AD-787 054

ADVANCED CONCEPTS OF SUPERCONDUCTIVITY

A COMPARATIVE REVIEW OF SOVIET AND AMERICAN RESEARCH. PART I. HIGH TEMPERATURE SUPERCONDUCTIVITY

RAND CORPORATION

PREPARED FOR

DEFENSE ADVANCED RESEARCH PROJECTS AGENCY

JANUARY 1974

The research described in this Report was sponsored by the Defense Advanced Research Projects Agency under contract No. DAHC15-73-C-0181. Reports of The Rand Corporation do not necessarily reflect the opinions or policies of the sponsors of Rand research.

AD 787 054

ARPA ORDER NO.: 189-1

3F10 Nuclear Monitoring Research

R-1401-ARPA

January 1974

Advanced Concepts of Superconductivity: A Comparative Review of Soviet and American Research. Part I. High-Temperature Superconductivity

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A Report prepared for

DEFENSE ADVANCED RESEARCH PROJECTS AGENCY

Rand
SANTA MONICA, CA. 90406

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Published by The Rand Corporation

PREFACE

This Report is part of a continuing Rand study, sponsored by the Defense Advanced Research Projects Agency, of significant aspects of Soviet scientific research. It is the first in a series that will consider superconductivity, an area in which the Soviet Union maintains a strong and viable technological posture. The present Report treats high-temperature superconductivity (HTS); subsequent reports will deal with high-pressure superconductivity (HPS) and high-critical-field (Type II) superconductivity (HFS).

The Report is based on a comprehensive -- although not exhaustive -- coverage of the open-source literature in the United States (and some Western countries) and the Soviet Union for the period from 1964 to September 1973.* A more detailed treatment of the analytical studies, while desirable, would have exceeded the scope of the present Report, which was designed to provide all of the essential concepts of HTS, the physical meaning of results (rather than mathematical detail), an evaluation of the relative positions of research in both countries, and a partial basis for the guidance of future work.

In general, we have chosen to devote more attention to the Soviet research than to the American in the belief that it will be of greater interest to the larger audience. It is apparent that the Soviet Union is more aware of the work done in the United States than vice versa.

We believe the publication of this Report to be timely because:

- The possibility exists of a major increase in the superconducting temperature, and such an increase would have pervasive effects on electrical technology, both industrial and military.
- Encouraging experimental data are emerging on new organic systems with extremely high conductivity.

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*It also reflects some of the most recent findings reported at the meeting on superconductivity held in Gatlinburg, Tennessee, 10-12 September 1973 [A48].

- o The USSR has a high degree of capability and preparedness in this field.
- o United States interest in theoretical and experimental approaches to excitonic superconductivity is increasing.

SUMMARY

This Report reviews novel mechanisms for achieving high temperature superconductivity (HTS), the most promising of which is the exciton process. It differs from the phonon process, which gives rise to conventional (low-temperature) superconductivity (LTS), by the manner in which the attractive interaction between electrons occurs. In the phonon mechanism of superconductivity two electrons are attracted to each other through a mutual interaction with a phonon. In the exciton mechanism, effective attractive interaction derives from excitation of electron-hole pairs (excitons).

Section I (Introduction) summarizes the HTS research programs in the United States and in the USSR, from the publication of the Bardeen-Cooper-Schrieffer theory (1957) in the United States and the Ginzburg-Landau theory (1950) in the USSR, and ending with the present. Preprints kindly made available by several U.S. authors should make this review current with the literature through September 1973.

The Introduction also cites examples of known superconductors and their critical temperatures, and it briefly discusses the conventional applications of superconductivity. Comments are made on the tradeoff between cryogenic devices and potential HTS variants. Cautious optimism is expressed toward work on excitonic superconductors currently under way in both countries. HTS technical material is reviewed in Sections II and III, which lay groundwork for the assessment of the American and Soviet efforts in the concluding Section IV.

American and Soviet HTS research institutions and their affiliated research personnel are listed in Tables 4 and 5 in an order that is meant to suggest the hierarchic standing of the individual authors and the relative significance of their activity.

