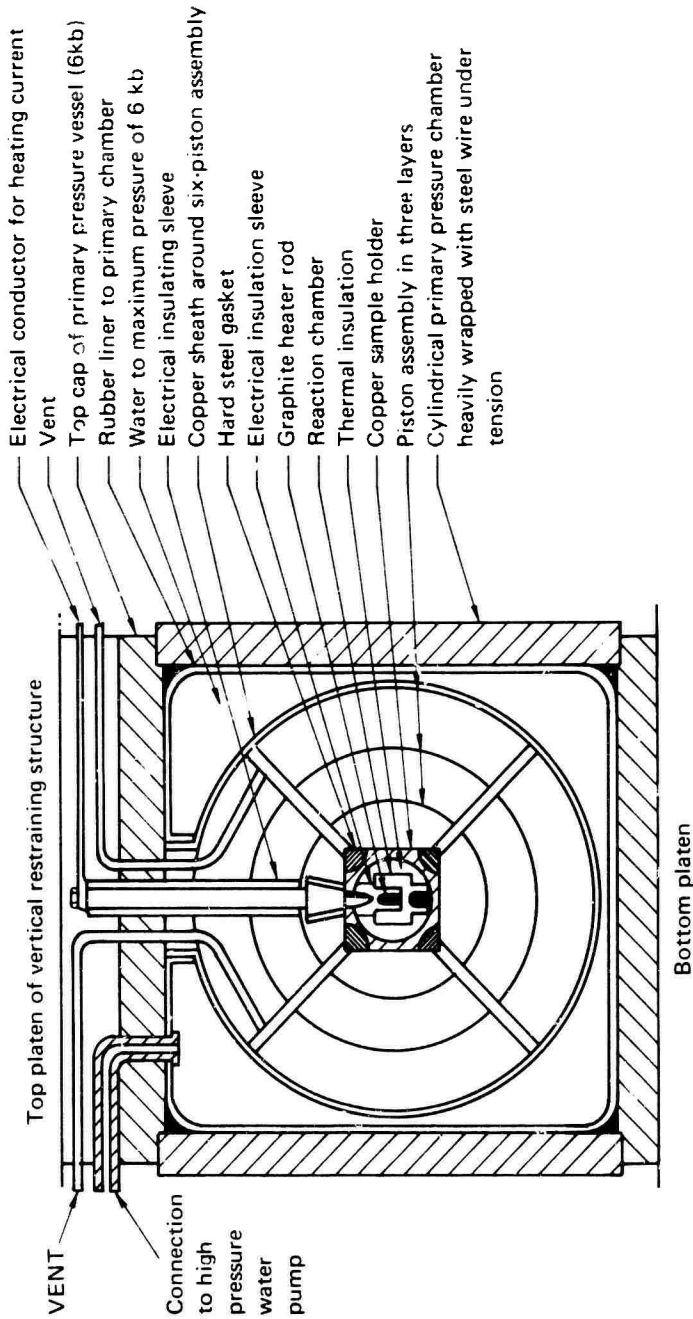
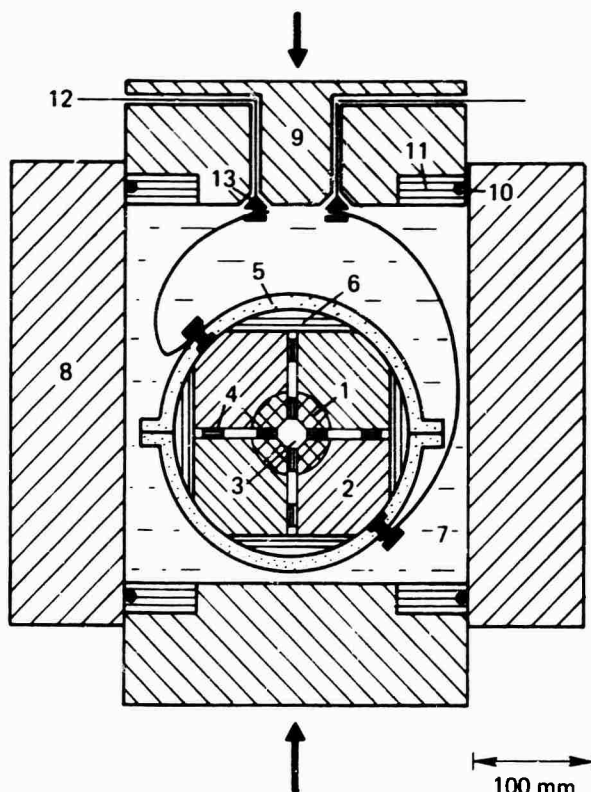


FIGURE 8 Von Platen's cube apparatus

Inner cube has 75 mm edge

Pressure limit: probably ~60 kbar

Reproduced from: J. Liander and E. Lundblad, "Some Observations on Synthesis of Diamonds," Arkiv. Kemi., 16, 139 (1960).



Single 8-anvil type split sphere apparatus in oil reservoir.
Only two of eight leads are shown here. 1—Tungsten carbide
anvil core, 2—steel backing block, 3—sample chamber, 4—
insulator sheet, 5—rubber shell, 6—corner cap, 7—copper
electrode, 8—cylinder, 9—piston, 10—O-ring, 11—nylon ring,
12—lead, 13—copper cone.

FIGURE 9 Kawai and Endo's split sphere apparatus
Pressure limit: probably >300 kbars

Reproduced from: N. Kawai and S. Endo, "The Generation of
Ultrahigh Pressures by a Split Sphere
Apparatus," Rev. Sci. Instru., 41, No. 8,
1178 (1970).

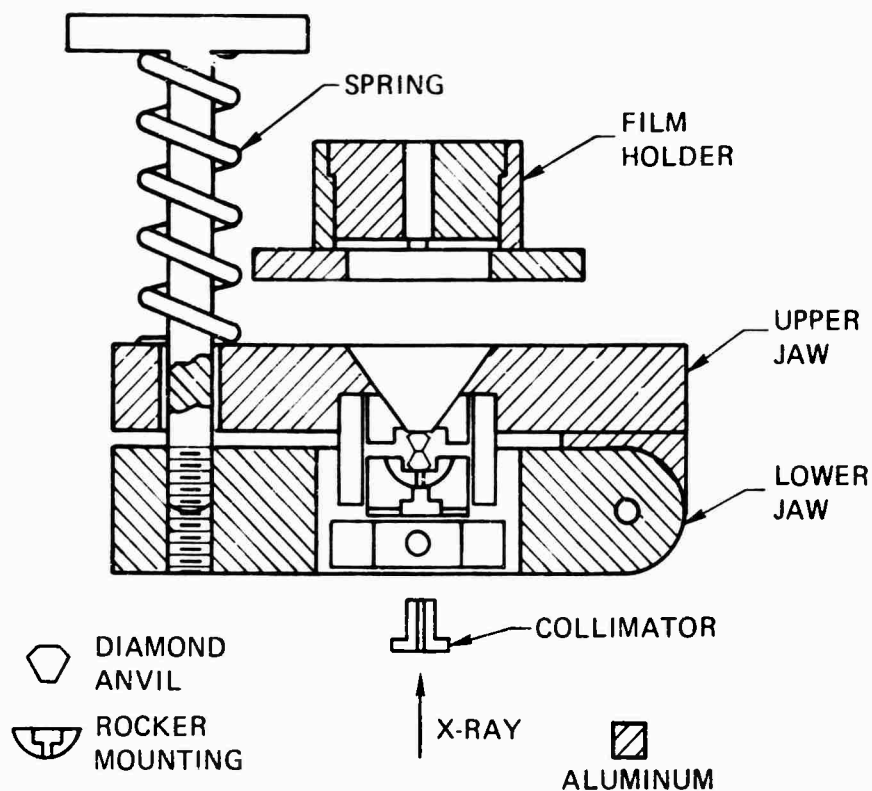


FIGURE 10 Diamond anvil apparatus for X-ray diffraction at high pressure.

Anvil face diameter: 1 mm 0.3 mm
Pressure limit: ~200 kbars ~300 kbars

Adapted from: C. E. Weir, E. R. Lippincot, A. VanValkenburg, and E. W. Bunting, Bur. Stds., J. Res., 63A, 55 (1959).

T. Takahashi and W. A. Bassett, Science, 145, 483- 486, 31 July 1964. Fig.1. (Copyright 1964 by the American Association for the Advancement of Science.)

See also: Rev. of Sci. Insts., 38, No. 1, 37-42, Jan. 1967 and Scientific American, 212, No. 6, June 1965 pp 100-108, for newer designs.

The pressures attainable in a laboratory are in principle without limit if one could increase the flank support to the regions of highest stress (i.e., piston tip and cylinder walls without limit). This corresponds to Bridgman's principle of "massive support," but one soon runs into unwieldy practical difficulties. The reaction volume becomes very small in comparison to the supporting structures; the available force budget is mostly consumed in supplying the support, and one tends to lose track of the pressure (P) actually being generated for the reaction in terms of applied force. The proper balance of flank support in relation to the piston face pressure becomes very difficult to achieve as P increases. In the present state of the art of applying flank support, the practical upper pressure limit for studies at room temperature was extended to about 300 kbar at very small volumes. For pressurizing at high temperature, the pressure limit presently is about 200 kbar.

The spherical apparatuses of VonPlatten and Kawai may have some advantages in volume and pressure capability over the more conventional piston or punch type since they probably give a more nearly spherically symmetrical distribution of stress than do other types. The proper flank support may be automatically achieved, and the central region, including the anvils, are more nearly hydrostatically compressed. Kawai's apparatus has probably exceeded 300 kbar.

The spherical types seem better adapted to scientific experiments than to routine production. Also, in prolonged high-temperature work, the need for cooling may be more difficult to satisfy.

Pressure apparatuses of the type illustrated are adapted for using solid pressure transmitting media (typically pyrophyllite) in which it is usually quite difficult to obtain a hydrostatic pressure distribution. A further complication arises when phase transformations start; as the transformation runs there will be an internal volume change that the apparatus may not follow. The large frictional forces between the compression members and gasket material as well as the rigidity of the pressure transmitting medium may easily bridge over the pressure cavity at the specimen when its volume shrinks, or it may contain the extra pressure when its volume tries to expand as in melting. Some alleviation of these problems is obtained when it is possible to surround the specimen with softer materials such as talc, silver chloride, lead, indium, or sodium chloride.

It is obviously not possible to use the simple force-divided-by-area formula to calculate the pressure on the specimen. Instead, a series of calibration reference points are used to calibrate internal pressure in terms of applied force. These reference points are phase transformations in the several elements listed in Fig. 11 (the former and 1970 revised reference points are given). The transitions may be detected by one of the following: (1) volume change; (2) electrical resistance change; or

CONVERSION TO NEW 1970 P SCALE FPB; 5 Jan '71

H. G. DRICKAMER
 Rev. Sci. Instr. 41, 1667 (Nov. '70)

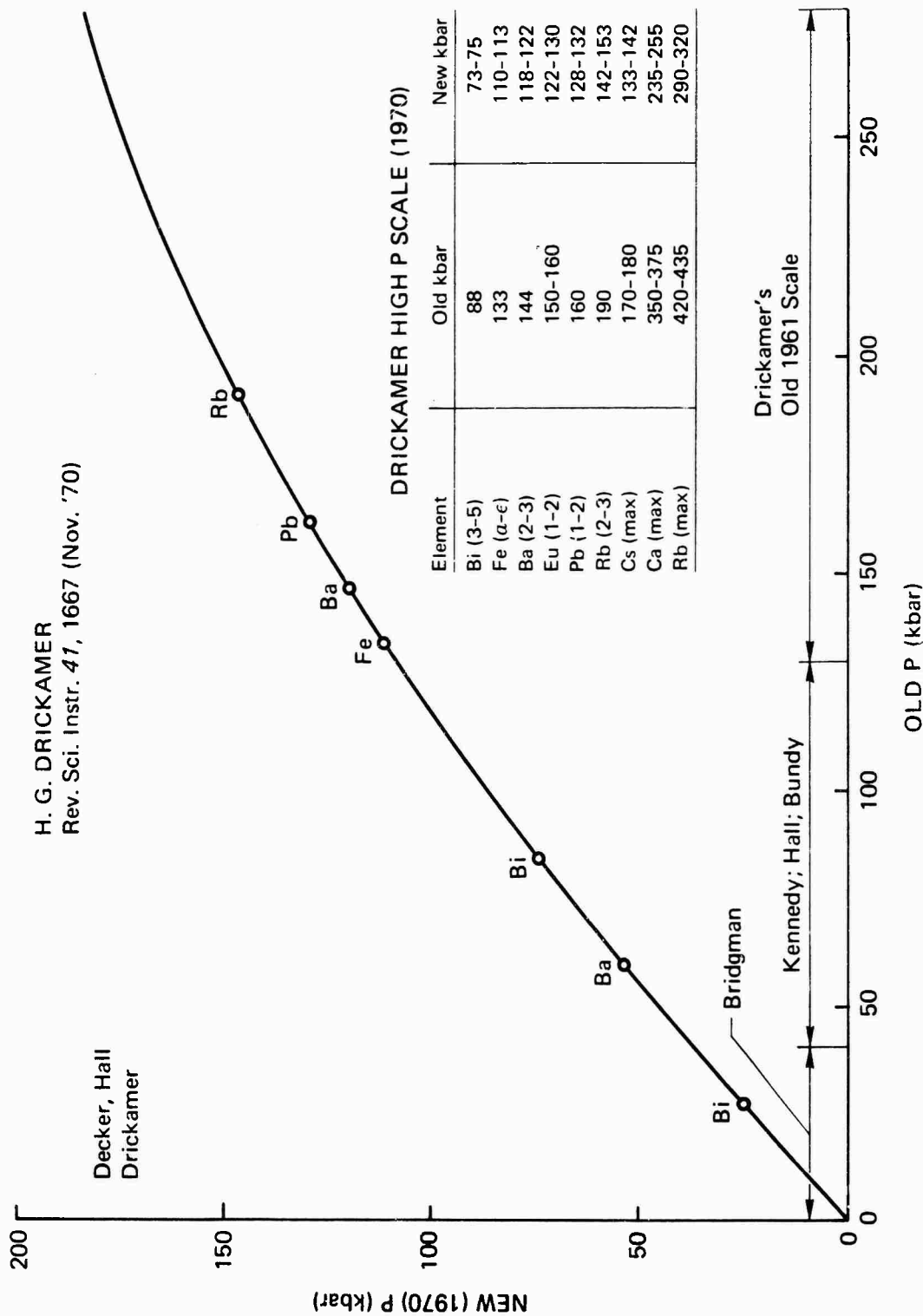


FIGURE 11

(3) structural change (X-ray diffraction). The higher the pressure, the more uncertain is the exact pressure location for the reference transition.

When applying internal heating, the experimenter is beleaguered by a new set of complications. With increase of temperature, the internal parts at first expand increasing the pressure along some inexactly known pressure-temperature (P-T) path until some transformation occurs in specimen or pressure medium, after which the pressure changes rapidly. Talc and pyrophyllite are particularly troublesome in this respect, because at temperatures near or above 1300° C, these materials increase their densities abruptly by modifications in their aluminum silicate structures. Internal pressure decreases of as much as 10; 15 kbar have been noted in heated pyrophyllite media (Strong, unpublished data and (1962).

Thermocouples are almost always used to measure internal temperatures. This method works quite well, but for precise work (determining the slope of a phase boundary), one must recognize that thermocouples wander off in calibration as the pressure increases (Bridgman, 1918; Bundy, 1961; Hanneman and Strong, 1965; Getting and Kennedy, 1970). At prolonged high temperature dwells, it is rather common for the thermocouple to suffer chemical attack or contamination, with loss of accurate calibration.

It is clear then that the high-pressure experimenter will need to recognize several possibilities for error. Sometimes it is possible to approach the problem of measurement from more than one direction to improve reliability. For example: one may observe two phase transitions in the same experiment, one being a more or less established reference point; one may measure the compression of a standardized cell companion material such as sodium chloride; or one may be able to do the experiment in more than one type of apparatus.

The lifetime of a high-pressure apparatus is highly variable but generally short compared to apparatuses used in the 1-to 10-kbar range. Structural materials used are selected for their high compressive strengths and are generally quite brittle. Their breaking points are consequently quite erratic in terms of breaking tension and number of excursions to high pressure. But the skillful experimenter using a well-balanced design can obtain several hundred experiments in a 60-kbar apparatus.

Occasionally, one hears about new apparatus designs having unusual pressure and/or volume capability, for example, in the paper of Vereschagin et al. (1970), the possibility of a static apparatus capable of generating a pressure of 1 megabar is discussed. The anvils in this apparatus were to be made of diamond composite material having an elastic modulus of 60×10^{11} dynes/cm². This modulus is the same as that of cemented tungsten carbide. However, it was suggested that the modulus would reach 75×10^{11} dynes/cm², a calculated value, after the pores

were squeezed out of the composite under high pressure. The matrix material was not described, but its elastic modulus suggests that it may be tungsten carbide. A demonstration of 1-megabar capability has not been reported at this writing.

Many high-pressure apparatus designs are available for selection of one adapted to particular needs. All of them depend for their success upon the principle of massive support to regions of greatest stress. Theoretically, there seems to be no limit to pressures attainable by extension of the principle of massive support, short of a phase transformation in the highly stressed portions of the pressure anvils.

While most apparatuses described are limited to a ~300 kbar pressure at room temperature and ~200 kbar at high temperature, the spherically symmetrical design may have a higher pressure limit. It may be that this latter design can most easily be adapted to extending the pressure range.

3. PHASE TRANSFORMATIONS

With the possibility of subjecting matter to a wide range of pressures and temperatures, the variety of new structures that can be experienced proliferates faster than it can be reviewed. A goodly number of them have been classified and catalogued by Klement and Jayaraman (1967), Wentorf (1969), and Rooymans (1969), whose reviews were a valuable aid in preparing this report.

The different phases of a substance (liquid, crystal type, vapor) each normally have sharply bounded definite regions in p and T space for thermodynamic stability. At a boundary line, two phases are in equilibrium in the sense that the Gibbs free energies, G, of the respective phases are equal, where $G = U - TS + pV$; U is the internal energy, T temperature, S entropy, p pressure, and V volume. For an infinitesimal variation, $dg = V dp - SdT$, and, along the i - j equilibrium-phase boundary, $dG_i = dG_j$. This leads to the Clausius-Clapeyron equation for first-order transformations,

$$\left. \frac{dT}{dp} \right|_{i-j} = \frac{V_j - V_i}{S_j - S_i} = \frac{\Delta V}{\Delta S} ,$$

It is convenient to express dT/dp in degrees/kbar, in which case,

$$\frac{dT}{dp} \text{ (in } ^\circ\text{/kbar)} = 23.9 \frac{\Delta V}{\Delta S} \text{ (in cm}^3\text{/g-atom)} \\ \text{(in cal/g-atom}^\circ\text{ or entropy units, eu).}$$

This defines the direction of the boundary line between the two phases i and j in pressure and temperature space at any p and T for which ΔV and ΔS are known, usually zero pressure. In order for a transformation to proceed across the boundary line from i to j, it must have thermodynamic permission to do so -- specifically, $G_i > G_j$. In many reactions, the application of pressure is a requirement for tipping the free energy balance in favor of j. The energy supplied to the system by pressure is $p\Delta V$ and is usually little more than a few hundred calories to one kilocalorie/mole in high-

pressure condensed-state reactions. Because solids are relatively incompressible (ΔV small), p must be large to generate even this small energy.

Most phase boundary lines are more or less curved. This curvature results from shifts in relative compressibilities, thermal expansions, and heat capacities of neighboring phases as compression advances. Such shifts, on occasion, can result from gradual promotion of an electron from its normal orbital to one of higher energy as in the curvature of the fusion curves of cerium and caesium. Quantitatively, the curvature may be expressed by differentiating the slope with respect to pressure:

$$\frac{d^2T}{dp^2} = \frac{1}{\Delta V} \cdot \frac{dT}{dp} \left[\left(\frac{\partial \Delta V}{\partial p} \right)_T + 2 \frac{dT}{dp} \left(\frac{\partial \Delta V}{\partial T} \right)_p - \left(\frac{dT}{dp} \right)^2 \frac{\Delta C_p}{T} \right]$$

The equation illustrates how changes in compressibility, thermal expansion, and heat capacity affect the curvature.