The major findings of this paper are:

1. Work in advanced concepts of superconductivity in the United States lagged badly for the major part of a decade (1964-1973), while that in the USSR progressed uniformly.
2. Within the last three years the United States has shown greater progress than the USSR.
3. Soviet HTS research is approximately on a par with our own, but has a greater potential for future advancement.
4. National policy on superconductivity exists in the USSR under unified leadership.
5. United States support of HTS research is more austere than Soviet.
6. Soviet HTS research is more organized and coordinated than American.
7. Soviet research staff population is more stable than American; institutional differences are held partly responsible for this.
8. American HTS research is conducted primarily by physicists; the Soviet approach tends to be interdisciplinary, involving physicists, chemists, materials scientists, etc.
9. Soviet research style is not generally conducive to rapid exploitation of its own theoretical and experimental results.
10. Soviet HTS studies are useful in assessment of developments of potential value.

ACKNOWLEDGMENTS

The authors wish to thank Prof. William A. Little of Stanford University, Dr. Robert B. Somoano of the California Institutute of Technology Jet Propulsion Laboratory, and Dr. Paul Chaikin of the University of California at Los Angeles for their useful comments and suggestions.

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I. INTRODUCTION

In 1969 Academician Pyotr L. Kapitsa, at the age of 75, made his first visit to the United States to receive an honorary degree from Columbia and to tour the California Institute of Technology and University of California at Berkeley. In response to a question from an American physicist for a comparison of Soviet and U.S. work, he commented rather cautiously that perhaps the Soviet Union does a little better in solid-state physics and in superconductivity. He said also that leadership alternates between the two countries and that Landau's death had weakened the Soviet position.

Kapitsa's short, unembellished assessment is strikingly confirmed by the material on research in advanced concepts of superconductivity in the two countries presented in this report. Although the initial suggestion -- which may be said to have instigated the most novel approaches -- came from the United States, *research in this country lagged for the major part of a decade, while experimental work in the Soviet Union progressed and expanded uniformly. Within the last few years, however, greater progress has been shown in the United States.* Nevertheless, the capability of the Soviet groups in the field -- manpower, experience, and presumably funding -- is such that they may well be in a better position to exploit the results of recent months.

EVOLUTION OF THE THEORY OF SUPERCONDUCTIVITY

The first experimental observation of superconductivity, in 1911, presented a theoretical puzzle on which physicists made very slow progress. Almost half a century passed before the physical process giving rise to the enormous electrical conductivity was deduced. Previous theories gave macroscopic and thermodynamic descriptions of the properties of superconductors largely without explaining what caused them. Then, in 1957, a detailed, microscopic, exact explanation of the process responsible for superconductivity was given by Bardeen, Cooper, and Schrieffer. The magnitude of this accomplishment was recognized by a Nobel Prize in 1972.

Great progress was made during the same period in the study of materials, and complex alloys retaining superconducting properties in high magnetic fields and at higher temperatures than the pure elements first investigated became available. Superconductors effective in fields of hundreds of kilogauss and at up to 21 K are known. These are used in electromagnets which produce hundred-kilogauss magnetic fields and in electronic devices such as Josephson junctions, which give sensitive switches and detect microscopic electronic processes.

After the development of the Bardeen-Cooper-Schrieffer (BCS) microscopic theory and considerable work on alloys in a search for superconductors that could be used at more convenient temperatures, it became evident that there are rather severe limitations on the maximum temperature for practical operation of the traditional substances. In 1964, W. A. Little proposed a theory for a new electronic mechanism by which superconductivity might be attained at much higher temperatures. The proposed mechanism would be expected in materials quite different from the usual metals and alloys of traditional superconductors. In contrast to the continuing, systematic, semiempirical work on development of conventional metallic superconductors we have just referred to, the investigation of materials based on an entirely new conductive mechanism was thus opened up. The study of novel materials is now expanding in a search for a major increase in superconducting temperature.

HTS VS. CRYOGENIC DEVICES

The necessity for raising the operational temperature of superconductors may be questioned in view of the well-developed cryogenics technology and established techniques for the maintenance of very low temperature by liquefied helium and hydrogen. Significant advantages derived from high-temperature capabilities can be cited in reply. Particularly in the high-field alloys, the desired superconducting properties degrade as the temperature approaches the critical or transition temperature T_c, at which superconductivity disappears and only normal conductivity is found. Further, even with relative facility in the use of cryogenics, operation at a temperature of only 10 K higher provides direct savings both in the quantity of coolant used, and in the type of coolant required. For potential technological applications, the decrease in cost and weight and the conservation of energy rapidly become appreciable.

SUPERCONDUCTOR APPLICATIONS

What are the applications of superconductors which, aside from scientific research, would justify interest in the hoped-for materials? Many reviewers of this field have suggested applications from the mundane to the exotic without giving an adequate picture of the potential of, for example, a room-temperature superconductor. In the field of transportation, several countries, including the United States, Great Britain, and Japan, are investigating train propulsion by linear motors and magnetic levitation of vehicles, processes which can hardly be considered without the use of the magnetic fields provided by superconducting metals. Experimental work and design analyses for such vehicles have advanced to construction and testing of motors.

In the Soviet Union Kapitsa's work with high-power, high-frequency sources inspired plans for electric-power networks utilizing these sources, with transmission in superconducting channels below ground. Cryogenic systems would be involved for the channels at 40 K, an operating temperature predicted for future superconductive alloys. Engineering studies in the United States include the design of both power generators and transmission channels or cables using superconductors.

Applications which have been examined at length include high-Q microwave cavities, switching devices, computer and other circuits in which reduction of random noise is critical, frequency detectors, and magnetic-field detectors. These applications are based on known superconducting materials and the associated requirements, as appropriate in engineering developments.

In contrast to these specialized uses, the potential application of a high-temperature superconductor would be extremely broad in electrical technology. Wherever a conducting material is found, the advantages of its replacement by a smaller, lighter, though more expensive, substance would come into consideration. Potential military applications include ship propulsion, on-site power generation, ELF communication, magnetic detection, and possibly magnetic guidance devices. *The extent of the future use of a favorable material can hardly be imagined.*

NEW SUPERCONDUCTING MATERIALS

The search for new superconducting materials occupies a comparable -- and major -- position of importance in both the United States and the Soviet Union. Large numbers of workers in the two countries have been investigating metallic compounds and alloys leading to increasingly higher critical temperatures (see Table 1). The production of superconducting metal in practical wire or ribbon form by an especially convenient method was recently reported by Tsuei of the California Institute of Technology. Heat treatment of copper containing 5% niobium and 1.5% tin, for example, gradually converts the material into a superconductor. It should be noted that the specific materials with the highest T_c were invariably first reported in the United States, even while some Soviet scientists were apparently studying the same alloys. The characterization of some of the essential properties of high-T_c substances was first published in the Soviet Union, and parity has been evident in current technical papers.

Table 1

CRITICAL TEMPERATURE OF SUPERCONDUCTORS

Substance	T_c °K	Year observed
Mercury	4.2	1911
Lead	7.2	1913
Niobium	9.5	1930
Vanadium-silicon (V_3Si)	17.1	1954
Niobium-tin (Nb_3Sn)	18.1	1954
Niobium-aluminum-germanium ($Nb_3Al_{0.75}Ge_{0.25}$)	20.5	1967
Niobium-gallium (Nb_3Ga)	20.3	1971
Niobium-germanium (Nb_3Ge)	23.2	1973

Outstanding among investigators in the area of conventional superconducting alloys and metals are N. Ye. Alekseyevskiy of the Vavilov Institute of Physics Problems, Academy of Sciences, USSR, and B. T. Matthias of the University of California (San Diego) and Bell Telephone Laboratories.

This report deals primarily with the new area of high-temperature superconductivity (HTS) in which the Soviets for almost a decade (1964-1973) devoted considerably greater effort than the United States. It should be noted that, even as recently as the beginning of 1973, there was widespread skepticism in this country of the primarily theoretical approach to very high superconducting temperatures. A considerable increase in interest followed rapidly on the publication by Allender, Bray, and Bardeen of the University of Illinois of detailed specifications for an experimental approach in layer substances, as well as the observation by Heeger, Garito, and their associates at the University of Pennsylvania of extremely high conductivity in a linear TCNQ complex at 60 K. At the same time, the published results of the two groups have been widely criticized by some researchers in the field.