It is clear, therefore, that pressure always favors the stability of the more dense phase. More often than not, the denser phase also has the lower entropy, but there are several exceptions as in the case of water-ice, liquid and solid germanium, α - γ iron, etc. For these substances the slopes of the phase boundary lines, dT/dp , are negative. There are a few substances for which the thermodynamic properties of adjoining phases are known and the initial directions, dT/dp , of their phase boundary

lines can be calculated, even extrapolated to several tens of kilobars pressure, with fair reliability. The diamond-graphite equilibrium to 40 kbars, 1200° K (Rossini and Jessup, 1938) is a classic example of an effective calculation and extrapolation.

From the viewpoint of the low-pressure phase alone, it is impossible to predict the occurrence or nature of a new high-pressure structure (except by comparing with similar materials as noted below) and to forecast the direction of the equilibrium line separating new and old phases. Molecular orbital theory has not yet developed the ability to decide how the bonding electron orbitals will rearrange their directions and spacings or how they will redistribute their energies. Thus, we discover phase boundary lines in p and T space running every which way without prior notice.

The surprising effects induced by pressure can be illustrated by the high-pressure properties of cesium studied by Jayaraman et al. (1967b). This metal exhibits several solid phases and a dimpled inverted V melting curve (Fig. 12).

- I = body centered cubic (bcc),
- II = face centered cubic (fcc)
- III = collapsed form of II but with 6s electron promoted to 5d with some collapse in volume.

In the upward sloping parts of the melting lines, the solid density is greater than the liquid density; however, in the downward sloping regions, their relative volumes are in reverse order.

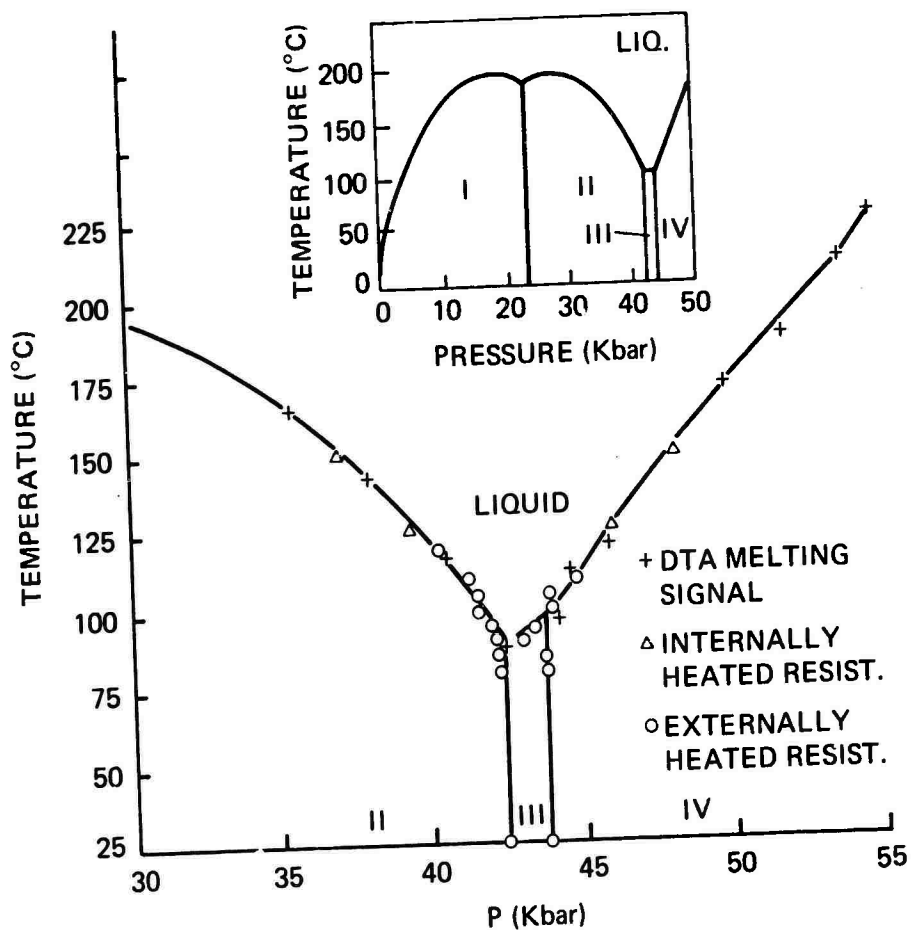


FIGURE 12 Pressure-temperature stability diagram for cesium in the range 30-55 kbar and 25-225° C. The insert shows the fusion curve and phase fields to 50 kbar, modified from Kennedy *et al.*, Physical Review, 126, 1363, (1962).

Reproduced from: Phys. Rev., 126, 1363 (1962).

While there are many surprises of this type, much help in guiding research to new discoveries has come from comparing structures in isoelectronic series of elements and compounds. These isoelectronic families tend to form progressions of similar structures with change of pressure and temperature. Thus, the group IV elements are isoelectronic with each other, differing in respect to total quantum number, n , which runs from $n = 2$ to 6. Group IV elements are likewise isoelectronic with III-V and II-VI compounds, again with total quantum number varying, $n = 2$ to 6. Cross combinations are permitted with n differing for the two elements. However, differences do creep in when the (Pauling's) electro-negativity differences become so large that the normal covalent-type bonding shifts gradually to ionic bonding with salt-like structures replacing the graphite, diamond cubic, Wurtzite, or metallic tin patterns of the group IV elements.

The group IV structure pattern with increasing pressure is graphite (carbon and BN only), diamond cubic (diam) or Wurtzite (Wtz), metallic tin, and fcc lead. The heavier elements may exist stably in structures for which the lighter elements require a great deal of pressure. Thus, silicon and germanium are diamond cubic at zero pressure, while carbon is as stable as diamond at room temperature only for pressures exceeding 16 kbar. Silicon and germanium are stable in the metallic white tin structure at pressures exceeding 100 kbar, and revert back to meta-

stable intermediate structures when pressure is removed (Bundy 1964). For the heavier elements in group IV to attain the more open structures of the lighter elements, negative pressures or reduced temperatures are required. Only white tin exhibits a shift of this sort: from metallic tin to the diamond cubic form when T is reduced.

Several isoelectronic families of elements and compounds may be cited. For example, GeO_2 , BPO_4 , and BeF_2 are isoelectronic with SiO_2 . Again, a structural pattern has been recognized in which, with increasing pressure, we find the sequence quartz \rightarrow coesite \rightarrow rutile $\rightarrow \alpha\text{PbO}_2^* \rightarrow$ possible fluorite or CaCl_2 structure*. Low-pressure SiO_2 has a succession of modifications with increasing temperature: quartz, tridymite, cristobalite, and liquid. But BPO_4 , which occurs in cristobalite structure at zero pressure, transforms to quartz at 40 kbar (Dachille and Roy, 1959). Again, the heavier members have served as prototypes to the high pressure modifications of the lighter members.

This characteristic relation between the high-pressure forms of the light members in an isoelectronic series vis-a-vis the low-pressure forms of the heavier members was extensively exploited by Ringwood and others. (Ringwood, 1969, and Akimoto et al., 1968 and 1971) to explore inaccessible high-pressure phase transformations of

*Nagel and O'Keefe (1971) claim that in TiO_2 and the difluorides, these are probably not thermodynamically stable phases.

the pyroxenes in the deep mantle by studies on various heavier isoelectronic analogues, especially the metal-germanates.

The most important technological outgrowth of reasoning from analogues was the discovery of cubic BN by Wentorf (1957). This material was formed from the low-pressure graphitic structure at pressures and temperatures approaching those needed for diamond growth. Cubic BN is technologically important because it is next in hardness to diamond but chemically different so that it supplements diamond in many industrial applications. Like diamond, two modifications are known: zinc blende (zb) and wtz corresponding to cubic and hexagonal or wtz diamond (Hanneman, Strong, and Bundy, 1967). These two modifications seem to differ little in entropy, density, and other physical properties.

Perhaps other technologically important materials will be uncovered with similar reasoning. Very likely, the new materials, with far-out properties, will be found among the lighter elements of the periodic table. In order that they may persist at zero pressure in their high-pressure modifications, like diamond and cubic BN, they may have to be formed at high temperatures. This will be explained below under general rules and limitations.

a. Certain guide lines for directing high-pressure research towards specific goals are described above. The following list of limitations, trends, and helpful hints may be useful to the high-pressure researcher:

(1) Solid-solid phase transformations tend to spread themselves over a pressure range instead of appearing sharply at the phase boundary line. This is especially true for solids at temperatures well below their melting points. Some over-pressure may be required to form nuclei of the new phase which must then grow. The growth advance can be hampered by intergrain boundaries and impurities or by loss of driving pressure in material adjacent to growing nuclei. The denser transformed material creates a pocket of reduced pressure which may be bridged over by the surrounding material. Finally, the pressure apparatus usually has poor follow-through characteristics so that the volume shrinkage in the sample is not compensated by piston travel. These are the sources of uncertainty in recorded solid-solid phase boundary lines which should be viewed as approximations.

A few solid-solid transformations can be accelerated by additions of a solvent or liquid catalyst to permit freer movement of transforming atoms or molecules. Small amounts of water are very effective in oxide and silicate systems; molten metals are effective in the carbon systems. But, the solvent introduces a second component which can interact with the solid to produce binary phases other than those desired (Wentorf, 1966, and Strong and

Hanneman, 1967).

(2) In transforming to denser states, most substances become more closely packed in the sense that the coordination between constituent atoms increases. The density of packing sequence in many elements in terms of structure is simple cubic (sc) → body centered cubic (bcc) → hexagonal close packed (hcp) → face centered cubic (fcc). Naturally, there are some exceptions wherein the bcc structure is more dense than fcc or hcp due to distortions of electron distributions, as in Yb, Sr, Zr, Ti, and Te.

In groups IV, III-V, II-VI, the succession of transformations, coordination numbers, and properties are: (1) graphite, coordination 3, light elements only, semiconducting in C-direction, metallic conducting in a-direction (carbon only); (2) diamond cubic (diam), zinc blende (zb), or wurtzite (wtz), coordination 4, semi-conducting; (3) metallic white tin, coordination 4 and 2, metallic conducting; (4) lead, fcc, metallic. The structures diam, zb, and wtz differ little from each other in density or entropy but have different stacking orders.

The elements in group IV have pure covalent bonding in the diam structure, but in the III-V and II-VI compounds (zb or wtz), the bonding is partly covalent, partly ionic.

In the heavier II-VI compounds, covalent bonding gives way to predominantly ionic bonding so that in place of the metallic tin structures, the sodium chloride (B1) structure, coordination 6, is found. When sufficiently compressed, B1 transforms to B2, cesium chloride structure, coordination eight.

In the SiO_2 series, and similarly in its analogues, the coordination of Si with oxygen increases in the sequence quartz, coesite, 4-fold coordination; rutile, α - PbO_2 structure, 6 fold coordination; possibly the fluorite structure at still higher pressures, 8 fold coordination.

(3) Very few high-pressure phases persist for long after the pressure is removed. Sometimes, as in the case of germanium, (Bundy, and Kasper and Richards, 1964) the high-pressure phase reverses to a metastable intermediate phase with the same coordination but higher density than the diam form. This inability to return alive most high-pressure forms deprives the researcher of the opportunity to more closely examine and use the interesting properties that might otherwise be available.

The exceptions to the usual behavior are found mostly in those forms that require both high pressure and high temperature to run the transformations. This implies that a substantial activation energy barrier normally retards the

rate of the transformation in either direction. Diamond and cubic BN, both formed at high temperature, are the best examples of persistent metastable forms at zero pressure. Coesite and stishovite (rutile structure) high-pressure high-temperature modifications of SiO_2 also persist at zero pressure. Both of these latter minerals were found in the Canyon Diablo Meteor Crater where they were formed by an impact which occurred at least 20,000 years ago.

There are a few instances in which stubborn-type transformations will run at moderate temperatures when the pressure is greatly in excess of equilibrium. The formation of cubic diamond, hexagonal diamond, and both zb and wtz BN are examples in which pressurizing to from 0.3 to 1.5 megabar causes the transformations to run in microseconds at temperatures $\approx 1,000^\circ \text{C}$. In these examples, the reaction paths are altered by the severe compression so that the activation energy barrier is greatly reduced.

Actually, these ultra-fast reactions may represent an example of Libby's (1962) proposal that materials compressed into the metallic state might transform into a non-metallic state (stable or metastable) upon release of pressure. The metallic bond's non-directional character, would offer no hindrance to directional bond formation. Dynamic shock compression brings carbon very close to the metastable metallic liquid state of graphite where

bond directionality may be largely erased permitting the rapid transformation to diamond.

(4) Many elements melt from the bcc structure which tends to be the predominant high-temperature form. The bcc phase of iron at just below the melting point persists to ~ 52 kbar, $1,718^\circ$ C where there is a triple point between liq, bcc, and fcc iron (Strong, unpublished data 1972). Above the triple point, iron melts from a fcc solid. Copper, silver, and gold are other exceptions which are fcc at the melting point.

(5) So far, there is no evidence for a solid-liquid critical point comparable to a liquid-gas critical point, in any substance. However, at extremely high pressures, it is expected that the difference between solid and liquid will gradually fade away as the increasing compression permits a closer approach to the Thomas-Fermi state of ions embedded in a sea of electrons.

It is fortunate that not all elements undergo high-pressure phase transformations within the explored pressure ranges. Some stable materials are needed for apparatus, lead wires, thermocouples, capsules, heaters, probes, etc., in high-pressure experimentation. The important stable elements are: (1) the "hard" metals V, Nb, Ta, Cr, Mo, W; (2) the group IB metals, Cu, Ag, Au; (3) the platinum-group metals Rh, Ir, Pd, Ni, Pt; and (4) the group III metals Al and In. Aluminum has been subjected to megabar pressures with no sign of solid-solid phase transformation. Amongst the high melting-point hard metals, only Ta and Mo have had their high-pressure

fusion curves determined: Ta from 2996° C at zero pressure to 3500° C at 60 kbar (Fateeva and Vereschagin, 1971), and Mo. No change in the solid structure of Ta or Mo was reported in these experiments.

In recent years, interest has been running high in binary and ternary oxides, chalcogenides, fluorides and chlorides, etc. Among these compounds, a seemingly endless variety of combinations are emerging, many with interesting properties, including magnetic, ferro-electric, optical, tunnel lattice passages (possible solid electrolyte), band gap materials, etc.

Formation of these interesting materials sometimes requires pressure at high temperature, which helps to insure their stable metastability at room conditions. The pressures required are generally less than 60 kbar.

Some of the persons who have published in this area are: Singh, Jayaraman, Chatterjee (1971); Yu and Geliessse (1971); Rooymans (1965, 1969); Goodenough, Kafalas, Longe (1972); Goodenough (1972); and Previtt and Shannon (1969).

b. Anticipating new forms of matter bears a likeness to weather forecasting; one relies largely on recognizing patterns. The thermodynamic approach is helpless without data on properties of both phases. The molecular orbital approach is also of little use because the structures are far too complex for mastery. But patterns of behavior there are; and as we have seen, these have been useful. Meanwhile, gradual progress is being made in analyzing structures, and measuring or calculating expansion and compressibilities of high-pressure phases (for example, the works of Decker, 1971;

Jamieson, 1960, 1963, 1964; Kasper, 1969; and Swenson, 1971, have contributed substantially in this area).

Plendl and Gielisse (1969) have proposed an interesting method for anticipating structural changes associated with either a temperature or a pressure increase. They noted that the compressibility of many substances followed a linear relationship with $\rho \frac{ZE_B}{r_0^3}$ in which r_0^3 is proportional to volume/atom in the crystal, Z the valence, E_B an energy constant identical with the stationary energy of an electron in the L-orbital corresponding to total quantum number $n = 2$ in the Bohr energy term,

$$E_B = \frac{2\pi^2 e^4 m_0}{n^2 h^2} = 5.448 \times 10^{-12} \text{ erg. } \rho \text{ is the ratio of coordination}$$

numbers in the modified state vs the "base state." For many materials $\rho = 1$ and a plot of compressibility vs $\frac{ZE_B}{r_0^3}$ yields a straight line. For $\rho > 1$, the material is said to be in an "elevated" state and may be brought back to the base state by a reduction of pressure or increase of temperature. For $\rho < 1$, the material is in a "reduced" state and may be transformed to the base state by means of increased pressure or reduction of temperature. Their results were applicable to some 90 binary, ternary, or quaternary solids having 25 different structural types and valences from one through six.

In a somewhat related development, Previt and Shannon (1969) have shown how effective ionic cation radii in oxide and fluoride crystal structures are related to the volume of the unit cell. They showed that in isotypic series of rutile structures or jadeite structures, the unit cell volume is a linear function of the cation radius cubed. For example, in rutile, RO_2 , structures where $R = \text{Si, Ge, Cr, Ti, Pt, Mo, Sn, Pb, etc.}$, unit cell volume is a linear function of r^3 for cation R radii. It is particularly interesting

that in the case of $R = \text{Si}$, SiO_2 is in the high-pressure stishovite form. This fact suggests that their empirical rule has predictive capability for new crystal compositions in various complex oxide structures that may be derived by using pressure to adapt either smaller cations (i.e., Si in rutile) or larger cations (i.e., In^{3+} , Tl^{3+} in corundum) into structures already well known as low-pressure forms. In this way, the variety of physical properties available may be greatly extended. Many oxide and di-fluoride structures formed at high pressure and temperature are recoverable at zero pressure.

Melting behavior under pressure continues to receive considerable speculative attention. During the past several years, a number of melting-point extrema have been observed, such as the melting-point minimum for cerium and the maxima among the alkali metals. It has been suggested by Yoshida and Okamoto (1971) that with continued compression, the potential energy of crystal-bound atoms can increase faster than those in the liquid state until the difference between the two energies becomes less than kT , when the crystal will melt. They have had some success applying their calculations to cesium and rubidium melting temperature maxima. The occurrence of maxima melting curves have been proposed as "normal" melting behavior by Kawai and Inokuti (1968). Maxima have not been seen in the more incompressible elements.

Looking far into the future, we may see more electronic transitions of the type already demonstrated in both cesium and cerium. Izmailov and Shuliman (1966) have suggested that under compression, states with higher orbital quantum numbers tend to become filled as compared to free atoms or low pressures where these states remain unfilled. Hence, if all atoms were sufficiently compressed, a new

periodic table of the elements could be generated. The pressures needed may be in the range of 3 to 40 mbars for many elements.

4. CHEMICAL SYNTHESIS

Sometimes high pressure is useful in the simple role of mechanical confinement, i.e., keeping volatile substances imprisoned while they participate in high-temperature reactions. Thus, Munson (1968) synthesized IrS_2 and NiAs_2 in the pyrite structure and Rooymans (1967) and others describe the synthesis of many spinels and chalcogenides. CrO_2 and PbCrO_3 were synthesized at 60 kbars, 1500°C by Devries (1967) and Devries and Roth (1968). Pressure confined the high oxygen or sulphur vapor pressures during the reactions. Forming alloys or intermetallic compounds between metals of widely separated melting points can likewise be aided by this technique, for example, Ti-Mg alloys (Oriani and Strong, 1966). In one of the very early high-pressure reactions, Bridgman (1964) polymerized CS_2 at ~ 30 kbars, 200°C .

The latter example illustrates the far reaching effects of high pressure on organic reactions, that may be radically altered in character, rate, or both. Thus the decomposition of acetone may be prevented by pressure and its polymerization greatly accelerated at 350°C , 40 kbars (Bengelsdorf, private communication, 1958). Bengelsdorf (1958) reported the rapid trimerization of aromatic nitriles to triazines at 30 to 50 kbars. In like manner, the dinitriles such as succinonitrile and malononitrile are rapidly polymerized in the solid state at 450°C , 50 kbars (Hara, 1970).

Pressure does not always aid chemical reactions constructively. In an opposite role, Bengelsdorf (private communication, 1959), found that when compressed at 35 kbars, 30° C, bicycloheptadiene was completely unstable and carbonized in 45 minutes.

In thinking about chemical reactions, one must consider the activated state of the reacting molecules in which the Gibb's free energy is higher than that of the reactants or products. Generally, the volume of the activated state is different from that of the reactants and products. Activation volumes commonly lie in the range $\pm 25 \text{ cm}^3/\text{mol}$ for organic reactions. If the activation volume change is $\Delta V^* = \pm 10 \text{ cm}^3/\text{mol}$, a pressure of 40 kbars will contribute 10 kilo calories to the free energy of the activated state; an amount approaching the chemical reaction energy. Thus, one can easily see that pressure will greatly affect the reaction rate through the term $p\Delta V$. For negative ΔV values, the reaction will be speeded up -- possibly beyond the need for catalysts if the final product is more dense than the reactants. For positive ΔV , the reaction may not occur at all or may seek some other reaction path and product with more favorable ΔV 's.