II. DEVELOPMENT OF CONCEPTS LEADING TO HIGH-TEMPERATURE SUPERCONDUCTIVITY THEORY

This section presents the modern basic concepts of superconductivity. We have attempted to provide sufficient material on conventional superconductivity to indicate the foundations on which the more controversial advanced concepts rest. A summary of the essential principles of many of the unconventional approaches to high-temperature superconductivity is followed by a discussion of the newer theories and the results of succeeding studies. Often these studies introduce negative aspects of the proposed high-temperature systems, and we attempt to present all available information on controversial or unresolved problems.

There remain unresolved theoretical questions, and a thorough understanding of the electrical properties of the substances under consideration is certainly still in the future. The present capability of the theory in this field, however, has provided quite a useful guide for experimental work and some critical problems have been studied in detail. A review by W. A. Little of Stanford University covering the mathematical aspect, minimized in this paper, will appear in *Reviews of Modern Physics* in early 1974.

A. GINZBURG-LANDAU THEORY

In 1950 Ginzburg and Landau contributed to the phenomenological descriptions of superconductivity a theory that is still of great utility in the field. Superconductivity was presented as a property of electrons regulated by an order parameter

$$|\psi|^2 = n$$

in which ψ is analogous to a wave function of the superconducting electrons of number density n. The free energy of the superconducting phase near the transition temperature at which it appears is expanded as a series

$$F = F_0 + \alpha|\psi|^2 + 1/2\beta|\psi|^4$$

in which F_0 is the free energy (density) of the normal state in zero field, $\psi(r)$ is the complex order parameter, and α and β are empirical coefficients, functions of pressure and temperature. At equilibrium, by minimizing the free energy, one obtains the following relationships for the coefficients

$$|\psi|^2 = -\alpha/\beta \quad \text{and} \quad F - F_0 = -\alpha^2/2\beta$$

At the transition temperature the order parameter $|\psi|^2 = 0$. The critical magnetic field H_c, just sufficient to destroy the superconducting state, is also related to the free energy difference by

$$F - F_0 = \frac{H_c^2}{8\pi}$$

The order parameter is 0 at the critical temperature and increases smoothly in zero field as the temperature decreases below this. The free energy of the superconducting phase in an external magnetic field is increased by a term given by Ginzburg and Landau as

$$\frac{1}{2m} \left| \left(-i\hbar\nabla - \frac{e^*}{c} A\right) \psi\right|^2$$

where m is the mass of the electron, e* is the charge, and A is the vector potential of the applied field. This additional free-energy term has been variously interpreted as the result of a spatial variation of the order parameter representing the supercurrent in a form analogous to a kinetic energy that acts to damp rapid changes. Chandrasekhar remarked on the difficulty of the interpretations of this term in the free energy; he considered the interpretations unsatisfactory, but concluded that the term represented an example of the deep physical intuition of Ginzburg and Landau.

In considering experimental behavior of superconductors, a dimensionless parameter k was defined

$$k = \frac{mc}{he^*}\left(\frac{\beta}{2\pi}\right)^{1/2} = \frac{\sqrt{2}}{2}\frac{mc}{he^*}\left(\frac{H_c}{\psi^2}\right)$$

which is temperature-independent near the superconductive transition temperature. The value of k is related to important properties of the superconductor. In particular the surface energy density between the normal and superconducting phases for the majority of elements and simple compounds is positive for very small values of k. Ginzburg and Landau noted that the surface energy is negative when k becomes greater than $1/\sqrt{2}$. This value, it is now known, is the demarcation between type I and type II superconductors.

Abrikosov's solution in 1956 of the Ginzburg-Landau equations for k greater than $1/\sqrt{2}$ has been called one of the greatest achievements of theoretical solid-state physics. It opened the completely new field of superconductivity of the second type. Type I superconductors exhibit one superconducting and one normal phase, whereas in type II *two* superconducting phases are observed. Most pure superconductors (excepting niobium and vanadium) are type I; type II superconductors are generally alloys.

Abrikosov's model of the second superconducting phase is one of a quantum-vortex mixed state. The mixed structure explains how superconductivity can persist even in high magnetic fields. Superconductivity remains appreciable after the magnetic field has penetrated a considerable portion of the material: Quite small but regular regions retaining superconductivity are sufficient to provide the whole material with the desired property. The most useful high-field superconductors are of this type. Curiously, the earliest experimental work clearly indicating the existence of type II superconductivity was published by Shubnikov in 1937. The mixed state, which is neither normal nor wholly superconducting, is generally known as the Shubnikov phase.

Abrikosov's early career was comparable in some aspects to that of Josephson* of the Royal Society Mond Laboratory of Cambridge University, who as a young student predicted the characteristics of superconductive tunneling through junctions. Abrikosov, one of Landau's most productive students, proposed the theory of quantized vortexes for type II superconductors in the early years of their collaboration, which extended over a decade. Acceptance (and publication) of the theory was delayed for four years, until 1957, after a similar concept had been described by Feynman of the California Institute of Technology to explain properties of helium II. Abrikosov was awarded the Fritz London Prize in Low-Temperature Physics (an honor also accorded Josephson) and is now a member of the Landau Institute of Theoretical Physics.

B. BARDEEN-COOPER-SCHRIEFFER THEORY

In 1956 Cooper, then of the University of Illinois, in considering the properties of electrons in a superconductor, found that if there was the slightest attraction, the electrons responsible for metallic conductivity tended to form pairs consisting of electrons of opposite spins and momenta. The physical process responsible for the attraction leading to pairing was revealed by the experimental observation of the isotope effect on the superconductive transition temperature. The transition temperature varies inversely with the square root of the atomic mass, $T_c \sim M^{-1/2}$. The microscopic process thus involves the lattice vibrations, the frequency of which were proportional to the square root of the reciprocal of the ion mass.

The concepts of formation of a preferred state of electron pairs and electron interaction through a lattice vibration were combined in 1957 in the BCS theory. *This theory, with subsequent improvements, constitutes the theoretical basis of the current field of superconductivity.* Its major premise is that the superconducting state is one in which electrons occupy spin- and momentum-pair states produced through an

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*Brian Josephson shared the Nobel Prize for physics in 1973 with L. Eisaki and I. Gievert.

electron-phonon process in the lattice. The electron attraction is ascribed to distortion of the lattice by a moving electron which then affects a second electron. The distortion produces a virtual phonon which the second electron reabsorbs when it encounters the lattice distortion.

Despite the preeminence of the BCS theory with its powerful microscopic analysis, the Ginzburg-Landau (G-L) theory which appeared some seven years earlier (in 1950), is still used and even preferred in many investigations. The continued utility of the G-L theory to the present time is a tribute to its effective formulation of significant properties of the superconductive state, when its extensions, particularly including time dependence, are considered.

In 1958 the BCS theory came under the scrutiny of Gor'kov, now of the Landau Institute of Theoretical Physics, who reformulated it in terms of Green's function -- its most powerful form -- and rederived the G-L equations on the microscopic basis. The charge unit appearing in the G-L theory is two electrons charges, in accordance with the picture of paired electrons as the operant unit of the superconductive state.

From BCS theory, the transition or critical temperature of superconductivity, T_c, occurs when all the electron pairs are destroyed

$$kT_c = 1.14\ \hbar\omega\ \exp\ [-1/N(0)V]$$

in which $\hbar$ is Planck's constant, k the Boltzmann constant, ω the appropriate phonon frequency, N(0) the density of states of electrons with one spin, and V the interaction parameter. The major part of the interaction V is from high frequency phonons, $\hbar\omega \sim k\theta_D$, where θ_D is the Debye temperature, the characteristic temperature of the lattice oscillations. Experimentally, $\hbar\omega$ is approximately 3/4 $k\theta_D$, resulting in

$$T_c = 0.85\ \theta_D \exp(-1/g)$$

with g the electron-phonon coupling constant.