For more complete discussions of high-pressure effects in organic chemistry see Weale's (1967) review of basic principles, techniques, and results of studies in 1- to 15-kbar range; Kohnst's (1970) discussion of kinetic effects of pressure; Gay's (1971) review of pressure dependence of activation volume; and R. E. Hanneman's "Effect of Pressure on Phase Transformation Rates," (1969).

5. OVERSEAS ACTIVITIES IN HIGH PRESSURE

The open literature, a few meeting summaries, and personal observations from some of General Electric Company's representatives in Europe and in Japan provide impressions about activities in high-pressure technology on the foreign scene. It seems clear that there are very many people engaged in this type of research and, in Japan at least, the number of people so engaged is still increasing. The research in which they are involved spans the same broad spectrum as U. S. work. In addition, some of the Europeans seem to have more background in the areas of supercritical fluids and mechanical extrusion than do Americans. In other areas, high-pressure work is still a novelty and researchers are happily engaged in redesigning and calibrating high-pressure gear. In this summary, Russia, Europe, and Japan are considered separately.

a. Russia: Russia has a large institute, located near Moscow and directed by L. F. Vereschagin, for high-pressure research. The Russians publish many papers on the subjects of apparatus, superconductivity, and phase transformations in mineralogic substances, diamond, and cubic BN. Most of their publications relate to the latter two topics and many of these are only one or two pages long, revealing little essential detail.

The Russians often refer to their 50,000-ton press and associate this press with their plans for generating one megabar pressures. However, no description of the apparatus that is to support this pressure has been seen, and no evidence has been offered for having attained pressures near one megabar.

Some of their work on superconducting materials and geologic minerals has been a first-rate pioneering effort. Their publications relating to diamond and cubic BN contain nothing significantly new or different from the U. S. contributions on these topics. A good portion of their diamond work is considerably behind U. S. work, while their cubic BN work runs about even in recent years.

The Russians have succeeded in growing diamond whiskers at low pressure and have made some progress in obtaining n-type diamond by ion implantation. The diamond whiskers, according to first-hand reports from their makers, have no technological value. The n-type diamond development could be useful because only p-type can be formed in growth.

b. Europe: There are many high-pressure research groups scattered throughout Western Europe, probably none of them as large individually as the Institute in Moscow. All of these laboratories are turning out a great deal of work on various kinds of electrical measurements under pressure, phase transformations and structure work, particularly with chalcogens and oxides of transition metals, and geophysical studies. An interesting type of study on supercritical liquids has been going on for many years at Karlsruhe under E. U. Franck. Ion mobilities, etc., are being measured under pressures ranging from 10 to 100 kbars. Another pioneering effort on metal extrusion and mechanical properties has been in progress for many years under H. Ll. D. Pugh in Scotland. Other laboratories seem to be

studying the types of things that have been done in the U. S. -- phase transformations, structures, electrical, magnetic, superconduction, and Hall-effect properties. A good deal of effort has been expended, probably needlessly, redesigning apparatus and elaborating on calibration. On the whole, European work seems to be of good quality.

c. Japan: The Japanese are very ambitious and this is reflected in the variety and quality of their work. Their high-pressure activities are widely scattered in Japanese industries and universities and are conducted individually or in small groups. The range of work includes theory, geophysical research, neutron diffraction, radioactive decay under pressure, organic reactions-- polymerization, diamond and cubic BN, phase transformations, structure and electrical conductivity studies down to liquid helium temperatures, and melting phenomena.

While their diamond and cubic BN work is virtually a duplication of U. S. work, in other areas they seem to be opening new ground and may have improved apparatus with greater than 300-kbar capability.

The Japanese have done well and are expanding their efforts.

d. Summary: The products of all the thousands of high-pressure experiments conducted all over the world represent great strides in understanding matter, structures, and geophysical problems of the deep mantle but have resulted in only two technological products, diamond and cubic BN.

The small, independent laboratories of Europe and Japan have been most effective in producing a large variety of innovative scientific and technological results. The concentration of effort into a single large institute has been effective in Russia for focusing on a few restricted areas such as diamond and cubic BN and for advancing their own technological skill with these materials.

6. RESEARCH RECOMMENDATIONS

In conclusion, it seems desirable to comment on a number of problem areas of relatively direct interest to the DoD.

a. Development of 1-Megabar Pressure Capability:

This problem was discussed in the apparatus summary. It is suggested that an apparatus project patterned after Kawai's spherical design may be effective. Tungsten carbide anvils seem to have given Kawai good results; however, some of the new tungsten-carbide-backed diamond compact materials might be useful as well for the anvil tips in the spherical design.

As a first step, 400- to 500-kbar pressure capability would be quite rewarding, but it is difficult to know when one of these higher goals has been achieved. One suggestion for a possible high-pressure reference point would be the direct transformation at room temperature of graphite to diamond, which should run at 400 to 450 kbar (Bundy, 1962). This transformation at room temperature has never been reported.

b. Material and Property Investigations: An example of possible technologically important products of high-pressure research are the alkali antimonates described by Goodenough. These compounds have tunneled structures that may be useful in energy storage as solid-state electrolytes in a battery. Inquiry into this development might lead to further useful research towards a product.

Another example is laboratory-made gem-quality diamonds with tailored properties. These have controllable properties of high purity, thermal and electrical conductivity, optical characteristics, abrasion resistance, and strength.

An analogous potential exists for unique electrical and optical properties in cubic BN crystals as new high-pressure growth methods now under development yield a variety of crystals. Fundamental property studies of such crystals will be required along with more practical problems, such as metal to boron nitride bonding with acceptable electrical resistance for device considerations.

These three examples: (1) tunnel structured dielectrics, (2) diamond with tailored properties, and (3) cubic boron nitride with tailored properties offer potential for unique physical properties over existing materials for helping to meet DoD needs, especially in device technology. One possibility is the use of high-purity laboratory diamonds in electronic devices as either: (1) "heat sinks," or (2) as Schottky-barrier diodes. Their suitability as heat sinks has already been proven. Their potential for diodes needs more study. The diode application is attractive because of the self-cooling property

of diamond not found in any other existing diode material. There is consequently the possibility of attaining higher power levels in diamond than is presently done in other diode materials.

The identification of a suitable material for a specific application would have to be followed by practical engineering work on crystal growing, purification, fabrication, device development and economic studies.

While many new forms of matter have been identified in high-pressure research, there are surely many more hidden from view that have some small chance of being technologically important. Consequently, the continuation at moderate funding of systematic materials research, guided closely by theory, to be conducted at several small laboratories will serve the human need-to-know. Also, it is the method by which progress in high-pressure research in other countries may be followed.

c. Superhard Bearing and Cutting Tool Materials:

These items are considered together because both are likely to have the same material-problem solution.

The question of whether there are better superhard materials has been reviewed by Prendl (1961), Prendl and Gielisse (1962), and by industry. There is a close correlation between crystal cohesive-energy density and abrasive hardness of materials (see Fig.13). Diamond remains unexcelled with a cohesive-energy density of 1400 kcal/cm^3 . Abrasion resistance, compressive strength, and friability of synthesized diamond and cubic

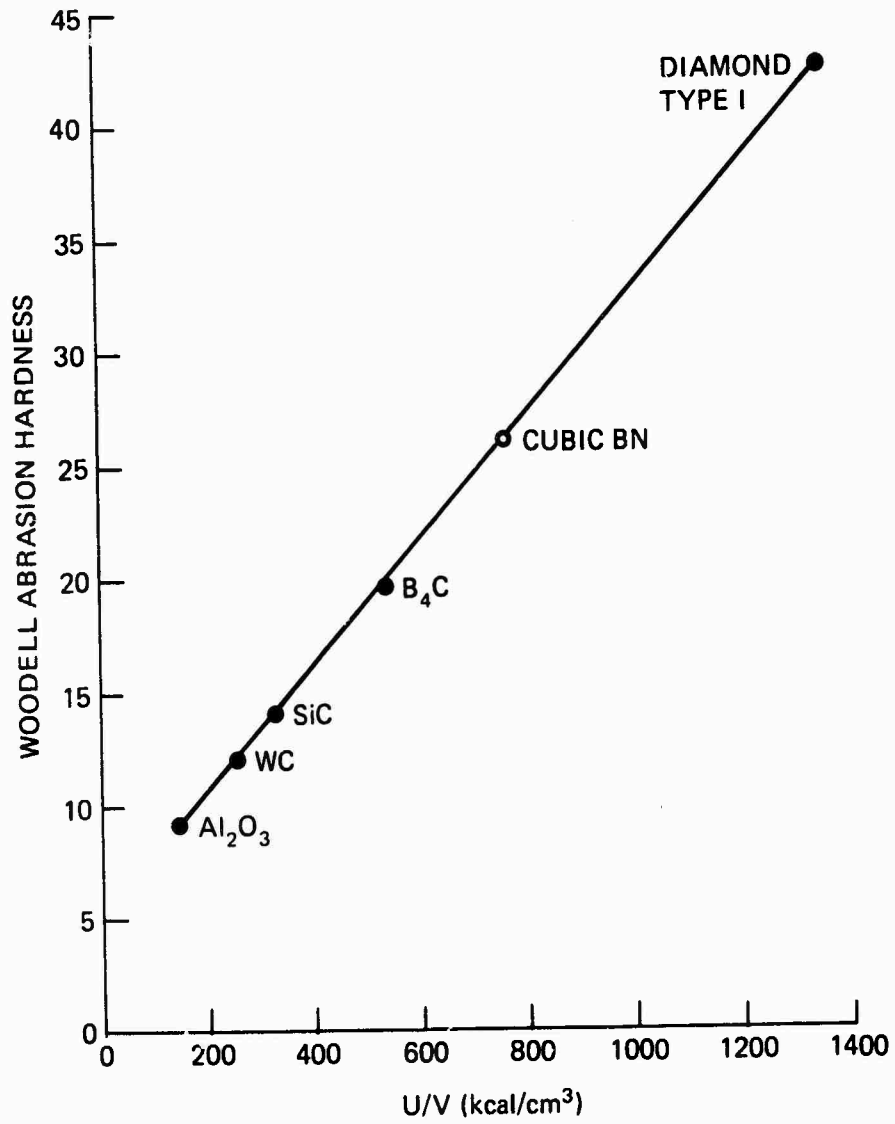


Fig. 13 Relation between density and hardness.

BN crystals can be altered considerably by impurity and process control.

It has been possible to enhance further the utility and application of diamond and cubic BN by forming densely sintered compacts of small crystals of these materials. In some cases, these compacts are bonded to a high-strength tungsten carbide substrate. The diamond and cubic BN crystals may be work-hardened somewhat in the sintering process and the random orientation of the crystallites block cleavage crack propagation. These very recent developments, proposed earlier as a need by DoD, have now gone through the laboratory development stage as well as extensive engineering development, practical trials in real production settings, and cost effectiveness and marketing studies. These unique new products represent a breakthrough in cutting tool technology that should have important impact in machining a wide range of ceramic and composite materials as well as difficult-to-machine alloys. Detailed studies of the mechanisms of tool wear and failure and a re-definition of machinability criteria and parameters will be required for this new class of tools to accelerate their use broadly. The preliminary indications are that benefits can include much higher material removal rates, improved surface integrity, and greatly extended tool life. Limited applications to date of DoD interest have included machining of missile nose cone materials, submarine bearing seals, ceramics, composites, and superalloys. In addition, superhard compact materials are being adapted for bearing materials, wire drawing dies, and other applications.

Among the problems listed by DoD were those of shaping boron nitride and sapphire. These are presently most easily handled with diamond tools, including diamond-studded saws, grinding wheels, and single point diamond tools. However, abrasive and cutting properties vary between diamonds. For single-crystal diamond tools, low-nitrogen type II diamonds may be more durable than the "run of the mine" nitrogen-containing diamond. In some problems of this type, it is quite possible that much help can be gained at no cost to DoD by consulting people with wide experience in industrial diamond applications.

The cutting tool business is a very active and highly competitive one. The motivation for new developments within the industry is intense so that there are frequent significant improvements being made. The DoD is sure to benefit by the efforts being made in the private sector on cutting tool problems and will be able to accelerate the adoption of these developments through substantial support in new machinability studies and fundamental analyses of machining processes involving new compacts of superhard materials. It is this limitation of machinability understanding that appears to be limiting the rate of adoption of these new tools in certain key areas at this time.

It is intriguing to consider possible new hard structures formed from one or more combinations selected from the elements C, B, N, Be, Si, Al, and P. While B and N substitute easily in diamond, it has not yet been possible to form a hybrid crystal of NBC or to form a two-phase system of BN in diamond, or inversely, diamond in cubic BN. The possibilities among these seven elements

have not been exhausted, but there are no uniquely promising leads at present. If it were possible to obtain the metallic states of SiC, BN, or diamond, it would be interesting to try again to form hybrid, or two-phase, crystal systems. Probably pressures in the 60- to 150-kbar range at high temperatures would be needed to induce new reactions of interest.

It is not likely that any of these would be harder than diamond, but they might have chemical characteristics that qualify them for cutting work not fully suited to diamond or BN.

A program of study of this type should probably have only fairly modest support at this stage.

d. Metallic Hydrogen: It has been suggested that metallic hydrogen would be a high-temperature superconductor and therefore a worthy goal for high-pressure research but all speculation relating to metallic hydrogen is very "iffy."

The pressure needed to induce the metallic state is presently estimated to be between 1.7 and 5.6 megabars; however, even this range is uncertain. The corresponding density was estimated at 1.6 gm/cm^3 . Comparing this with its S T P density, 0.00089 gm/cm^3 , it would seem fairly unlikely that the metastable phase of this material could be frozen-in at atmospheric pressure.

Another unsolved problem is that of introducing the hydrogen into the high-pressure cell.

For the present, the pressure and the handling techniques are not available to start this project. Two parallel approaches appear to be justified at this stage regarding metallic hydrogen. First, a more adequate theoretical study of the metallic hydrogen transition should be considered now that includes the more advanced molecular orbital approaches successfully being adopted recently to other solid-state materials. Such treatments could probably be adopted to the metallic ammonia transition. Secondly, it is suggested that with the possible extension of the pressure range to 500 kbars, the metallic ammonia problem might be a good place to start experimentally. As pressure equipment and capability evolve, metallic BN and SiC might occur and finally, metallic carbon and metallic hydrogen might be obtained. Any experimental program on metallic hydrogen should await a more thorough theoretical evaluation of the properties and transition conditions.

e. Superhard High-Density Materials for Penetration:

There does not seem to be any better generally available material than tungsten carbide for penetration. The properties of tungsten carbide have recently been improved by a hot pressure sintering method.

Any new, more dense, hard material generated by high pressure is likely to be too expensive for large volume application to projectiles. Therefore, this is not a promising project for high-pressure research and does not justify significant support.

f. Summary: Our consideration of the opportunities for the application of high-pressure research to technological materials and properties advances of relevance to DoD shows substantial promise for only selected areas.

This is partly the case because of the inherently small volumes that are achievable at very-high-pressure conditions, partly because of the very high intrinsic costs of high-pressure process, and partly because of the difficulty to "freeze-in" certain phases or properties achieved upon return to atmospheric pressure. The most promising opportunities appear to lie in: (1) the processing and use of very high unit value high-pressure materials such as diamond or cubic BN for tailored applications ranging from devices to cutting tools, and (2) unique high-pressure processing of "low pressure materials" (such as extrusion, drawing, and deformation of metals, and sintering of ceramics). Significant contributions to other carefully selected technological and scientific problems will be made by both theoretical and experimental studies using pressure as a key variable, but these should be carried out on a more modest basis.

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APPENDIX E
CALIBRATION OF THE SUPPORTED TAPER
CELL FOR ELECTRICAL WORK

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In Appendix D Dr. Strong indicates the pressure limitations on various types of equipment as seen by the General Electric Company. It seems desirable to include a note on the calibration of the tapered piston cell for electrical work to permit people to judge the methods of calibration and the pressure limitations. It is important to note that all the results discussed were obtained using tungsten carbide pistons with 3% binder. The pistons were thoroughly work-hardened and reground as described in the original papers. Failure to work-harden provides a very severe limitation on the pressure range.

In 1960 a high-pressure electrical resistance cell was developed in the University of Illinois laboratory,¹ utilizing the supported taper principle previously applied to an optical apparatus.² The calibration of the electrical cell was tenuous since it was based on some poorly located phase transitions at low and moderate pressure plus a gross extrapolation of Bridgman's electrical-resistance data for platinum.³ Since that time a number of transitions have been located more accurately and x-ray diffraction techniques utilizing the tapered piston cell⁴ have become available.

A new calibration, based largely on x-ray diffraction work, is presented here. The piston diameter and

internal geometry of the x-ray cell can be made identical to the electrical cell (22 mm in diameter, 2 mm flat, 18° taper), but the x-ray cell contains a layer of lithium hydride and boron with platinum collimation in addition to pyrophyllite, while the electrical cell contains only pyrophyllite. Nevertheless, this calibration represents a considerable advance over the previous one. Many of the calibration data were taken with Al or Ag powder, using the shock data of Rice et al.⁵ interpolated to room temperature.⁶ The 111, 200, 220, and 311 lines were utilized. Above 250 to 300 kbars, the dishing of the pistons made it impossible to obtain the 220 and 311 lines clearly. Data were also obtained for NaCl to over 200 kbars. Applying Decker's calculated p-v values for NaCl,⁷ the Al and Ag data were closely checked. MgO⁸ also gave consistent results to 300 kbars.

The calibration is established as follows: The pressure is a linear function of applied force to 100 kbars (and substantially linear to 130 kbars). For higher pressures the change of pressure (from 100 kbars) vs fractional change in applied pressure is shown in Table I. This was obtained by taking the fractional change in pressure with the fractional change in applied force from the x-ray data to 400 kbars and extrapolating primarily by assuming the relative pressure is a linear function of the logarithm of the relative applied force at pressures above 400 kbars. (This condition holds quite well in the range 300 to 400 kbars.) X-ray data above 400 kbars are limited. There are a few x-ray data (e.g., on the 111 and 200 lines of Ag, which extend to 475 kbars). X-ray data on CsCl⁸ to 450 kbars fit very closely

the extrapolation of shock and other data by the Born-Mayer or Mie-Grüneisen equation.

In Table II appear the old and new pressures obtained from typical calibration curves for a number of transitions. These are not presented as standards. The CdS maximum has been reproduced in several laboratories. By 450 to 460 kbars the resistance of CdS has dropped to ~60% of the maximum. By ~460 to 440 kbars the resistance in ZnS has dropped by 20% from its maximum value at ~420 kbars. Another possible point involves the rather distinct increase in resistance for barium at ~420 kbars and 77° K. By 500 kbars it has increased about 70% from the value at the shallow minimum near 400 kbars. This point is of use only at 77° K. It is of interest to note that the transitions in the low pressure region generally agree reasonably well with recent values obtained in other laboratories.

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TABLES

TABLE I. Electrical Cell Calibration. Pressure vs. Applied Pressure. (Related to pressure necessary for 100 kilobars.)

Pressure (in kilobars)	P_{APP}/P_{100} kilobars
100	1.00
130	1.32
150	1.60
200	2.50
250	3.80
300	5.60
350	8.20
400	12.00
450	16.70
500	24.00

TABLE II. Approximate Location of Transitions.

	Old	New
Bi	88	73-75
Fe	133	110-115
Ba	144	118-122
Eu	150-160	122-130
Pb	160	128-132
Rb	190	142-153
Cs ^a (max)	170-180	133-142
Ca ^a (max)	350-375	235-255
Rb ^a (max)	420-435	290-320
CdS ^a (max)	460	320-340
ZnS ^a (max)	550	410-420

^aMaximum in resistance-pressure curve.

APPENDIX F
SOME KINETIC PROBLEMS IN
VERY HIGH-PRESSURE RESEARCH

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The effects of pressure on kinetics of reactions and phase changes in condensed systems have been reviewed elsewhere.¹ In this appendix some high-pressure kinetic phenomena that are not well understood, in particular marked pressure enhancements of crystal growth rates in some systems, will be discussed. A satisfactory understanding of these effects would provide valuable guidance for high-pressure synthesis. Also the problem of retention of phases, formed in high-pressure synthesis, upon the release of pressure will be discussed.