A number of apparent experimental discrepancies from theory have led to criticism from Matthias, who on the basis of his detailed experimental knowledge of superconductors, pointed out that the electron-phonon lattice interaction of the BCS theory described only one type of superconductor, although four different types were indicated by observed properties [A35]. The electron-phonon process is held decisive for metallic-state s-d metals and their compounds found in Groups IIB to VIA in the Periodic Table largely in the third, fourth, and fifth periods (ranging from zinc and aluminum to bismuth and tellurium). Matthias proposed as the second major type the s-d electron transition elements (metals) in which the superconductive transition temperatures vary markedly with the number of valence electrons per atom (Fig. 1). An optimum ratio is indicated, the superconducting transition temperature decreasing again strongly when higher-than-optimum electron ratios occur in the elements or compounds. The highest temperature superconductors presently known ($T_c \sim 20\text{-}21$ K) were formulated with the aid of the "critical-electron-ratio" concept. A third group of superconductors contains the nonmagnetic compounds and elements of the first period from beryllium to nitrogen with very high Debye temperatures (excepting carbides and nitrides). The fourth empirical type of superconductor is that of the magnetic 4f and 5f rare-earth and transuranium elements, from uranium to lawrencium and cerium to ytterbium, attributed to f-level interaction.

The deviation of the isotope effect from a value of -1/2, noted generally in the transition metals but especially in ruthenium (with exponent 0) and uranium (exponent reported as high as +5), has been cited by Matthias and others as evidence against the phonon mechanism of the original BCS theory. Deeper consideration of BCS parameters, however, indicates that additional interactions change the numerical value of the isotope effect and cause the apparent deviation. The electron-phonon process may still be the ruling interaction in the (theoretically) "recalcitrant" superconductors. Part of the difficulty lies in the lack of sufficient knowledge of the properties of even normal metals. The specific parameters in question include (1) the density of states (or the band structure) in the region of the Fermi

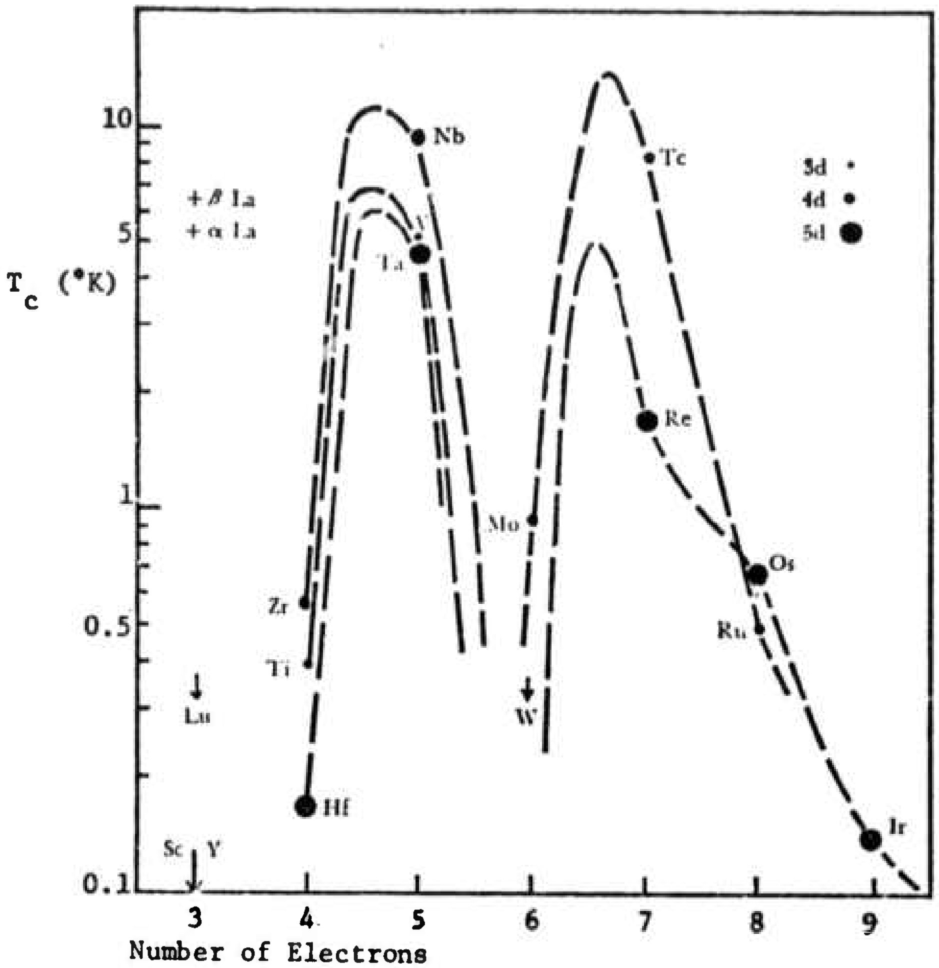

Fig. 1 -- Transition temperatures as a function of the number of valence electrons