1. ENHANCEMENT OF PHASE-TRANSFORMATION RATES BY APPLICATION OF PRESSURE

The frequency of a kinetic process can be considered to consist of the product of a thermodynamic and a kinetic factor. The thermodynamic factor is some function, $f[\Delta G(P,T)]$ of the Gibbs free energy change $\Delta G(P,T)$ accompanying the process and it is expected to vary rather slowly with pressure. Considered here are kinetic effects so large that they imply marked increases in the kinetic factor $k_1^0(P,T)$ with pressure. Examples are the large pressure enhancements of crystal growth rates in amorphous B_2O_3 ^{2,3} and SiO_2 ⁴ at quite low temperatures and in transformations generated by shock waves. The pressure effects on the crystallization of amorphous B_2O_3 are especially striking. At low pressure even seed

crystals which have been melted back fail to grow at measurable rates in the undercooled region. However, substantial growth occurs even at quite low temperatures upon application of 10 to 30 kbars of pressure.

It has been found that the kinetic time constants for crystal growth usually scale roughly as the shear viscosity of the melts into which the crystal is growing. Since the activation volumes for viscous flow are generally observed to be positive, the marked pressure enhancements of crystal growth were quite unexpected. Three sorts of explanations have been offered for these effects. The first explanation is that the structure of the melt changes with increasing pressure to configurations more conducive to crystal growth. The second explanation is that the increase in driving free energy due to pressure application markedly increases the fraction, f , of growth sites in the crystal surface.⁵ The effect of pressure on f could be marked if there were large potential barriers to monolayer nucleation on the surfaces of the crystal normal to the growth direction. In the simple theory for two-dimensional nucleation, the parameter which largely determines this barrier is σ_e , the edge tension of the monolayer in contact with the melt. Increasing pressure could change the melt structure in a way such that σ_e would be reduced or it might increase $|\Delta G|$ with the result that the barrier to two-dimensional nucleation would decrease--in particular, the radius, r^* , of the critical monolayer is $r^* = -\frac{\sigma_e \bar{V}}{\Delta G}$ and the thermodynamic barrier to monolayer nucleation is $\pi \lambda r^* \sigma_e$ where \bar{V} is the molar volume of the crystal and λ is the monolayer height. Finally the third explanation main-

tains that impurities catalyzing crystal growth might be retained in larger concentrations at the higher pressures.

a. Effect of Pressure on Melt Structure: As pressure is increased, systems tend to evolve toward structures in which the binding is less directional and the number of nearest neighbors is increased. In this evolution the nearest neighbor separation might also increase but the effect of this on specific volume would be more than offset by the increased coordination number. Thus, covalently bound systems tend to be transformed by increasing pressure into structures with binding that is more ionic or metallic in nature. The atomic mobility in the liquid states of these systems, owing to the greater interatomic separations and non-directional binding, is likely to be much greater than in covalently bound liquids at equivalent specific volume and composition. Crystal-growth kinetic constants are expected to be similarly scaled.

By this mechanism the resistance to crystal growth in a molten state, in which the binding was mostly covalent initially, might be decreased markedly by application of high pressure. As has been recognized, this effect may account for some of the anomalously high rates of transformation produced by shock waves. It may also be an important factor in the lowered resistance of fused silica to crystallization at high pressure. However, the similar effect in B_2O_3 may be more complicated in view of the large apparent disparity between resistances to melting and crystal growth in B_2O_3 at ambient pressures.

b. Effect of Pressure on Fraction of Surface Growth Sites:

Some possible phenomenological causes for the effect of pressure on the growth-site fraction, f , have been indicated already. If screw dislocations emerge in the surface of the growing crystal the growth-site density/area will scale approximately at $\frac{1}{r^*}$, meaning that a relatively large value of σ_e can lead to a slow growth rate even if the crystal is imperfect. On the other hand, the melting-site fraction, and hence the melting rate, can be much greater than the corresponding quantities for growth, owing to the finiteness of the crystal surface area. Thus, the growth and melting behavior of B_2O_3 at the ambient pressure might be explicable in terms of a relatively large σ_e for this system. Application of pressure might reduce σ_e by effecting some change in structure of the melt (e.g., the "boroxyl" type of short-range order suggested for B_2O_3 glass by Mozzi and Warren⁶ might transform to a type of short-range order more similar to that in B_2O_3 crystals; also r^* might fall with increasing pressure due to the concurrent increase in $|\Delta G|$).

c. Retention of Catalyst Impurities at High Pressure:

High pressures may be applied to extend greatly the range of compositions at high densities in monophasic systems. Such systems often are especially well adapted to rapid growing of crystals with satisfactory perfection. One of the best known of crystal-growing techniques of this type is hydrothermal crystallization.⁷ In this method a high temperature solubilizes the crystal nutrient in a fluid medium while the application of pressure maintains the medium at a high density.

It is possible that similar growth processes may occur at high pressure when the amount of solvent is small relative to that of the crystallizable material, CM. For example, suppose that at high temperature and pressure the binary system H_2O -CM can phase separate into nearly pure CM and a concentrated fluid solution of CM in water. Then a concentrated H_2O -CM solution could form from a very small amount of water and serve as a medium for rapid transport of CM from some metastable to a more stable crystalline state. Similar processes can occur at the ambient pressure (e.g., in the devitrification of GeO_2 glass, when the solubility of CM in H_2O is high enough).

Impurities either localized or adsorbed at interface also may catalyze crystal growth, especially in covalently bound systems, without the separation of an impurity-rich fluid phase. Application of high pressure can lead to the retention of high concentrations of these impurities to much higher temperatures than would be permitted at low pressure. This provides an additional mechanism for the pressure enhancement of crystal growth rate.

2. RETENTION OF PHASES SYNTHESIZED AT HIGH PRESSURE

Phases, β , formed by application of high pressure may revert to the initial low-pressure, α , phase by nucleation and growth or by a spinodal mechanism.⁸ Spinodal reversion might occur if the new structure developed a compositional or a shear instability upon removal of the pressure.

It would be extremely difficult to eliminate the heterogeneities, impurity particles, and imperfections, that

might serve as centers for a nucleation and growth reversion of β to α . Consequently, the most practical approach to the problem of retaining phases synthesized at high pressure is to find conditions in which the rate of growth from the α nucleation centers, or, in spinodal decomposition, the amplification rate of fluctuations, is negligible. If the kinetic factor in the growth or amplification process is thermally activated, it should be possible, in principle, to select for the pressure release a temperature that is low enough so that the β will be retained. However, there are a number of "shear-type" transformations, especially in metal systems, in which the propagation or amplification process apparently requires no thermal activation. In the event that such a shear mode is possible for the reversion of β to α , it would seem difficult, if not impossible, to retain β , at least in substantial quantities, after the pressure release.

It is interesting to consider the problem of the retention of a metallic phase of hydrogen if it were synthesized. It appears that one of the main mechanisms of decomposition of this phase would be the association of hydrogen atoms at the surface. This process would ultimately be limited by the frequency of dissociation of atoms from surface kink sites. The number of atomic layers/time, \dot{n} , evaporated by this mechanism might be specified approximately by

$$\dot{n} \sim f\nu e^{-\epsilon/kT}$$

where f is the fraction of kink sites in the surface, ν is a vibration frequency, and ϵ is the energy required to dissociate an atom from a kink site. Setting $\nu f \sim 10^{12} \text{ sec}^{-1}$ the condition that \dot{n} not exceed 1/sec is that $T < \frac{\epsilon}{28k}$. The magnitude

of ϵ is difficult to estimate, but it seems unlikely that it would exceed $\frac{1}{2}$ of the cohesive energy/atom of metallic hydrogen.

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APPENDIX G

SUPERCONDUCTIVITY*

by C. W. Swenson**

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Superconductivity is of technological interest because of the possible use of superconducting components in such diverse areas as power transmission lines, electric motors and generators, magnetic bottles for power generation by fusion, and high-speed ground transportation.¹ Existing superconductors must be kept at temperatures near the boiling point of liquid helium (4°K, -269° C, -452° F) if they are to be used in these applications, and refrigeration problems become important.

Hence, one concern of modern superconductivity research is the discovery of superconductors with ever high-transition temperatures and two approaches may be defined. The first uses qualitative theoretical guidelines and empirical rules in survey-type investigations of metallurgical systems.^{1,2,4} The highest known superconducting transition temperature of 21° K (for $Nb_3(Al_{0.75}Ge_{0.25})$) was discovered, or more correctly, was produced in an investigation of this type.¹ A second approach attempts to understand the basic

* This general discussion of superconductivity and the role high pressures have played in superconductivity research is based in part on a number of recently published general articles.¹⁻⁴ These articles should be consulted for details and additional references.

** In consultation with T. H. Geballe of Stanford University.

mechanisms that bring about superconducting behavior with the hope that these can be used to predict either favorable conditions for high transition temperatures or to set fundamental limits for the occurrence of superconductivity. To some extent the two approaches are concerned with quite different types of systems, since the empirical approach tends to concentrate on relatively complex systems similar to those for which high transition temperatures have been observed, while the more theoretical approach must make its beginnings in the understanding of relatively simple, often purely elemental, systems.

High-pressure methods have played an important role in both of these types of investigations. The experimental methods used have been surveyed by Brandt and Ginsburg³ who reference both their own and other Russian work as well as work done in the United States and other countries. Matthias' survey article,² which appears in a special low temperature issue of Physics Today (August, 1971), outlines the current status of superconductivity research and the semi-empirical search for ever higher transition temperatures. His survey shows that the superconductivity of a number of the elements has been discovered only through the use of high-pressure techniques and that phase transitions can produce a material which is a superconductor only at high pressure. This is the case for the semiconductor-metal transitions of germanium and silicon, for instance, and for transitions in which magnetically ordered phases are destroyed (such as for cerium), while cesium is the first normally monovalent metal which has been shown to be a superconductor. Matthias² makes the interesting, challenging, and broad comment that "Many elements have become superconducting under pressure but none has ever lost this property yet!"

However, not all high-pressure modifications of the elements have been investigated for superconductivity. Typical examples are iodine (which has a semiconductor-metal transition), rubidium, and potassium (which have unusual high-pressure modifications), chromium (for which a special type of magnetic ordering disappears under pressure), and the rare earth metals (which have electronic transitions at high pressure to what could be non-magnetic phases). One of the challenges is that no definite predictions can be made as to whether or not a new phase will be superconducting. The experiments are difficult and require pressures of up to several hundred kilobars at temperatures of less than 1° K. Apparatus of this type has been designed and used for some applications.³

High-pressure methods can be used to generate superconducting modifications of solids which remain stable when the pressure is released, although often only at low temperature. Brandt and Ginsburg³ give several examples, including metallic indium antimonide, antimony, and bismuth. The alloys of the yttrium-thorium sesquicarbide system,⁵ which can be produced only at high pressure and high temperature, are stable at low pressure and are particularly interesting since they show a systematic variation of the superconducting transition temperature with lattice parameter with a maximum at 17.6° K. The low-pressure stability of a given compound that can be produced only under pressure cannot be predicted beforehand, and indeed this is a major unanswered question common to all high-pressure syntheses.

One of the most important objectives of work in this area is the understanding of the basic mechanisms

leading to superconductivity. Many phenomena are explainable in terms of the electron-phonon interaction and the BCS theory, but feelings often are expressed² that different mechanisms must exist to explain the occurrence of superconductivity in various classes of metals. Non-transition metals (such as tin, lead, and indium) appear to be BCS-like and are said to be "understood." The transition elements (niobium, tantalum, and vanadium, for instance) may belong to another distinct category, while the rare earth-type metals (lanthanum, cerium, yttrium, and possibly uranium) show somewhat different behavior. Why is lanthanum a superconductor with a relatively high transition temperature (5° K), yttrium a superconductor only under pressure, and scandium never a superconductor? The high-pressure measurements of the superconducting transition temperature for lanthanum⁶ must be considered in answering this question since they show a variation which is anomalous both in sign (the transition temperature rises with increasing pressure) and in magnitude (an increase from 5° K to 12° K in 140 kbar). The increase appears to be linear in volume to a first approximation for the 25% volume change of these experiments. Lanthanum represents an extreme case; yet transition metals in general show quite different pressure effects from non-transition metals. There are no ground rules to use in determining the region of stability of the superconducting state, although Brandt and Ginsburg³ suggest that both zinc and cadmium should become normal metals at very high pressures at absolute zero. What is a valid extrapolation procedure? Any phase transitions that occur can be expected to affect the transition temperature, and Matthias² suggests a general tendency towards increase. Experiments designed to establish or differentiate between

various mechanisms for superconductivity are badly needed, as are theories that can suggest such critical experiments.

The major concern in the above paragraph would appear to be in the relatively simple elemental superconductors for which theories can be proposed. Most of the high-temperature superconductors that have technological applications are more complex, and it is not clear that the same considerations will apply. For instance, Geballe¹ has suggested that transition temperatures greater than 12° K occur mostly in materials that have lattice instabilities. Many of these (such as Nb₃Sn) have the cubic beta-tungsten structure in which there are unbroken linear chains of the transition metal ions. This one-dimensional structure appears to be very important for superconductivity, and Smith⁷ recently has reported on a systematic investigation of pressure effects on the superconductivity of many of these compounds in an attempt to test various theories, with inconclusive results. Various layer-structure chalcogenide compounds have been discovered recently to be superconducting¹ in a manner which appears to be two-dimensional. The complexity of these effects is evident not only in the rapid rise of T_c with pressure as has been observed for NbSe₂,⁸ but also by the discovery of high superconducting transition temperatures (10 to 13° K) for ternary alloys of similar compounds⁹ which are of the form Li_xTi_{1.1}S₂. Any mechanisms proposed for superconductivity in these materials certainly must predict the results of high-pressure measurements.

The above survey then suggests several potentially profitable applications of high-pressure techniques to research on superconductors including:

(1). Routine testing of new high-pressure metallic modifications of all solids for superconducting behavior, and the systematic study of promising ternary systems. Particular emphasis should be given to systems which are metastable at low pressure since apparently metastability is important for high transition temperatures. While the mass production high-pressure synthesis of superconducting materials may never be feasible economically, these studies should be encouraged since they can give guidelines as to the existence of other, more easily produced materials. A portion of the above program should be devoted to studies of the high-pressure modifications of the elements that have not been tested for superconductivity, since in this case the role of crystal structure is most clearly evident, and theoretical calculations could be possible.

(2). Systematic studies of the effects of high pressure on the superconductivity of existing systems (such as the study carried out by Smith⁷). Such studies could make particularly valuable contributions to our understanding of superconductivity, initially through correlations and ultimately through direct tests of theories. Theoretical work is needed that can suggest critical experiments which can be used to differentiate between various mechanisms.

(3). An investigation of the effects of defect structures on superconducting behavior. Very little is known about these effects. The superconducting transition temperature of TiO^{10} for instance has been increased from 1° K to over 2° K by a high-pressure anneal in which the vacancies in the as-grown normal crystal are squeezed out. Similar effects should be observed for other compounds such as NbN.

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APPENDIX H

FERROMAGNETIC MATERIALS

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Much of the high-pressure work on ferromagnetic (FM) materials has been aimed at a better understanding of the physical phenomena involved and was motivated by the early recognition that the exchange forces which govern ferromagnetism are strong functions of interionic distances. In principle, the variations of the magnetization (or magnetic moment) and the Curie temperature T_c with pressure reflect important changes in the inter- and intra-atomic interactions. In practice, however, these exchange interactions are fairly complicated and generally not understood, especially in the case of metals, and progress towards the better fundamental understanding has been somewhat limited. Nevertheless, the use of high pressure in FM materials science and technology has been and will continue to be an important and fruitful endeavor.

A few pertinent points covering both science and applications are commented on here. These comments are intended to complement Goodenough's contribution, Appendix J, and are restricted to ferro- and ferrimagnetic substances. Pressure studies on antiferromagnetic and paramagnetic materials are of much scientific interest but will not be considered here.

1. FM MATERIALS RESEARCH

a. Insulators: Insulators are the simplest FM materials. Here the inter-atomic exchange forces are of the direct, indirect, or superexchange type, and the effects of pressure on the magnetic properties are qualitatively and, in some cases, semiquantitatively understood. Good examples are ferrites ($\text{MeO} \cdot \text{Fe}_2\text{O}_3$) and garnets ($3\text{Me}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$), where Me is a transition metal ion. Though complicated both chemically and structurally, these materials are rather simple magnetically. The dominant interactions are of the superexchange type operating between neighboring magnetic ions via the intermediate oxygen ions. The strength of the interactions is proportional to the amount of overlap between the $3d$ wave functions of the metal and the $2p$ wave functions on the adjacent oxygen. This overlap should increase with pressure and the Curie (or Néel) temperature can be expected to increase. Indeed that is what is observed experimentally with dT_c/dP typically in the range $1-2^\circ \text{K/kbar}$. In many of these substances the magnetic moment per unit mass has its spin-only value and should not be affected by pressure. This has been confirmed by experiment (e.g., yttrium iron garnet and magnetite).

In the presence of anisotropic (nonhydrostatic) stress, strain-induced magnetic anisotropy effects can become important especially for materials with large magnetostriction. This anisotropy induces an easy direction of magnetization which can be different from the applied magnetic field direction and thus competes with

the field. For low values of the applied field the magnetization can rotate away from the field direction towards the easy direction. Materials such as nickel ferrite exhibit strong strain-induced anisotropy effects, and these are reflected in the large rotations in magnetization at low fields observed in shock-wave compression experiments in the elastic range. In this range the stress is anisotropic.

b. Metals: In the case of FM metals interactions between conduction electrons and magnetic spins are complicating factors, and the question of the localized versus the itinerant nature of the magnetic moment remains generally unresolved. Although the pressure results on the magnetic properties of these metals are usually difficult to interpret, they remain important. This is especially so in cases where the results might be used to assess the validity of an existing model or perhaps to choose between competing models. Two examples of recent work, which may come close to achieving this goal, serve to illustrate the point.

(1) ZrZn₂

This is thought to be perhaps the best example of a weak itinerant ferromagnet. It has a small magnetization and a low Curie temperature ($\sim 20^\circ \text{K}$) which decreases with pressure. The initial decrease is linear with a slope $dT_c/dP = -1.9^\circ \text{K/kbar}$. Recent results¹ have shown that the decrease continues to be linear up to $\sim 7.5 \text{ kbar}$ and then T_c decreases rapidly to zero, the FM state vanishing for pressures $> \sim 8.5 \text{ kbar}$. At present this is

the only known example of the vanishing of ferromagnetism at high pressure and 0°K . The observed pressure dependence of T_c has been discussed¹ in terms of a model for weak itinerant ferromagnets,² and, in fact, such a model is capable of qualitatively reproducing certain aspects of the experimental results. In particular the model predicts a decrease of T_c with pressure and that $(dT_c/dP) \rightarrow -\infty$ as $T_c \rightarrow 0^\circ \text{K}$, as observed. Careful examination of the results, however, shows that the initial linear decrease of T_c extends to a much higher pressure than is predicted by the simple model.^{1, 3} It may be possible to give a better account of the results by a model that combines an itinerant and a localized description--a so-called modified Zener model.³ This model is essentially an itinerant one but with some localized character. It does away with the neglect of Hund's rule effects and degeneracy of the d bands effects which are assumed in the simple itinerant model and deemed objectionable.

(2) Invar Alloys

Face-centered cubic iron-nickel alloys in the Invar region ($\sim 25\text{-}45\%$ Ni) exhibit many anomalous properties including large decreases in magnetization and Curie temperature with decreasing Ni content, large volume magnetostriction, negative thermal expansion at low temperature, and large compressibilities. In agreement with the predictions of the weak itinerant model, their magnetizations and Curie temperatures exhibit large

decreases with increasing pressure. This behavior combined with observations that many of their atmospheric pressure properties are consistent with this model have led to the belief that these materials are weak itinerant ferromagnets. Recent extensions of the pressure measurements to much higher pressures for some of these alloys have, however, yielded results not consistent with the simple itinerant model.⁴ In particular T_c decreases linearly over a large pressure range with indications that vestiges of the FM state will persist to very high pressures (i.e., the FM state may never vanish). It appears that the results can be described by the modified Zener model mentioned above.³ It must be emphasized, however, that this description as well as that for $ZrZn_2$ is rather phenomenological in that it does not incorporate any details of the electronic structure of these materials--details that must certainly be important. Unfortunately our present knowledge of these details is either primitive or nonexistent, and phenomenological treatments can be quite useful in correlating and examining trends in experimental data.

High-pressure results of the type described above for the Invar alloys and $ZrZn_2$ constitute significant knowledge which should ultimately enhance our understanding of ferromagnetism in metals. It is in studies of this kind, and on select materials, that high pressure can be expected to have an impact on this field.

2. APPLICATIONS

Some of the possible direct applications of high pressure in magnetic materials science and technology are discussed by Goodenough. In addition to these, there are some unique applications that deserve brief mention. These are based on pressure-induced changes in magnetization and can be utilized specifically under shock-wave conditions. Examples are FM shock-wave stress gages and electrical power sources. The power sources are capable of producing relatively large current or voltage pulses in a manner similar to the ferroelectric power sources described elsewhere in this report. The electrical pulse results from the pressure-induced change in magnetic flux detected by a pick-up coil wound on the FM material.

The change in magnetization with compression results from any of the following causes: (a) an intrinsic change in magnetic moment or a shift of the Curie temperature with pressure, or both; (b) a pressure-induced phase transition to a nonferromagnetic phase or to an FM phase of different magnetization; or (c) a strain-induced magnetic anisotropy.

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APPENDIX I
DIELECTRIC AND FERROELECTRIC MATERIALS
AND APPLICATIONS

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The use of pressure in the study of dielectric and ferroelectric materials has made contributions in three general areas: (1) basic understanding, (2) materials synthesis and fabrication, and (3) device applications. Much of the work has been devoted to the first and second areas and significant contributions have been achieved. Device applications, on the other hand, have been rather limited since they are generally restricted to very low pressures or unique environments. In this appendix the present status of the field will be assessed and certain aspects of the above areas and contributions will be discussed.

1. EFFECTS OF PRESSURE ON DIELECTRIC AND FERROELECTRIC PROPERTIES

a. Introduction

The interatomic forces and interactions which determine the structure and properties of matter are strong functions of interatomic separation (and volume), and, therefore, pressure is a fundamental variable in the study of physical properties. Results of pressure experiments lead to a better understanding of these properties and often make it possible to test the validity of theoretical models. It is in this general context of understanding physical properties that high-pressure work has its greatest impact (though perhaps indirect) on dielectric materials science and technology. The direct use of pressure in

material synthesis and in device applications, though sometimes unique and important, will always be more limited.

Pressure studies are necessary and sometimes essential for understanding physical properties and, in particular, the temperature dependence of a given material property. The measured change in property with temperature at constant pressure arises from two contributions: (1) the change that arises solely from the change in lattice spacing or density (i.e., the explicit or pure volume effect), and (2), the explicit or pure temperature effect that would be present even if the volume of the sample were to remain fixed. Isothermal pressure measurements give the pure volume effect directly and thus make it possible to evaluate the two contributions to the isobaric temperature measurements. The pure temperature contributions arise from anharmonic lattice effects, and as shall be pointed out later, play predominant roles in ferroelectrics and certain dielectrics.

In addition to the above-mentioned volume effects there are some property changes unique to the high-pressure environment. Most important among these are a wide range of pressure-induced phase transitions which are accompanied by large, often drastic, changes in physical properties. For example, dielectrics (=insulators) may become good semiconductors or metals, normal dielectrics may become ferroelectrics, and ferroelectrics may lose their spontaneous polarization and become normal dielectrics. In addition to their scientific interest such changes have applied implications.

b. Dielectrics

Comments here shall be restricted largely to the effects of pressure on the dielectric constants. Other important aspects such as optical properties and electrical con-

ductivity are treated in another section of this report. A knowledge of the static (ϵ_s) and high-frequency (ϵ_∞) dielectric constants of a substance and their temperature and pressure dependences is of great interest because these properties enter into the treatment of and/or determine various physical properties (e.g., problems of electron-electron and electron-phonon interactions and dispersion, optical properties, and effective field considerations). Such important properties of dielectrics as the capacitance, dielectric loss or Q factor, dielectric strength, electrical transport, optical refraction, electro-optical effects, and laser beam-medium interactions are determined, or strongly influenced, by these dielectric constants. Future progress in the development of high energy storage capacitors, nonlinear dielectrics, and improved piezoelectrics can be strongly influenced by a better knowledge of electric polarization phenomena. Three sources of polarization are induced by the application of an electric field to a dielectric. These are (1) electronic, (2) ionic, and (3) dipolar. Electronic polarization results from the displacement of the electron distribution relative to the nucleus for each atom or ion and thus produces an electric dipole moment. Ionic polarization, on the other hand, is caused by the opposite displacements of positive and negative ions from their equilibrium positions. This mechanism of polarization is operable in the infrared and lower frequency regions. At higher frequencies the ions cannot follow the variation in electric field, and the ionic polarization vanishes. Dipolar polarization comes into play at sufficiently low frequencies and is associated with substances made up of molecules that possess a permanent electric dipole moment or with substances containing dipolar impurities.

(1). High Frequency Dielectric Constant: The high-frequency dielectric constant is determined by electronic polarization and is given by $\epsilon_{\infty} = n^2$, where n is the index of refraction. The electronic polarizability α_{elec} is determined by the electronic structure of the ion or atom, and its value can be calculated, in principle, from a solution of the differential equations of motion for the perturbation by an external field of the electronic wave functions for the various electronic shells. This is a complex theoretical problem even in the free ion or atom because of the quantum and many-body nature of the interactions; it is further complicated in the case of ions and atoms in condensed media where added interactions and distortions of the electronic distributions occur. Theoretical calculations are most successful for the smallest (containing fewest number of electrons) atoms and ions and become less satisfactory for the larger ones. Because of the complexity of first principles calculations, however, it has proved very useful, at least in the case of ionic crystals, to determine empirical values of the electronic polarizabilities of ions from measured values of the index of refraction. This is generally done on the basis of the additivity rule (i.e., the total α_{elec} is taken as the sum of the individual polarizabilities of the constituent ions). Refinements which introduce the effect of the lattice environment on the individual α 's have also been made, and tabulated values of electronic polarizabilities are available and widely used.^{1, 2}

Changes in the refractive index of a substance with temperature and pressure (or stress) can result

from changes in (a) the Coulomb and local fields in the medium, (b) the density of the medium, and (c) the intrinsic α_{elec} 's of the constituent ions or atoms. For isotropic dielectrics and uniform stress (a) is negligible; however, for anisotropic substances and/or nonuniform stress, changes due to (a) have to be taken into account.

An examination of data on a wide variety of isotropic dielectrics shows that the pressure (P) and temperature (T) derivatives of n (or ϵ_{∞}) can be either positive or negative.^{3,4} For example, (dn/dT) is negative for the alkali halides and positive for diamond and MgO, whereas (dn/dP) is positive for the alkali halides and negative for diamond and MgO. The effects due to the change in density can be readily understood: n increases with increasing density of polarizable entities. Analysis of the pressure results shows that in all cases the electronic polarizability increases with increasing volume, i.e., $(\partial \ln \alpha_{elec} / \partial \ln V)_T$ is positive. This means that α_{elec} decreases with increasing pressure leading to a negative contribution to the pressure dependence of n and ϵ_{∞} . This is what one might intuitively expect. The distortion of an ion (and thus its polarizability) in an electric field becomes smaller when the space available for distortion (i.e., the volume) becomes smaller. In the case of the alkali halides the increase in density dominates and n increases with pressure and decreases with temperature. For diamond and MgO the opposite is true with $(\partial \ln \alpha_{elec} / \partial \ln V)_T$ dominating. In all cases, except diamond, the volume-independent, or pure temperature contribution, $(\partial \ln \alpha_{elec} / \partial T)_V$, to dn/dT

is very small and negligible. This is an important conclusion with practical as well as scientific implications -- it means that to a good approximation, α_{elec} is a function of volume only. Thus, knowing either the temperature or pressure dependence of n we can estimate the other provided, of course, that the compressibility and thermal expansion are known. For diamond the pure temperature contribution, though small, is comparable in magnitude to the pure volume effect and cannot be neglected.

(2). The Static Dielectric Constant: The values of the static dielectric constant ϵ_s of normal ionic crystals (i.e., nonferroelectrics) varies from $\sim(4$ to $5)$ up to several hundred. A comparison between values of ϵ_s and the high-frequency constant ϵ_∞ shows that ϵ_s is much larger. Thus, for example, for NaCl $\epsilon_s = 5.90$ and $\epsilon_\infty = 2.33$ and for rutile (TiO_2 , c-axis) $\epsilon_s = 166$ and $\epsilon_\infty = 7.2$. The difference $\epsilon_s - \epsilon_\infty$ is a measure of the lattice (ionic) contribution to the dielectric constant (i.e., a measure of the lattice or infrared polarizability). This important mechanism of lattice polarization arises from opposite displacements of positive and negative ions in the presence of an electric field, and thus has its origin in the lattice vibrations of the crystal. Its treatment is a problem in lattice dynamics. The general theoretical treatment is complicated by the fact that lattice vibrations are not completely harmonic, and the introduction of high-order anharmonic potential and dipole moment terms makes an exact solution of the problem impossible. One of the benefits of pressure

studies is that they make it possible to estimate the anharmonic contribution to the isobaric temperature variation of ϵ_s . In some crystals such as rutile, these contributions dominate and, as shall be seen later, play an all important role in ferroelectrics.

Theoretical models show that for ionic crystals ϵ_s is determined by the infrared resonance frequency of the crystal and the ionic charge as well as ϵ_∞ . Comparisons between calculated and experimental values of ϵ_s for many crystals show that the ionic charge does not have its formal value of Ze , where Z is the valence. For this purpose the concept of an effective ionic charge Ze^* has been introduced.⁵ In the ideal case of deformable ions that do not overlap, the ratio e^*/e is unity. In real solids, however, the ions overlap, and the concept of an effective ionic charge serves to account for the polarization effects associated with the overlap. Deviations of e^*/e from unity arise from three effects: (a) short-range repulsive interactions between the electron clouds on adjacent ions which modify the electronic dipole moments, (b) redistribution of charge and overlap when the ions move in the course of lattice vibrations, and (c) modification of the local electric field at a given lattice site by the distortion of neighboring ions. Using the earlier examples, analysis of experimental data including pressure measurements shows that $e^*/e \approx 0.77$ for NaCl and 0.64 for rutile.

High pressure measurements of ϵ_s for ionic crystals can be used to determine the magnitude of the anharmonic contribution to ϵ_s and to obtain better values of e^*/e

than those which were based on a completely harmonic model, reported in the earlier literature. This can be seen simply in the following way: ϵ_s is given by⁵

$$\begin{aligned} \epsilon_s - \epsilon_\infty &= \frac{4\pi (Ze^*)^2}{\mu V \omega_{TO}^2} \left(\frac{\epsilon_\infty + 2}{3} \right)^2 + G \\ &= \eta + G \quad , \end{aligned} \quad (1)$$

where μ is the reduced mass, V is the volume per molecule, and ω_{TO} is the IR resonance frequency. The term denoted by η is the lattice contribution to ϵ_s in the harmonic approximation and G represents the anharmonic contributions. G is a complicated function, but in the high temperature limit (i.e., for $T > \theta_D$), it reduces to

$$G = T[\partial(\epsilon_s - \epsilon_\infty)/\partial T]_V \approx T(\partial\epsilon_s/\partial T)_V . \quad (2)$$

The right-hand side, and therefore G , can be readily evaluated from the measured pressure and temperature dependences of the dielectric constants, and then e^* is calculated from Eq. 1 using appropriate values for the other variables. G can be quite large, for example, at 300° K G amounts to 3-10% of the lattice dielectric constant, $(\epsilon_s - \epsilon_\infty)$, in the case of the alkali halides, over 30% in the thallos halides, and over 40% in rutile.

A very useful relationship in the study of the dielectric properties of ionic crystals in the Lyddane-Sachs-Teller (LST) relationship. It is based on the harmonic approximation, and for diatomic crystal, takes the simple form

$$\frac{\epsilon_s}{\epsilon_\infty} = \left(\frac{\omega_{LO}}{\omega_{TO}} \right)^2, \quad (3)$$

where ω_{LO} is the long wavelength longitudinal optic phonon frequency. From Eq. 3 it is seen that large values of ϵ_s can be associated with small values of ω_{TO} . This has an important implication in the case of some ferroelectrics for which it is now established that $\epsilon_s \rightarrow \infty$ and $\omega_{TO} \rightarrow 0$ as the temperature approaches the transition or Curie temperature.

The effects of pressure and temperature on ϵ_s have been determined for a large number of dielectrics.⁶⁻⁸ As was the case for ϵ_∞ , both positive and negative values of $d\epsilon_s/dP$ and $d\epsilon_s/dT$ are observed. Analysis of the data in terms of the pure volume and pure temperature contributions to $\epsilon_s(T)$ is quite revealing and has led to some deeper insight and generalizations concerning the dielectric properties of solids. Particularly interesting are the changes in behavior as ϵ_s increases in value for different solids. In general, $d\epsilon_s/dT$ starts out positive for small ϵ_s (e.g., NaCl, $\epsilon_s = 5.9$) and becomes increasingly more negative as ϵ_s increases (e. g., TlBr, $\epsilon_s = 30.4$ and c-axis rutile $\epsilon_s = 166$). Since, in general, ϵ_s decreases with increasing pressure reflecting the fact that the ionic polarizability decreases with decreasing volume (i.e., the solid becomes stiffer) despite the increase in density, the above trend in $d\epsilon_s/dT$ reflects an increase in the influence of the pure temperature effect $(\partial \ln \epsilon_s / \partial T)_V$ as

ϵ_s increases. As mentioned earlier, this pure temperature contribution arises from anharmonicities in the crystal potential and dipole moment. It is also found that the sign of $(\partial \ln \epsilon_s / \partial T)_V$ depends on crystal structure (e.g., it is positive for crystals having the NaCl structure and negative for crystals having the CsCl structure). This reflects important differences in the nature and origin of the anharmonicities in different crystal structures. These differences, however, are not well understood.

Much information about anharmonic interactions in dielectrics can be gained from detailed studies of the pressure and temperature dependences of vibrational spectra. Particularly important from the standpoint of the dielectric response is the behavior of the IR resonance frequency ω_{TO} in Eq. 1. Pressure measurements on ω_{TO} have been performed on a number of ionic crystals using far IR techniques.⁹ Unfortunately, the accuracy of the data thus far has been limited. Accurate measurements are important, since a knowledge of the pressure dependence of ω_{TO} combined with the pressure dependences of ϵ_s and ϵ_∞ allows one to determine the pressure or volume dependence of the effective charge. At present, values of $(\partial \omega_{TO} / \partial P)_T$ are generally not known accurately enough to allow this, since $(\partial \ln \epsilon^* / \partial P)$ turns out to be determined by the difference between large and nearly equal quantities. Intuitively, one suspects that $(\partial \ln \epsilon^* / \partial P)_T$ should be negative -- the decrease resulting from increased electronic distortion as the solid is compressed.

Available $\omega_{TO}(P)$ data suggest that both positive and negative values of $(\partial \ln \epsilon^* / \partial P)_T$ may be obtained, but in view of the poor accuracy of the data, positive values have to be viewed with caution.

More generally, pressure and temperature studies of phonon spectra of solid dielectrics are attracting more attention and much more work is needed in this important area in order to obtain quantitative estimates of anharmonic effects, as well as to shed some light on the origin of these effects. Understanding of lattice anharmonicities is important from the point of view of ferroelectricity since many ferroelectric transitions are believed to be driven by anharmonic effects. Such studies are also important from the standpoint of lattice stability and phase transformations since some transformations result from the instability of the crystal against a certain mode of vibration, i.e., the frequency of the mode becomes so low (with temperature or pressure) that the restoring force for the atomic displacements associated with the mode vanish and a transition sets in. Optical phonons can be studied by far IR absorption, Raman scattering, or inelastic neutron scattering; acoustic phonons can be studied by ultrasonic propagation, Brillouin scattering, or neutron scattering. The ultrasonic technique, which gives information about the long wavelength modes, has been very widely used to study the pressure dependence of the elastic properties (elastic constants) of solids and for high-pressure equation of state considerations.

Finally, measurements of ϵ_s provide an excellent and relatively simple probe for studying the detailed behavior and kinetics of phase transformations under pressure. Often apparatus design and other constraints limit the kind of probes available for such studies.

c. Ferroelectrics

Studies of the effects of pressure on ferroelectric (FE) crystals have shown that FE properties are among the most pressure (or volume) dependent of all physical properties. This is perhaps not too surprising since ferroelectricity is a structure-sensitive phenomenon and there is intimate coupling between the onset of FE ordering and lattice strain. Anharmonic interactions are of utmost importance in ferroelectricity, and, as pointed out earlier, pressure measurements are very useful for separating out anharmonic effects. Pressure studies can thus provide important information concerning the nature of ferroelectricity, and in the case of some ferroelectrics such as KNO_3 and $\text{LiH}_3(\text{SeO}_3)_2$, such studies turn out to be essential for elucidating the FE behavior. In addition, as will be discussed later, pressure (or stress) effects on ferroelectrics have some direct practical applications.

The properties of a large number of FE crystals have been investigated under pressure. Recent reviews and assessments of the field are available in the literature.¹⁰ It is difficult to draw general conclusions based on these investigations because of the varied nature of different classes of FE crystals (i.e., each crystal class exhibits a different mechanism for its ferroelectricity). Thus, the following remarks will be restricted to a few instances where pressure studies have led to significant advances in the basic and

phenomenological understanding of ferroelectricity -- understanding which has indirect practical implications and which illustrates the importance of pressure as a variable in the study of physical phenomena.

(1) Soft Mode Ferroelectrics: It is now established that the dielectric properties and ferroelectric transition in some ferroelectrics, most notably the perovskites such as BaTiO_3 and PbTiO_3 , can be understood in terms of soft optical phonons. The FE transition is caused by an instability of the lattice against a long-wavelength transverse-optic mode caused by the cancellation of the short-range forces by the long-range Coulomb forces. Schematically the frequency of this mode is depicted by $\omega_{\text{TO}}^2 \propto$ (short-range forces) - (Coulomb forces). As $T \rightarrow T_0$, the transition temperature, $\omega_{\text{TO}} \rightarrow 0$ and the static dielectric constant, $\epsilon_s \rightarrow \infty$, ϵ_s and ω_{TO} being related by a generalized LST relationship with the result that $\epsilon_s \omega_{\text{TO}}^2 = \text{constant}$. The strong dependence of the properties on pressure can be qualitatively appreciated by noting that the short-range forces are much more strongly dependent on interionic distance r than the Coulomb forces -- the latter vary as $1/r^3$ whereas the former vary more like $\sim 1/r^{11}$. Thus the application of pressure causes the short-range forces to increase much faster than the Coulomb forces leading to an increase in the soft mode frequency and a corresponding decrease in transition temperature. It can also be readily appreciated that the fractional increase in ω_{TO} with pressure becomes larger as T approaches T_0 , and this is reflected by the fact that the Grüneisen parameter γ for this mode,

$\gamma \equiv -(\partial \alpha_{TO} / \partial \ln V)_T$, is found to increase very rapidly, reaching values of hundreds to thousands near T_0 .

(2) Antiferroelectrics: Recent pressure studies have also played an important role in our present understanding of some antiferroelectric (AFE) crystals such as PbZrO_3 . Because of the antiparallel nature of the displacements of similar ions in adjacent unit cells, the transition to an AFE state is associated with an instability of a lattice mode whose wavelength is of the order of a lattice parameter (i.e., a zone boundary mode). The experimental situation (at 1 bar) in PbZrO_3 and related AFE crystals suggested the presence of two, nearly "degenerate," low-frequency modes: a zone center TO (or FE) mode which is responsible for the large dielectric susceptibility and a zone boundary (AFE) mode which causes the transition. On lowering T at 1 bar, the crystal becomes unstable against the AFE mode just before the instability due to the FE mode is reached. While the validity of this description can in principle be checked by measuring the temperature dependence of the phonon dispersion curves by optical and neutron scattering techniques, such data are not available due to the lack of suitable single crystals. Recent dielectric constant pressure measurements on polycrystalline samples have, however, given the first experimental confirmation that the properties of these crystals are indeed determined by two separate modes. With increasing pressure the frequency of the FE mode increases (as discussed earlier) while that of the AFE mode decreases leading to a removal of the near "degeneracy" that exists between the two modes at 1 bar.

(3) Hydrogen-Bonded Crystals: Pressure studies have proven to be important in the study of the FE and AFE properties of hydrogen-bonded crystals of the KH_2PO_4 -type. The protons play crucial roles in the transitions in these crystals as evidenced by the large changes in transition temperatures and other properties observed on replacing the protons by deuterons. It is now believed that above the transition the protons exhibit tunneling motion between two equilibrium positions along the hydrogen bonds that connect adjacent PO_4 groups. This motion is coupled to that of the other ions in the crystal. The transition is triggered by the ordering of the protons in their potential minima. The details of the potential and thereby the tunneling frequency are strong functions of the hydrogen bond length. Pressure can be expected to strongly affect the transition temperatures and properties of these crystals and this is found to be the case. One of the most significant findings is the recent observation of the vanishing of the FE and AFE states at high pressures and 0°K in KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ at 17 and 33 kbar, respectively.¹¹ This is believed to result from the increase in proton tunneling frequency which causes the disordering tendency of the tunneling field to be larger than the ordering tendency of the dipolar field at all temperatures.

The possible vanishing of the FE state in other classes of ferroelectrics has not been investigated experimentally. It is expected, however, that this will occur for soft T_0 mode ferroelectrics because of the rapid increase of ω_{T_0} with pressure. The manner in which T_0 approaches 0°K at high pressure is par-

ticularly important from a theoretical point of view since it may help decide between competing models. For example in KH_2PO_4 , $T_0 \rightarrow 0^\circ$ with infinite slope, i.e., $dT_0/dP \rightarrow -\infty$, and this is consistent with the tunneling model.

(4) Other Ferroelectrics: Studies of $\text{LiH}_3(\text{SeO}_3)_2$ illustrate another aspect of high-pressure research. This crystal has by far the largest spontaneous polarization of any hydrogen-bonded ferroelectric, and it is unusual in that the forces responsible for the ordering of the dipoles are strong enough for the crystal to remain ferroelectric up to its melting point of 110°C . A ferroelectric-to-paraelectric transition can be (and has been) induced in this crystal only at high pressure. This results from the simultaneous increase in the melting point and decrease in the Curie point with increasing pressure. Thus, pressure studies made it possible to examine the details of the FE behavior at and near the transition, and these details provide important clues as to the nature of the ferroelectric ordering in this class of crystals.

KNO_3 is another interesting example in that its FE phase is thermodynamically stable only at high pressure. This phase can be obtained metastably at 1 bar over a very narrow temperature range of $\sim 10^\circ \text{C}$. At high pressure the FE phase becomes stable over wide temperature ranges. It is quite likely that many of the high-pressure phases observed in a variety of dielectric crystals are ferroelectric; however, very little work has been done in this regard.

In view of these examples, it can be seen that high-pressure studies have provided important information concerning the nature of ferroelectricity. For perovskite- and KH_2PO_4 -type ferroelectrics the pressure results are in qualitative agreement with the accepted model theories and, therefore, lend some support to these models. Quantitative treatments are hampered by the complicated nature of the phenomena and the fact that the models have not been developed in sufficient detail. Important theoretical questions remain unresolved and offer challenging problems. For example, the exact origin of the temperature dependence of the soft-mode frequency in the perovskites and the nature of the proton-lattice coupling in the hydrogen-bonded crystals are not clear. These are complex problems, but they deserve additional investigation.

2. DIELECTRIC MATERIALS SYNTHESIS AND FABRICATION

a. Synthesis

The successful high-pressure synthesis of diamonds in the late 1950's generated a great deal of research effort in the United States, U. S. S. R., Japan, and other countries, and there was high expectation that the high-pressure techniques might lead to new and exotic dielectric materials for a wide variety of applications. Unfortunately, with very few exceptions (notably, diamond and cubic boron nitride which are discussed elsewhere in this report), this expectation has not materialized. Although a substantial number of new compounds and new polymorphs have been prepared under pressure, none of these has found practical applications and they remain largely objects of academic interest. This is not to say, however, that high-pressure synthesis is not a worthwhile

endeavor; rather, it is a specialized and expensive process that holds promise when used judiciously on sound scientific grounds.

The materials and processes listed below are some of those used in pressure synthesis of dielectric materials.*

- (1) The syntheses of diamond and cubic boron nitride are by far the best and most important examples of high-pressure synthesis.
- (2) Hydrothermal synthesis is of course a very widely used commercial process for producing such crystals as quartz and CrO_2 , but the pressures here are very low -- up to a few thousand psi. There may be potential for extending the process to higher pressures, but the equipment becomes more involved and costly.
- (3) The high-pressure synthesis of stishovite, the tetragonal rutile form of SiO_2 , has been considered one of the important successes of Russian workers in this area. This material is of considerable geophysical and geochemical interest.
- (4) There has been considerable expectation, largely on the part of Russian workers, for synthesizing new ferroelectrics of the ABO_3 type (e.g., perovskites) under pressure. This was motivated by ionic size considerations as discussed by Goodenough elsewhere in this report. A number of these oxides have been prepared under pressure

* The use of pressure in the chemical process industry (e.g., polyethylene) is extremely important but not considered here.

(e.g., RbNbO_3 and RbTaO_3), but at present none seems to have any especially attractive properties for practical applications.

- (5) A number of high-pressure phases can be retained metastably at 1 bar. Some examples include high-pressure modifications of SiO_2 , ZnF_2 , and TiO_2 , the latter having been first recovered in shock-wave experiments. Many high-pressure phases can be easily retained by quenching to liquid nitrogen temperatures and retaining at low temperatures before releasing the pressure. One of the best examples is the metallic high-pressure phase of InSb. The technique allows one to study the properties of the high-pressure phase in much more detail than is possible at high pressure and is largely of scientific interest.
- (6) The apparent success in making diamonds on a commercial scale by shock-wave compression is an important achievement. The potential of the method for other syntheses is not known but it is most likely limited because of the unique nature and short duration ($\sim 1 \mu\text{sec}$) of the compression.
- (7) High-pressure single-crystal growth is an area that has received little attention. The pressure range will be necessarily limited, but the process may have considerable potential in growing crystals of substances having high vapor pressure or in cases where pressure may suppress a phase transition which might interfere.

b. Fabrication

High-pressure materials fabrication as referred to here relates primarily to uniaxial and isostatic pressure sintering. These are important, but mainly low-pressure (< ~2 kbar) operations that are discussed elsewhere in the report. Important examples of dielectric materials produced this way are optical quality ceramics such as MgO, Y₂O₃ and a family of lanthanum-doped lead zirconate-lead titanate ferroelectrics.

The use of pressure in other fabrication areas such as forming and hydrostatic extrusion of dielectrics will not be discussed here.

3. DEVICE APPLICATIONS

The large pressure-induced changes in dielectric properties such as refractive index, optical absorption, conductivity, static dielectric constant (capacitance), ferroelectric polarization, phase transitions, etc., can in principle be utilized in a variety of practical applications, much in the same way as temperature-induced changes are utilized. In practice, the requirements for a pressure generating system make such applications unfeasible and/or impractical. However, in a few instances this is not the case. These are either such low-pressure (stress) applications so as not to present any apparatus difficulties or very specialized applications.

In the realm of low pressures (or more properly low stresses) there are a wide variety of strain and stress-biased devices and electromechanical transducers, many using piezoelectrics such as quartz and ferroelectric ceramics. The most recent application involves the use of strain to

cause a change in the birefringence of optical quality ceramics for electro-optic image storage and display. In all of these applications the stresses are so low that they are outside the scope of our immediate concern.

In the area of high pressures there are a few unique and important applications of dielectric phenomena which are worth mentioning. Most of these involve shock-wave compression. Areas of additional needed research are mentioned.

a. Piezoelectric Shock-Wave Stress Gages

These gages yield stress-time records of shock-wave events with submicrosecond resolution.¹² The application of stress produces a change in polarization of the piezoelectric material and this in turn causes an electrical current to flow in a low impedance external circuit. The current is proportional to the stress. The amplitude and time dependence of this current are functions of the piezoelectric and dielectric constants and the mechanical properties of the material under shock-loading conditions. The gages operate in the elastic compression range, and fortunately there are a number of piezoelectric materials, such as quartz, lithium niobate, and lead zirconate-lead titanate ceramics, which have rather high Hugoniot elastic limits and make it possible to use such gages over a wide range of pressure. Quartz is by far the most widely used piezoelectric for this application. It remains elastic up to ~ 60 kbar under shock conditions. Its piezoelectric, dielectric, and mechanical properties under shock have been investigated in some detail. Similar knowledge of the properties of other piezoelectrics is rather limited and much more work is needed in this specialized but important area.

The application of very high stress to a strongly piezoelectric material produces very high electric fields within the material. In quartz these fields can be and often are in the 10^5 -to 10^6 - volt/cm range. Such high fields can cause conduction or severe dielectric breakdown which interfere with the normal operation of the gage. Evidence for conduction and breakdown has been observed under certain conditions in quartz gages and these conditions have been experimentally defined. Again similar data are lacking for other piezoelectrics. In all cases the mechanism for the electrical conduction and the nature of the breakdown under the dynamic conditions in question are not understood and represent areas sorely in need of more research. The more general problem of dielectric breakdown in shock-wave environments often causes experimental and systems failure and is a matter of serious concern. Dielectric breakdown under normal conditions is poorly understood and much less is known about the problem under shock. Studies of dielectric strength at high static pressures might be helpful, but these will not serve as a substitute for the dynamic case.

b. Capacitive Shock-Wave Stress Gages

The operation of such gages is based on the change in the capacitance of a solid dielectric disc resulting from the changes in the static dielectric constant and thickness produced by the application of shock pressure. A gage of this type utilizing sapphire discs has been used successfully.¹³ It is capable of measuring stress-time profiles with resolution limited only by the rise-time of the recording equipment and the planarity of the shock-wave front. The change in capacitance of the electroded disc, across which an electrostatic

potential is applied, causes a current to flow in a low impedance circuit. The current is instantaneously (very small circuit time constant) proportional to the particle velocity at the stressed electrode.

Sapphire is well suited for this application because it behaves elastically to large compressions. Its Hugoniot elastic limits along different crystallographic orientations are unusually high, varying from 120 to 200 kbar. However, the change in the dielectric constant of sapphire with stress is very small and large potential differences of the order of kilovolts have to be applied across the disc to produce useful currents especially at low stress. It would be desirable to find other suitable dielectrics with larger pressure-induced changes in dielectric constant for this application.

c. Power Sources

Some unique power sources, capable of delivering large electrical voltage or current pulses to a load, can be made. These are one-shot devices that operate on the basis of the charge released from a polarized ferroelectric disc by the application of shock compression. The amount of charge release or depoling depends on the stress, and above a certain stress complete depolarization may occur. This would correspond to a transition from the ferroelectric to the paraelectric phase. In its ferroelectric phase a ferroelectric material is also strongly piezoelectric and the application of shock stress causes rather complicated non-linear electromechanical effects. More work is needed in order to quantitatively understand these effects.

Strongly piezoelectric (but nonferroelectric) dielectrics such as quartz can also be used for such power sources. For example, quartz discs are capable of producing kilovolt pulses.

d. Other Electrical Pulses

Useful current and voltage pulses have been obtained from a variety of dielectrics exposed to shock-wave loading. For example, very thin (~ 0.005 -cm thick) anodized aluminum layers produce a voltage that increases with stress and amounts to more than 1 volt/kbar up to 100 kbar.¹⁴ Thin layers of plastic tape produce tens of volts.¹⁵ Such effects have been successfully used as inexpensive methods for detecting the arrival of shock waves at surfaces.

Electrical signals from other shock-loaded dielectrics, especially ionic crystals such as the alkali halides, have been observed and some speculative explanations based on the generation and motion of dislocations given. In general, all of these phenomena are poorly understood, and more work is needed in this area.

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APPENDIX J

HIGH-PRESSURE TECHNOLOGY AND MAGNETISM

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1. MOTIVATIONS

High-pressure technology provides an additional physical variable that is useful in three primary areas: (a) devices, (b) materials preparation and processing, and (c) exploration of physical phenomena.

To date, relatively little attention has been given to the use of high pressures in devices. This is primarily due to the stationary, expensive character of most high-pressure installations. However, mobile units of quite compact size have been built. At Lincoln Laboratory, there is a mobile "hydrostatic"-pressure unit capable of 14-kbar pressure over a temperature range from 1.5 to 1000° K. Such a unit can be brought to different measurement stations in the laboratory, thus greatly enhancing the range of investigations that are readily accessible to high pressure as a variable. Once relatively inexpensive, mobile pressure units become available, their use as control elements becomes feasible. For example, the energy gap between the valence and conduction bands of a diode laser can be significantly modulated by high pressure, so that pressure provides a control of the laser frequency. A modification of the Lincoln Laboratory mobile pressure unit is now being constructed to provide a tunable diode laser.

Uniaxial (tensile or compressive) stress may also provide an important control variable. For example, the simple strain gauge, which monitors electrical resistance as a function of tensile strain, provides a sensitive sensor. Uniaxial stress on a magnetostrictive ferromagnet can completely alter its permeability, or the shape of its $B-\mu_0 H$ hysteresis loop and a modest uniaxial stress on a metamagnetic material may change an antiferromagnetic-to-ferromagnetic transition temperature by tens of degrees centigrade. Although such phenomena have not been exploited by present technology, they may prove important in the future.

The preparation of optical-quality ceramics by hot-pressing techniques is of particular interest for transparent dielectrics useful for light modulation. However, magnetic properties are also sensitive to pores and grain boundaries. Furthermore, control of a transition-metal valence state often required a low-temperature preparation that may only be possible under high pressures. Therefore high pressure is an important processing variable in the preparation of dense magnetic ceramics by solid-state reactions at relatively low temperatures.

High pressure as a thermodynamic variable enlarges the range of compounds and structures practically available to synthesis. This enlargement manifests itself in four ways: (a) new compounds, such as ferromagnetic CrO_2 ; (b) new polymorphs metastable at ambient temperature, such as diamond or ferrimagnetic CsNiF_3 ; (c) phases with smaller numbers of native defects, such as superconducting TiO

and a stoichiometric FeO; and (d) easier synthesis of compounds marginally accessible by preparation at atmospheric pressure. (Illustrative examples may be found elsewhere;^{1,2} a few are presented later in this appendix.)

Many solid-state phenomena have been explored with high pressure as a physical variable. Of particular interest is the variation with lattice parameter of the various phenomenological constants directly accessible to measurement. These constants are interrelated by microscopic solid-state theory. Therefore, their relative variation with pressure provides an important test of existing theory as well as a demonstration of pressure sensitivities that may have technological significance.

Generally, but not always, the easiest phenomena to monitor are phase transformations. Magnetic phase transformations occur at critical temperatures and at critical volumes. Changes in only magnetic order occur at critical temperatures that vary with volume, and changes in the magnitudes of ordered atomic moments occur at critical volumes that may have little temperature dependence. Transitions involving changes in the magnitudes of disordered atomic moments may be first-order, occurring at well-defined transition temperatures, or they may be higher-order. Such transitions are to be distinguished from changes with temperature in the relative populations of ground and excited states of localized-electron f^n or d^n manifolds having the same n , but different net atomic moments. Changes in magnetic transition temperatures with pressure are commonly obtained by monitoring electrical resistivity or inductance. However, DTA, neutron-diffraction, Mössbauer,

and/or x-ray measurements under pressure may be necessary supplements to a meaningful interpretation of the data.

Measurements of atomic moments and magnetic anisotropy may be obtained from magnetometer measurements. The most versatile instrument for this purpose, developed at Lincoln Laboratory, is the vibrating-coil magnetometer that permits continuous monitoring of sample magnetization as a function of applied magnetic field, temperature, and pressure. The Japanese have used portable pressure bombs in conjunction with a pendulum magnetometer, but this method does not provide simultaneous monitoring of the pressure and the magnetization. Magnetometer measurements with pressure have one important advantage over electrical measurements: there are no electrical leads, and measurements on polycrystalline samples are independent of any cracking of the specimen with pressure.

Problems of particular interest for magnetism include: (a) shifting with pressure of a conduction-band edge relative to a donor level or a valence-band edge; (b) critical lattice parameters for strong vs weak electron correlations; (c) variations with pressure of charge-transfer exchange processes, which are responsible for couplings between excited states in optical devices as well as for the couplings between ground states that are responsible for any long-range magnetic order; and (d) exploration of temperature-bandwidth phase diagrams, the bandwidth of allowed energies for magnetic electrons being sensitive to pressure. Closely related to this latter problem is the use of pressure to distinguish between the influence of chemistry and of lattice parameter on the physical properties of alloys and mixed systems.

2. SOME ILLUSTRATIVE EXAMPLES

a. New Compounds

(1) CrO₂

Where chemical reaction does not take place at atmospheric pressure, high pressure may induce synthesis by lowering the free energy of the compound relative to that of the components. It is useful to identify those cases where this situation may occur. A rather interesting case appears to apply to the stabilization of octahedral-site Cr⁴⁺ ions in oxides.

Outer d electrons at transition-metal cations may be either localized or itinerant, depending upon the magnitude of the coupling energy between d electrons on neighboring cations. Where the coupling is of intermediate strength, the d electrons are relatively unstable. Application of pressure enhances the interactions between d electrons on neighboring atoms; therefore, it increases any itinerant-electron bandwidth. If only bonding d orbitals are occupied, increasing the d-electron bandwidth stabilizes the phase, and the increase in stabilization with pressure is particularly sensitive where the d bands are very narrow at atmospheric pressure. The Cr⁴⁺-O²⁻-Cr⁴⁺ interactions via the 2p_π orbitals on the anions are of intermediate strength in the perovskites A²⁺CrO₃ -- SrCrO₃ is metallic and Pauli paramagnetic whereas CaCrO₃ and PbCrO₃ are spontaneously anti-ferromagnetic and exhibit Curie-Weiss paramagnetic

susceptibilities -- and in the ferromagnetic metal CrO_2 . These compounds have only been synthesized under pressure. Hydrothermal synthesis is used to prepare CrO_2 for high-quality magnetic recording.

(2) RbNbO_3

Many oxides, fluorides, and chlorides of chemical formula ABX_3 crystallize in one of the hexagonal-perovskite polytypes.^{1,3} These structures consist of ordered, close-packed AX_3 layers stacked in cubic or hexagonal or mixed cubic and hexagonal stacking sequences. The smaller B cations occupy all the interlayer X-anion octahedral interstices, and stabilization of these structures requires not only that the larger A cation have a radius $r_A > 0.9\text{\AA}$, but also that the B cation be stable in an octahedral interstice.

If the stacking of AX_3 layers is entirely cubic, the B-cation octahedra share only corners to form the 3C structure of cubic perovskites. In this structure the A cations are confined to a cubic cage of edge B-X-B, where the B-X bond length is a characteristic of the B and X ions that requires considerable energy to increase. This cage creates an upper limit on the A-cation size that can be accommodated in a given BX_3 cubic array. Such geometrical reasoning gives the Goldschmidt tolerance factor

$$t = (r_A + r_X) / \sqrt{2}(r_B + r_X) \quad (1)$$

and the ideal cubic structure is anticipated for

$t = 1.0$. In fact, the cubic perovskite structure is found over a range

$$t_l < t < t_u \quad (2)$$

where the upper limit is anticipated to fall close to $t_u = 1.0$. For smaller values of t , distortions from cubic to rhombohedral or orthorhombic symmetry optimize the A-X bonding at lower temperatures.

If the stacking of AX_3 layers is entirely hexagonal, the B-cation octahedra form face-shared linear chains parallel to the c-axis of the hexagonal (2H) cell. Since these chains are isolated from one another, relatively large A cations can be accommodated by adjustment of the c/a ratio. Therefore, this hexagonal perovskite structure is competitive where $t > 1$, as t becomes larger. However, accommodation of the larger A cation is at the expense of considerable Madelung energy, a large electrostatic repulsive force occurring between B cations in face-shared octahedra.

In a narrow, intermediate range of t , three intermediate stacking sequences have been identified: two-to-one cubic to hexagonal stacking (cchcch of the 6H structure), a one-to-one stacking (chch of the 4H structure), and a one-to-two stacking (chhchhchh of the 9R structure). In these intermediates, the loss of Madelung energy is reduced by displacing oppositely along the c axis the B cations in face-shared octahedra. However, chang-

ing the stacking sequence also requires energy, so that the 4H polytype is only found in oxides. In fluorides, where the Madelung energy is relatively small, the various polytypes occur in definite ranges of t :

Orthorhombic distortion of 3C (GdFeO ₃ -type)	$0.78 < t \leq 0.88$
Cubic 3C	$0.88 \leq t \leq 1.0$
Hexagonal 6H (Hex. BaTiO ₃ -type)	$1.0 < t \leq 1.06$
Rhombohedral 9R (CsCoF ₃ -type)	$t = 1.07$
Hexagonal 2H (CsNiF ₃ -type)	$t \geq 1.08$

In oxides, both t_U and the ranges of t over which the given polytypes are stable depend upon the effective charges of the B cations. Nevertheless, pressure always stabilizes cubic relative to hexagonal stacking.

Stoichiometric BaTiO₃ has the 3C structure, even though $t = 1.06$. At lower temperatures it exhibits ferroelectric distortions having technological importance. In these distortions, the Ti⁴⁺ ions are displaced cooperatively from the center of symmetry of their interstices to form one, two, or three shortest Ti - O bonds. The fact that CaTiO₃ ($t < 1.0$) undergoes no ferroelectric distortion has suggested that the ferroelectricity of BaTiO₃ is due to a stretching of the Ti - O bond by a $t > 1.0$. Furthermore, a 3C polytype having $t = 1.06$ is stabilized because the large effective charge on the Ti⁴⁺ ion inhibits the formation of a face-shared octahedra.

This reasoning suggested that RbNbO_3 and RbTaO_3 , which have $t = 1.08$, cannot be synthesized at atmospheric pressure because the large B-cation charge prohibits the formation of hexagonal polytypes and the large A-cation size inhibits formation of the 3C structure. However, it followed that their synthesis should be accessible under pressure, and RbNbO_3 was prepared at 65 kbar and 900°C , RbTaO_3 at 90 kbar and 900°C . Whereas RbNbO_3 exhibits the ferroelectric distortions of BaTiO_3 at atmospheric pressure, RbTaO_3 remains cubic. This information indicates that not only stretching of the B - O bonds, but also a small octahedral vs. tetrahedral site-preference energy are required for a ferroelectric displacement of the B cations.

b. New Polymorphs

From the above discussion, it is apparent that ABX_3 polytypes having a larger fraction of cubic stacking can be prepared at high pressures. In the case of oxides and fluorides, these high-pressure structures are metastable at atmospheric pressure to high ($T \sim 1000^\circ \text{C}$) temperatures. The high-pressure formation of polytypes having a greater fraction of cubic stacking is a general phenomenon and has been extensively studied in the rare-earth metals.

A ferrimagnetic material that is transparent in the visible and in the IR out beyond $10\mu\text{m}$ would be technologically important, especially where the Curie temperature is above room temperature. At atmospheric pressure, RbNiF_3 forms in the 6H structure and is ferrimagnetic below $T_c = 139^\circ \text{K}$. Although transparent in the near IR, lattice absorption begins to be

intolerable at $7\mu\text{m}$. In order to push the absorption edge out to longer wave lengths, it is necessary to have a compound containing heavier ions. Although CsNiF_3 crystallizes in the hexagonal 2H polytype, a metastable 6H structure can be formed at $P = 60$ kbar. This phase is also ferrimagnetic with a $T_c = 111^\circ\text{K}$ and an IR cut-off beginning at $9\mu\text{m}$. To extend the limit beyond $10\mu\text{m}$, it appears necessary to go to heavier anions. Unfortunately the ferrimagnetic $\text{ABC}\ell_3$ compounds are unstable at room temperature. Nevertheless, this example illustrates how high pressure may be useful for the synthesis of a metastable polymorph, other than diamond, of technological importance.

c. Reduction of Native Defects

The preparation of wide-gap semiconductors for efficient light-emitting diodes or for diode lasers at visible frequencies has proven an illusive goal. The principal reason is the existence of native defects that prevent the preparation of both n-type and p-type semiconductors of the same wide-gap material. Evidence that this situation might be alleviated by high-pressure synthesis comes from successful improvement of the stoichiometry in several transition-metal oxides.

Antiferromagnetic FeO_{1+x} is oxygen-rich if prepared at atmospheric pressure. However, the high-pressure preparation of stoichiometric FeO has recently been reported. Similarly, $\text{A}^{2+}\text{FeO}_{3-x}$ is always oxygen-poor if prepared at atmospheric pressure, but synthesis under high oxygen pressure yields stoichiometric compounds. A high oxygen pressure can be obtained with a double cell having CrO_3 in one chamber and the sample in the other chamber.

Superconducting TiO contains about 16% cation and anion vacancies that order below 900° C. These vacancies may be at least partially removed by high-pressure synthesis.

d. Easier Synthesis

Many solid-state reactions are extremely slow or lead to poorly crystallized products if carried out at atmospheric pressure. Where the product is stabilized by pressure, high pressures may reduce reaction times to less than an hour and/or markedly increase the crystallinity of the product. For example, synthesis of the orthoferrites LnFeO_3 by normal ceramic techniques usually requires several days of regrinding and firing, whereas they may be prepared in half an hour at 50 kbar and 1200° C.

Although NaSbO_3 and KSbO_3 have a tolerance factor t compatible with the formation of a perovskite structure, these compounds crystallize in the ilmenite structure at atmospheric pressure. However, KSbO_3 transforms to a cubic structure -- space group $\text{Pn}3$ -- if annealed at 1000° C for several weeks. Treatment of the ilmenite phase for only 5 minutes at 800° C and 20 kbar is sufficient to transform it to a disordered, cubic $\text{I}23$ structure. The $\text{Pn}3$ and $\text{I}23$ structures each have the same $(\text{SbO}_3)^-$ array, which contains tunnels along the body diagonals. The difference between the structures is due to ordered vs disordered arrangements of the alkali atoms in the tunnels. Given KSbO_3 in the $\text{I}23$ structure, it is possible to prepare NaSbO_3 , LiSbO_3 , and AgSbO_3 compounds with the same $(\text{SbO}_3)^-$ array by ion exchange. Such tunnel structures may be useful as solid-state electrolytes.

e. Shifting a Band Edge

The ferromagnetic compound EuO may be made either europium-rich or europium-poor. The stoichiometric compound is an insulator having a $4f^7$ localized-electron manifold near the bottom of a large energy gap between the $O^{2-}:2p$ valence and $Eu^{2+}:5d$ conduction bands. If the compound is europium-rich, anion vacancies serve as electron traps for the excess electrons, and above the Curie temperature EuO_{1-x} is an n-type semiconductor. The trap, or donor, states appear to have energies that are relatively independent of the position of the 5d band edge, and below the Curie temperature $T_C \approx 70^\circ K$ the edge of the parallel-spin 5d band is stabilized by the Weiss molecular fields to below the trap level. Therefore a metal-to-semiconductor transition occurs near the ferromagnetic Curie temperature. An alternate method of changing the relative position of the 5d band edge is high pressure, which broadens the 5d band. Monitoring the change in resistivity and in optical absorption edge with pressure at room temperature provided an excellent test of the model.

In the case of SmS, a localized $4f^6$ level lies just below the 5d band edge, and 6.5 kbar causes sufficient broadening of the 5d bands to induce a first-order volume reduction due to $4f^6 \rightarrow 4f^5 5d^1$ electron transfer at each samarium atom. The device potential of such a phenomenon has yet to be explored.

f. Critical Atomic Volumes

The d electrons of neighboring transition-metal atoms may interact directly (M-M interactions) or via an intermediary anion (M-X-M interactions). In either case,

reduction of the atomic volume enhances the strength of the interaction. Three critical volumes are of fundamental interest: (1) that at which the pressure dependence of the magnetic-ordering temperature changes sign, (2) that at which spontaneous magnetism disappears, and (3) that at which there are abrupt changes in the magnitude of the atomic moments.

To date, there are no known examples where a change in sign of $\partial T_c / \partial P$ has been observed. This fact is, in itself, informative since it suggests two distinguishable thermodynamic states for the outer d electrons. Transitions from a semi-conducting, spontaneously antiferromagnetic phase to a metallic, Pauli paramagnetic phase have been observed in several compounds. Metastable, hexagonal NiS, for example, exhibits a first-order semimetal-to-metal phase change at an antiferromagnetic Néel temperature T_N , and the antiferromagnetic phase can be completely quenched by hydrostatic pressures $P > 20$ kbar. There appears to be no symmetry change across this transition. The compound MnAs exhibits a first-order change in the magnitude of its atomic moment at the Curie temperature. Experiments with hydrostatic pressure on this compound and on the systems $\text{MnAs}_{1-x}\text{P}_x$, $\text{MnAs}_{1-x}\text{Sb}_x$ have established that there is a sharp change in the magnitude of the intra-atomic exchange energy at a critical atomic volume. The system $\text{V}_{2-x}\text{Cr}_x\text{O}_3$ has a low-temperature, anti-ferromagnetic phase that can be quenched by high pressure ($P > 26$ kbar for V_2O_3). For small x , it also has a high-temperature metal-to-semiconductor transition that reflects changes in electron correlations as well as shifting band populations. There are several interesting features of this system that have important theoretical implications, including evidence of a critical

lattice parameter in the basal plane, and hence a critical bandwidth, for the support of spontaneous magnetism.

g. Exchange Processes

The most straightforward way to investigate the sensitivity of interatomic-exchange couplings to the lattice parameters is to monitor changes in magnetic order, magnetic-ordering temperatures, and the paramagnetic Weiss constant as a function of pressure. The sign of $\partial T_c / \partial P$ may reflect competing exchange interactions, but where these complications are missing it provides an interesting criterion for distinguishing localized from itinerant electrons. Measurements of $\partial T_c / \partial P$ for several itinerant-electron ferromagnets have provided important checks on the Stoner theory of ferromagnetism. Neutron-diffraction measurements of elemental chromium under hydrostatic pressure have provided constraining data for any theory of the spin-density waves in this itinerant-electron antiferromagnet. In particular, any theory of the spin flip relative to the propagation direction of the spin-density wave must also account for the pressure dependence of this phenomenon. In the system $Mn_{2-x}Cr_xSb$, an exchange-inversion temperature is found in a small interval of x . This appears to be intimately associated with the atomic volume and could profitably be investigated as a function of pressure.

h. Chemical vs Volume Effects

Investigations of the temperature dependence of magnetic properties as a function of magnetic-electron bandwidth must make use of chemical substitutions as well as of pressure. However, chemical substitutions require one to distinguish between the influence of chemical and of volume changes. In

the perovskite system $\text{Ca}_{1-x}\text{Sr}_x\text{MnO}_3$, for example, the Néel temperature increases with x , or $\partial T_N / \partial a_0 > 0$, whereas a $\partial T_N / \partial P > 0$ indicates just the opposite dependence on cell size. A distortion of the perovskite to orthorhombic symmetry gives rise to a weak ferromagnetism due to a canting of the antiferromagnetically coupled spins. The cant angle, and hence the magnetization σ_0 , varies with the magnitude of the distortion. Therefore, by monitoring both $\partial T_N / \partial P$ and $\partial \sigma_0 / \partial P$ for different values of x , it was possible to show that $\partial T_N / \partial x > 0$ is due to chemical rather than geometrical effects. This finding has important implications for any interpretation of the variations in magnetic properties found among the transition-metal oxides having the perovskite structure.³

3. FINAL REMARKS

No attempt has been made here to summarize the considerable amount of work that has been done on the preparation of magnetic materials and the investigation of their properties under hydrostatic or uniaxial stress. Rather, emphasis has been given to the principal motivations for use of high-pressure techniques in this field, and the few illustrative examples have been chosen to indicate how this tool is being used in exploratory research. Only oblique references are given to the technique's potential impact on technology. It seems clear, however, that a properly orchestrated effort could sharply enhance the influence of high-pressure technology on all three aspects of the materials field: devices, materials preparation and processing, and understanding and control of physical phenomena. However, proper orchestration would make high-pressure technology a tool within a larger materials effort rather than an end in itself.

The experimentalist responsible for the high-pressure apparatus and measurements at Lincoln Laboratory is James A. Kafalas. The vibrating-coil magnetometer was developed by Kirby Dwight and Norman Menyuk after an early design by Donald O. Smith.

4. RECOMMENDATIONS

The topics covered in this presentation may be related to the stated DoD pacing material problem areas as follows:

a. Pressure as a Variable (Evaluation of Pressure Effects on....)

- (1) Diode lasers: -- tuning
- (2) Electro-optic materials: -- pressure-induced metal-insulator transition introduces a mirror-to-window transition in the near IR.
Examples: SmS, $(V_{1-x}Cr_x)_2O_3$
- (3) Magnetic materials: -- (a) permeability changes induced by tensile stress, as in Permalloy, and (b) pressure-induced magnetic transitions, as in MnAs.
- (4) Dielectric materials: -- pressure modulation of the dielectric constant in the vicinity of a ferroelectric Curie temperature.

b. Materials Processing

- (1) Vacuum hot pressing: -- (i) Removal of pores from sintered specimens may yield (a) optical-quality, polycrystalline windows of greater mechanical strength than single crystals, (b) optical-quality Faraday rotators, and (c) higher magnetic permeabilities in ferrite materials.

(ii) Sintering at lower temperatures helps to control cation valence and hence to reduce dielectric loss.

(2) High-pressure preparation:

(i) Reduction of atomic vacancies as demonstrated in TiO and SnTe (tin vacancies reduced by a factor of five) improves stoichiometry and may permit the fabrication of p-n junctions in wide-gap semiconductors for LED and diode (tunable) lasers in the visible.

(ii) Reduction of sintering temperatures offers control of cation valence and hence reduction of dielectric losses.

(iii) Extrusion: -- fabrication of polycrystalline rods and plates.

c. Synthesis (Search for New Supermaterials)

It is generally possible to extrapolate from known materials to the design of unknown materials that would improve a desired physical property. It is also possible, in general, to determine whether pressure is a variable that makes synthesis of the unknown material more or less probable. The following examples (see 2. (a)) are illustrative:

(1) New compounds: -- CrO_2 is a hard magnet that can only be prepared at pressure (hydrothermal synthesis is used industrially) and that gives magnetic tapes of higher performance.

- (2) New polymorphs: -- The 6H form of CsNiF_3 is an example of a new ferrimagnetic material transparent to optical and IR frequencies, and NaSbO_3 having the cubic structure of KSbO_3 is a new solid-state electrolyte of considerable promise as a higher efficiency electrolytic power source material.
- (3) Easier synthesis: -- The orthoferrites LnFeO_3 exhibit a weak ferromagnetism that is of potential interest for "bubble-domain" devices. Preparation of sintered samples is greatly facilitated by high pressure. High pressure might also aid single-crystal preparations.

5. Comments

- (1) There is a clear need to develop techniques other than hydrothermal synthesis for the growth of single crystals at high pressures.
- (2) High-field superconductors and compounds exhibiting some types of metal-insulator transition generally have structures that tend to be unstable. If metastable phases can be prepared, these may exhibit interesting transitions at lower temperatures. For example, the stable low-temperature form of NiS is millerite, but quenching from 900°C retains the hexagonal B8_1 structure, which is metastable below 300°C . This metastable phase undergoes a first-order isosymmetric transition below room temperature from an antiferromagnetic semimetal

at $T < T_N$ to a Pauli paramagnetic metal at $T > T_N$. Since many high-pressure phases are metastable at atmospheric pressure, new metastable compounds with exploitable properties may be discovered with high-pressure techniques.

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APPENDIX K

VERY HIGH PRESSURES USED IN POLYMER TECHNOLOGY

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This survey omits the important use of elevated pressures in the synthesis of high polymers. As in areas of chemistry that pertain to organic and inorganic chemistry, so also is the use of high pressure an important variable in synthetic processes.

The exploitation of elevated pressures has great potential in adding to an understanding of polymeric substances. This statement can equally be made with respect to virtually the entire catalog of useful compounds; indeed, there are many examples of technological studies that have hinged upon information derived from the pressure dependence of key parameters. With polymers, regrettably, this information is still sparse. The relative complexity of these materials, both in structure and in thermodynamic state, makes them unattractive as candidates for investigation at elevated pressure. This situation is unfortunate, for this very complexity requires the use of every powerful variable to clarify the fundamental properties and behavior of the substances.

High polymers occur in technology either as partly crystalline substances or as wholly amorphous materials. Fully crystalline polymers are experimentally contrived oddities of some theoretical interest. No meaningful studies

of the use of elevated pressure on these materials have been reported. On the other hand, partly crystalline and wholly amorphous polymers comprise all the polymers of technological importance. The properties of these materials are strongly influenced by pressure.

We identify three categories of structural organization for bulk polymers: (1) crystalline regions; (2) rubbery structures; (3) glassy arrays. Depending upon the molecular character of the compound, the temperature, and the pressure, transformation from one to another of these organizations can be effected on a given time scale. We speak of two characteristic temperatures: (1) the melting point (T_m), and (2) the glass temperature (T_g). In contrast to the behavior of compounds of low molecular weight, T_m is affected by many variables (e.g., molecular weight, time scale, pressure). Similarly, T_g is also pressure-dependent.

In the case of T_m , the pressure dependence is evidently related to variations in the morphology. Information is largely confined to the behavior of polyethylene. This partly-crystalline polymer has been shown by Geil, Wunderlich, and others to have a lamellar crystalline structure that depends on pressure. In studies by electron microscopy, it is found that moderately high pressures during crystallization from the melt (e.g., pressures in the range 10^4 atmospheres and higher) lead to morphologies in which the crystalline lamellae consist of folded chains, with a fold length of $\sim 100 \text{ \AA}$. The technological value, if any, of these high-pressure forms of polyethylene (and other polymers yet to be studied) is still unknown, since current techniques of extrusion and molding occur at pressures well below this

range of unusual behavior. Certainly there is fundamental information to be gathered with respect to the kinetics and thermodynamics of crystallization in polymers, but it is not yet known if there is also technological promise.

The variability of T_g with pressure is known both for polymeric and monomeric substances. The rubbery "state" of polymers is fairly well understood, but the glassy "state" is the object of considerable dispute. It has been proposed, by Gibbs and DiMarzio and others, that T_g is in fact not very different from a thermodynamic transition temperature, T_2 , which is defined as a temperature that corresponds to the vanishing of free volume upon cooling. The existence of a temperature T_2 is postulated as being necessary in order to avoid the paradox of a lower entropy for amorphous regions than for crystalline regions with decreasing temperature. The state of this argument is in considerable doubt. It would be greatly aided if there were extensive measurements and correlated models as to the role of pressure-sensitive parameters such as the heat capacity, the thermal expansion coefficient, and the molar volume. Data on such parameters are sparse and often conflicting.

Elevated pressures and major pressure gradients are common to the important commercial processes of extrusion and molding of polymers. The absolute pressures are not great, but since the materials are characterized by quite large compressibilities in the molten state, gradients in pressure are empirically found to be important. For example, in the extrusion of a molten polymer such as polyethylene, there is found to be a limiting condition of mechanical shear forces

and temperature for a compound of given molecular weight (M.W.) and M.W. distribution at which a turbulent effect develops. This phenomenon has sometimes been called "melt fracture", a term that is outwardly descriptive but not authentic in molecular terms. With the acute demand for higher efficiency in the processing of plastics, the contributions of high pressure and of pressure gradients will have to be explored in vastly greater scope than has been undertaken so far.

APPENDIX L

HIGH-PRESSURE EQUATION OF STATE AND LATTICE DYNAMICS STUDIES

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Static high-pressure experiments to determine the thermodynamic properties of solids can use bulk measurements, x-ray and neutron diffraction techniques, or ultrasonic velocity measurements.¹ The highest pressure data have been achieved with x-ray methods,² while the greatest precision (at relatively low pressures) is obtained in elastic constant determinations using ultrasonic methods.³ The primary interest in these equation of state (EOS) data (phase transitions are not included) is fundamental and involves, for instance, correlations between classes of solids or tests of theoretical models for a given solid. In this sense, the maximum information about lattice properties could be obtained by studies of lattice vibration properties (lattice dispersion relations) of single crystals as a function of both temperature and pressure using inelastic neutron scattering experiments. These experiments are possible only for the highly compressible rare gas solids for which significant density changes can be realized at small pressures (a few kbar) in fairly thin-walled aluminum or stainless steel pressure vessels.⁴ The scattering of neutrons from pressure vessel walls is a major source of background in experiments of this type and provides a practical limitation to the pressure range hence to the substances which can be

studied. Somewhat the same type of information is obtained from ultrasonic measurements on single crystals for various wave polarizations and directions of propagation, although the data are restricted basically to the low frequency end of the lattice vibration spectrum. At present, these experiments are being carried out at pressures (of up to 10 kbar) where the second-order effects in the pressure dependence of the elastic constants (proportional to P^2) are important.³ The need for hydrostatic pressure to obtain data for single crystals restricts somewhat the pressure range which is available. X-ray¹ and neutron diffraction⁵ measurements of lattice parameters can be used to obtain information about linear compressions of anisotropic solids, with x-ray data extending at room temperature to 450 kbar.² Single-stage bulk piston displacement measurements of volume compressions can be made to roughly 40 kbar,⁶ although Bridgman reported compression data to approximately 100 kbar with a two-stage system.

The usefulness of all of these data in a technological sense probably is second-order; they are needed to convert other data from a pressure dependence to a more useful volume dependence or to provide the more detailed information required for a fundamental understanding of another phenomenon such as superconductivity or the equilibrium between two crystallographic phases. Guidelines exist⁷ so that available data can be utilized to predict qualitatively the high-pressure EOS for a new alloy or compound, although the need sometimes arises for a direct determination. More subtle problems can be studied only through direct experiments. For instance, lattice instabilities that are believed

to be associated with superconducting behavior⁸ and with the occurrence of some crystallographic transformations⁹ can be studied only through the transverse lattice vibrational dispersion relations or, alternatively, the pressure dependence of the elastic shear constants of the solid. In these instances, a study of the EOS (in a general sense) possibly can lead to a more fundamental understanding of the phenomena involved and thus could be of considerable technological importance.

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APPENDIX M
ELECTRONIC PHENOMENA AT HIGH PRESSURE

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1. INTRODUCTION

There are several areas of solid-state science in which high pressure has had important impact. These involve (1) studies of cohesive energy and the equation of state, (2) studies of morphology and structure, including phase diagrams and the synthesis and recovery of high-pressure phases, (3) studies of translational and rotational motion, and (4), studies of electronic behavior. After a couple of paragraphs outlining the situation of (1), (2), and (3) above, the bulk of this appendix relates to electronic phenomena.

Measurements of compressibility are perhaps the oldest form of high-pressure solid-state research. In recent decades there have been extensive advances based on a number of developments, including the extension of the static pressure range to several hundred kilobars, the development of high-pressure ultrasonic and x-ray diffraction techniques, the development and refinement of shock measurements, the development of techniques for high-pressure p-v measurements down to temperatures of a few degrees K, and, not the least, improvements in the theories of cohesive energy.

Between 1930 and 1945, P. W. Bridgman demonstrated that the first-order phase transition (the rearrangement of atoms into a new lattice) was a common phenomenon. This was perhaps his central contribution to solid-state science. The

study of high-pressure phase diagrams has flourished, aided by many of the developments mentioned in the preceding paragraph, as well as the possibility of doing work at pressures above 100 kbars at high temperature. It has formed the basis of a synthetic chemistry involving primarily "quenched in" high-pressure phases which has been significant both in this country and abroad, especially in France, Japan, and Sweden (see appendices D and J). For a long time theory did not keep pace with experiment in this area. Recently, the important early work of Löwdin and of Born and Huang has been supplemented by the important analyses by Phillips and by Van Vechten. For certain relatively simple classes of systems there appears to be a reasonable possibility of predicting first-order transitions. The measuring of phase diagrams of specific materials with potential practical interest, as well as a certain amount of systematic investigation, will always be of importance. There are, however, phenomena associated with first-order phase transitions that are very imperfectly studied, either experimentally or theoretically. These phenomena include metastability, which forms the basis for the quenching in of high-pressure phases, and the rates of first-order phase transitions including melting. In these areas experiments are in a rudimentary stage, and adequate theory is almost nonexistent. These studies would be intensely practical as well as interesting to the scientific community. Most high-pressure synthesis depends on the possibility of quenching in a metastable phase. The use of solids as "cushions" to absorb rapidly high energy pulses depends on the utilization of the volume change and latent heat associated with a phase transition and on the rate at which these can be made available.

In contrast to the situations associated with crystalline materials, as described above, the use of pressure to investigate the morphology of polymers and glasses is in a much more rudimentary stage. It would appear, however, to be a field of considerable promise (see appendix K).

A third area of active high-pressure research is that of atomic or ionic motion in solids. There have been extensive studies of diffusion in metals in the hydrostatic range, pioneered by D. Lazarus, as well as some measurements on ionic and covalent crystals. These studies have been essential to the understanding of the role of impurities in determining the properties of solids. Decker has recently extended diffusion measurements into the higher quasi-hydrostatic range. In addition to the studies of translational motion usually accomplished by tracer techniques, the use of nuclear magnetic resonance relaxation methods to follow rotational, translational, and other motions in solids, liquids, and solutions is a technique of growing significance in chemistry. In particular, the study of motion in polymers under pressure has important practical implications.

Somewhat in contrast to the areas discussed above, the study of the electronic structure and electronic behavior of solids is strictly a phenomenon of the past 25 years. In the late 1940's, A. W. Lawson demonstrated that hydrostatic pressure studies in the 12-kbar range could yield important information about electrons in solids. This approach has been pursued vigorously by physicists and most of the measurements of solid-state physics are now made in this pressure range. The possibility of measurements at a few degrees K

and several kilobars has greatly extended the applicability of high pressure to the problems of physics.

During the past 15 years it has been demonstrated that quasi-hydrostatic measurements at higher pressures (in some cases as high as 500 kbar) are significant to the understanding of electronic behavior. The major development has been the possibility of making a variety of types of measurements that are sensitive to the relative displacement of electronic and nuclear energy levels at these high pressures. These include optical absorption and emission (fluorescence and phosphorescence), nuclear magnetic resonance, Mössbauer resonance and susceptibility, and dielectric measurements, in addition to electrical resistance. The extension of the pressure range has been essential to the discovery of many of the electronic transitions discussed below. Recently McWhan and Lyons have developed a technique for making electrical resistance measurements to 100 kbar at a few degrees K, which has already had important consequences for the understanding of insulator-metal transitions. Jayaraman's extension of the static pressure range to 50 kbar has been significant in understanding semiconductor behavior. In this appendix it will be possible only to outline briefly the basic effect of pressure on electronic behavior and the types of studies made, with a few comments about applications.

The essential effect of pressure is to increase overlap of adjacent electronic orbitals. One result of this increased overlap is a broadening of energy bands and an increased electron delocalization. A second result is a shift in the energy of one type of orbital with respect to another.

Since orbitals of different quantum number may differ in radial extent or shape, this is a common phenomenon. Much of our understanding of electronic properties of solids comes from a study of these shifts. For many systems the shifts due to pressure are quite analogous to the shifts in going from a dilute gas to a solution, but the pressure shifts are frequently more susceptible to analysis.

Many systems have excited states which lie not too high in energy with respect to the ground state. For such systems the relative shift in energy may be sufficient to give a new ground state for the system, or a ground state grossly altered by configuration interaction. This event is called an electronic transition. These events may occur discontinuously at a fixed pressure or over a range of pressures. The prediction, discovery, and elucidation of electronic transitions is one of the most important aspects of solid-state science. It has primarily been an activity associated with physics, but it has recently been demonstrated that electronic transitions can also have significant chemical consequences.

The above phenomena can be described in terms of one electron theory. Pressure also has significant effects in truly cooperative phenomena such as ferromagnetism and antiferromagnetism, ferro-electricity, and superconductivity. In such a brief discussion, however, it is possible only to touch on those areas where high-pressure studies have had important impact and to include a few predictions about future possibilities.

The measurement of the shift of energy levels with pressure has been important to a wide variety of problems, both

theoretical and applied. The shifts of the absorption edge in semiconductors, and the evaluation of the deformation potential is an important feature in the design of electronic components. Shifts of the absorption edge also play a role in the study of the approach to the metallic state discussed below. High-pressure studies have been important in understanding the nature of color centers in alkali halides and of other impurity centers in a variety of crystals. High-pressure studies of transition metal ion spectra in a wide variety of environments is a very significant feature of coordination chemistry, High-pressure optical studies have similarly contributed to our understanding of the π energy levels of aromatic compounds. Both absorption and emission measurements (fluorescence and phosphorescence) and been important in this regard. Finally, high-pressure optical studies have made a basic contribution to the analysis of forces involved in electron donor-acceptor complexes.

2. ELECTRONIC TRANSITIONS

One of the most active branches of high-pressure experimentation is the prediction, discovery, and explanation of electronic transitions -- new electronic ground states. As we shall indicate below, these new ground states may have different chemical as well as physical properties. They may also have geophysical and biological implications.

Table 1 may be helpful in trying to understand the nature of these transitions. The types of transitions observed in solids are divided into four classes. Class I refers to events that involve rearrangement of the atoms, ions, or molecules with no electronic implications. Class II contains

TABLE 1 - Types of High-Pressure Transformations

Class I 1st Order Transition- Electronic Negligible	Class II 1st Order Transition- Significant Electronic Component	Class III Electronic Transition- Significant Volume or Structure Change	Class IV Electronic Transition- Continuous
fcc → sc KCl, KBr, KI fcc → hcp Lead	bcc → hcp Iron (Ferro → paramagnetic) diamond → white tin Si, Ge, InSb, GaAs etc. (semiconductor → metal)	s → d Cesium Rubidium Potassium? f → d cerium other rare earths Mott Transition doped V ₂ O ₃ ?	reduction of Fe(III) to Fe(II) spin changes in partially filled shells reactive ground states of aromatic hydrocarbons and electron donor-acceptor complexes rare earth salts

events whose main feature appears to be polymorphism, but where there may be drastic changes in electrical or magnetic properties. Class III contains essentially electronic transitions that occur discontinuously and are accompanied by a volume discontinuity. Class IV involves new ground states established over a range of pressures, cooperative phenomena, or events involving continuous change in the degree of configuration interaction. The equilibrium between states here is like the equilibrium between reactants and products in any chemical reaction.

The boundaries between the various classes are, of course, somewhat arbitrary. Any rearrangement of atoms or ions implies some change in electronic interaction because of change of local symmetry. Whether the electronic component of a transition is major or minor is, to some degree, a matter of viewpoint. Whether a transition occurs continuously or discontinuously may depend on the temperature at which it is studied. Nevertheless, the classification affords a basis for understanding many electronic phenomena. Outlined below are three classifications of electronic transitions -- those in metals, insulator-metal transitions, and those in organic and inorganic insulators.

a. Metals

Electronic transitions were first discovered in metals. Over 20 years ago a cusp in the resistance of cesium near 40 kbar was associated with a change in character of the conduction band from 6s to 5d. A second transition was discovered some ten years ago which is probably associated with the introduction of 4f and 5d characters to the conduction band. A sharp rise in the resistance of rubidium near 145 kbar probably involves

involves a $5s \rightarrow 4d$ promotion, and a maximum at 300 kbar may be established by introduction of 4p character. Potassium exhibits a sharp resistance rise near 280 kbar at low temperature probably associated with a $4s \rightarrow$ transition. The magnitude decreases with increasing temperature and it disappears near 250°K . This may be an example of a critical point for an electronic transition.

Some rare earth metals also exhibit electronic transitions probably involving promotion of a 4f electron to the 5d shell or to the conduction band. The transition in cerium has been most thoroughly studied as it initiates at a few kbar pressure. It has been shown that it disappears at a critical point with increasing temperature. There are numerous cusps and resistance maxima in various rare earth metals (e.g., praeysidymium, neodymium, europium, etc.). In several cases these are very sharp at low temperature and broaden out near room temperature so that there may be critical points for these transitions. In addition to these static high-pressure studies to pressures of 500 kbar, there have been shock-wave studies to well over a megabar. These reveal discontinuities in compressibility at very high pressure and temperatures of several thousand degrees Kelvin. It is, of course, difficult to interpret events electronically when the thermal energy is a significant fraction of an electron volt.

Finally, metals like calcium, strontium, and ytterbium exhibit a metal to semiconductor or metal-semimetal transition. The free atoms of these materials have filled electronic shells, and they are metals because the conduction band is of s-p-d character. The Fermi surface has thus a complex intersection with the Brillouin zone boundary. With

pressure the holes and overlaps merge to give semiconducting character. At sufficiently high pressure, there is a first-order phase transition to a metallic state.

b. Insulator-Metal Transitions

In a simple band picture of solids, insulators have filled bands separated by energy gaps large compared with kT . Metals have partially filled bands or filled bands overlapping empty bands as in the alkaline earth metals discussed above. Since many transition metal oxides are insulators, although in the simple picture the partially filled band arising from the atomic d orbitals should give metallic conductivity, it is clear that more than the simple picture is needed. Mott has developed an analysis that predicts that such materials will be insulators below a certain electron density and metals above that density.

Since increasing pressure tends to broaden energy bands and to shift one set of bands with respect to another, one might expect that insulator-metal transitions would occur by a number of different mechanisms with increasing pressure. In molecular crystals like iodine or pentacene, metallic conductivity occurs at sufficiently high pressure with no apparent discontinuity in physical properties. It would appear that in these very compressible materials the primary mechanism is the broadening and shift of energy bands.

Silicon, germanium, and the related III-V compounds, which are useful transistor materials, exhibit the diamond (zinc blende) structure which is relatively open. At sufficiently high pressure these materials show first-order transitions to the white tin or an analogous structure which is metallic.

Van Vechtin has developed a theory which is remarkably successful in predicting the pressure associated with these transitions. This theory should be useful in predicting the possibilities of transitions of a practical nature.

Compounds like ZnS, ZnSe, ZnTe, and CdS also have the zinc blende (or wurtzite) structure. Since these are practical phosphors, the understanding of their properties is of practical importance. The zinc compounds transform at high pressure to a form of low resistivity and metallic or semimetallic behavior. They apparently have the NaCl structure. The high-pressure phase of ZnS exhibits a maximum in resistance near 425 kbar with a drop of about 25% by 500 kbar. CdS transforms to the NaCl structure at 25 kbar. The high-pressure phase is semiconducting and exhibits a large maximum in resistance near 330 kbar with a drop of 40% by 450 or 460 kbar. The unusual resistance behavior in the NaCl phases of ZnS and CdS may involve further electronic transitions. A thorough study could reveal information of importance about these useful materials.

The transition metal oxides have been widely studied. Perhaps the most broadly based, thorough, and useful study has been by McWhan and his colleagues at Bell Laboratories. Their studies on mixed V_2O_3 - Cr_2O_3 crystals have been especially interesting. The material $V_{0.96}Cr_{0.04}O_3$ can exist as either a paramagnetic or antiferromagnetic insulator or a metal depending on the pressure and temperature. The insulator-metal transition approximates very closely to the transition predicted by Mott. An important feature of the McWhan study is the relationship exhibited between changing chemical composition and changing pressure on electronic properties.

There are many ways in which changing pressure has effects analogous to changing composition in a wide variety of solids and liquid solutions. For many systems pressure can be used as a simple way of explaining and predicting composition effects. This has not been hitherto widely understood. This understanding could lead to the "design" of solids which, at one atmosphere, would have the desirable properties which may first be observed only in materials under very high pressure.

Insulator-metal transitions have also been observed in rare earth calcogenides. These are associated with changes in the occupation of the 4f orbitals and may occur discontinuously or over a range of pressure.

c. Insulators

Electronic transitions have been observed in a variety of insulators with consequences of considerable chemical importance. The relative shift of electronic orbitals with pressure, combined with increased configuration interaction can give a new ground state with very different chemical properties. These transitions typically fall in Class IV of Table 1.

Aromatic hydrocarbons with low-lying excited states, such as pentacene and hexacene, react at high pressure and room temperature to form highly stable polymers. The reaction takes place via thermal occupation of the polar, reactive, excited state at high pressure. Some hydrocarbons, like pyrene and perylene, have excited states too high in energy to be thermally accessible at the highest available pressures, so they are not reactive. They form donor-acceptor complexes with acceptors such as iodine. These complexes have low

lying excited states that can be thermally occupied at high pressure. These materials then react. The iodine can be recovered qualitatively from the product leaving dimers and tetramers of the hydrocarbons of a type not hitherto seen. It is thus possible, by means of an electronic transition, to create a new class of hydrocarbon compounds.

A combination of Mössbauer resonance and optical absorption has revealed an extensive high-pressure chemistry of iron compounds. There are at least three kinds of electronic transitions resulting from interaction of the ligands (the surrounding atoms or ions) with the iron. The normal state of iron in ionic compounds is high spin. Transformations to the diamagnetic low-spin state have been observed, resulting from the increase in the splitting of the iron 3d orbitals by the field of the ligands at high pressure. Low-spin compounds exist if the ligands have available orbitals of appropriate energy and symmetry (π^* orbitals) which can be occupied by metal d_{π} electrons. This "back donation" provides the large ligand field necessary to give a low-spin ground state. At sufficiently high pressure the ligand excited states are occupied by ligand π electrons by a process similar to that observed for the aromatic hydrocarbons discussed above. This forces the metal electrons back into the metallic 3d orbitals and results in a low-spin to high-spin (diamagnetic-paramagnetic) transition. This can be classified as an "induced electronic transition," since a transition on the ligand induces one on the iron.

Finally, the reduction of ferric iron to the ferrous state is frequently observed. This takes place because the

3d orbitals lower in energy, vis-a-vis the ligand nonbonding orbitals, until the electron transfer is feasible. All of these processes take place over a range of pressures and are reversible, with considerable hysteresis. An analysis has been presented which accounts for the continuous nature of the process and for the hysteresis.

All the processes described here are thermal processes resulting from the relative shift of one type of orbitals with respect to another. Such shifts are normally measured by optical absorption. There are a number of reasons why optical processes involve different energies from thermal processes. These include the Franck-Condon principle (optical processes are rapid compared with nuclear motions), differences in selection rules, differences in the configuration coordinates involved in the two types of processes, and the effect of configuration interaction. An analysis has been presented which relates the two processes and which permits the prediction of thermal electron transfer from optical absorption studies. Specifically, the thermal energy is given approximately by the relationship

$$E_{th} \approx h\nu_{max} - \frac{1}{16 \ln 2} \frac{(\delta E_{1/2})^2}{kt} \left(\frac{\omega'}{\omega}\right)^2$$

where ν_{max} is the frequency of the maximum in optical absorption, $\delta E_{1/2}$ is the full width at half maximum for the optical peak, and ω and ω' are force constants associated with the ground and excited states. This relationship permits a semi-quantitative prediction of the pressure at which a (thermal) electronic transition will occur, from high pressure optical absorption data.

3. COOPERATIVE PHENOMENA

As mentioned earlier, there are classes of phenomena which can only be described in terms of interactions of electronic arrays. These include ferromagnetism, antiferromagnetism, ferroelectricity and superconductivity. Samara discusses ferroelectricity in Appendix I. In ferromagnetism and antiferromagnetism the relevant measurements are for the effect of pressure on the size of the field and on the Curie (or Néel) temperature. These studies have been important in understanding electron-electron correlations, alloying effects, "giant moments" in palladium alloys, and spin states in metals, as well as super-exchange and related phenomena in insulating antiferromagnets.

Pressure has been important in superconductivity research. Changes in critical temperature with pressure have formed important tests of theories. Most spectacular has been the creation of new superconducting phases at high pressure, and especially the superconductivity of metastable phases. The possibilities of high-temperature superconductors, especially hydrogen, have been widely discussed (see Appendix G).

4. PROSPECTS AND APPLICATIONS

Much of the work on electronic behavior at high pressure involves processes of current practical importance. In a number of cases (e.g., semiconductors) the work has been rather directly relevant to engineering design. Studies of pressure and electronic structure will continue to be a significant part of basic research. Listed below are several

aspects where such studies would appear to be rather directly relevant in the near future:

- a. The study of high temperature superconductivity.
- b. An elucidation of the properties of ferrites as related to local symmetry and orbital overlap.
- c. A better understanding of luminescence.
- d. New chemical reactions and new products based on novel electronic ground states. In this connection an important aspect is the ability to predict electronic transitions from optical absorption data.
- e. An understanding of the relationship between pressure effects and effects of changing composition to permit one to obtain at one atmosphere materials with properties only presently accessible at high pressure or in high-pressure phases.
- f. An understanding of the mechanism of protein denaturation.

In the past two decades high-pressure studies of electronic behavior have been very largely the domain of the solid-state physicist. There will be a considerable relative increase in the fraction of this activity relevant to chemical (and biochemical) problems.

Reviews devoted in large part to electronic phenomena include:

W. Paul and D. Warschauer, (eds.), "Solids Under Pressure," McGraw-Hill, New York 1963.

C. T. Tomizuka and R. Emrick, (eds.), "Physics of Solids at High Pressure," Academic Press, New York 1965.

D. Bloch, (ed.) "Proprietes Physiques des Solides Sous Pression," CNRS, Paris 1969.

D. B. McWhan, "The Pressure Variable in Materials Research," Science 176, 751 (1972).

H. G. Drickamer and C. W. Frank, "Electronic Transitions and the High Pressure Chemistry and Physics of Solids," Chapman and Hall, London, February 1973.

There are also articles in "Solid State Physics," F. Seitz, D. Turnbull and H. Ehrenreich (eds.), especially Vols. 11, 13, 17 and 19, Academic Press, New York, and in various volumes of "Advances in High Pressure Research," R. S. Bradley (ed.) and R. H. Wentorf (ed.), Academic Press, New York.