surface of a given material and (2) the phonon interaction. Use of the Debye temperature, for example, limits the range of frequencies considered effective in the electron lattice interaction. The apparent deviation in the variation of T_c with the exponent of the isotopic mass of uranium, $T_c \propto M^5$, from the normal $T_c \propto 1/M^{1/2}$, conceivably can occur with very sharp peaking of bands (i.e., exceptionally high state density), with pairing still a result of the usual electron-phonon interaction. The investigators who observed this isotope effect, on the other hand, suggested that a different attractive mechanism was indicated.

Within the frame of the BCS theory the transition temperature for superconductivity may be estimated by the equations given above. The difficulties indicated in the very limited knowledge of parameters (for example, the strength of the electron interaction V) permit virtually only order-of-magnitude results. For most superconductors $g \equiv N(0)V$ falls in the range 0.1 to 0.4, and the Debye temperature θ_D varies from 100 to 600 K. Within the coupling constant g, the density of states N(0) may range from 0.1 to 1.45×10^{23} $(eVcm^3)^{-1}$ and the interaction potential V from 0.1 to 2.7×10^{-23} $eVcm^3$. From these parameters the superconducting temperatures given by the BCS equations vary from a very small fraction of a degree up to approximately 9.5 K for pure elements in reasonable accord with the range of observed transition temperatures. The equation for the transition temperature may now be considered from the view of attaining higher superconducting temperature. Such an approach is largely limited to one of general principle; in the past, the temperature equation has been more effective for revealing information on the nature of the superconductor after the transition temperature had been measured (e.g., the strength of the electron interaction) than for accurate prediction of the transition temperature itself.

Evidently, a high Debye temperature is favorable for a high transition temperature. Hydrogen with $\theta_D \sim 3.5 \times 10^3$ K has long been considered of interest from this point of view. The suggestion has been made that at high pressures -- which have only recently become accessible in the laboratory, but which are found in conjunction with appreciable concentrations of hydrogen on the planets Jupiter and Saturn -- metallic hydrogen may be a superconducting material [S26]. Using a value of 0.25 as a reasonable lower limit of the coupling coefficient g [A3], an estimate of 55 K is obtained for the transition temperature. With higher coupling parameters, higher temperatures up to 245 K are predicted. A major goal of Soviet high-pressure research has been the study of hydrogen transitions. The density change from 1.08 to 1.3 g/cm^3 at a pressure of 2.8 Mbar, which they reported in September 1972, was taken as evidence of a change to the metallic state. Predictions that a transition would occur at approximately this pressure are found in both Soviet and U.S. literature.

The Soviet Union appears to lead in research on very high pressures by static methods, as evidenced by the existence of the largest presses. In addition to this, the Soviets are examining other methods in materials research, in which the study of metallic hydrogen is often acknowledged as of major interest. According to one proposed method, shock waves could be used for isentropic compression by proper selection of the mass density as opposed to the usual adiabatic compression [S38]. The possibility that metallic hydrogen will be metastable and, thus, remain in existence at pressures below those required to produce it, has also been mentioned [S43].

C. STRONG COUPLING

An alternate way to obtain increases in the transition temperature for superconductivity is found in the effect of the coupling or interaction constants of the equations presented. The "normal" substances, which were initially found to be satisfactorily described by the BCS theory in its original form, are the so-called "weak-coupled" metals with $g \ll 1$. First mercury ($g \sim 1$) and lead ($g \sim 1.1$) and then niobium ($g \sim 0.8$) were noted, with interaction parameters near 1 or even greater, and with somewhat higher T_c. The stronger electron interactions showed their effect in modification of the BCS form of the exponential coupling. McMillan found, further, that in strong-coupled superconductors the product of the coupling constant, the ion mass, and the square of the phonon frequency is a constant within certain classes of materials; for example, aluminum, indium, and lead comprise such a class [A39]. This provides a method of calculating the maximum T_c expected within a given class in which the phonon frequency, for example, may be subject to control by alloying to obtain the maximum of the exponential temperature function. High values of the coupling constant approaching 2 give the maximum in the transition temperature, as indicated in Fig. 2.

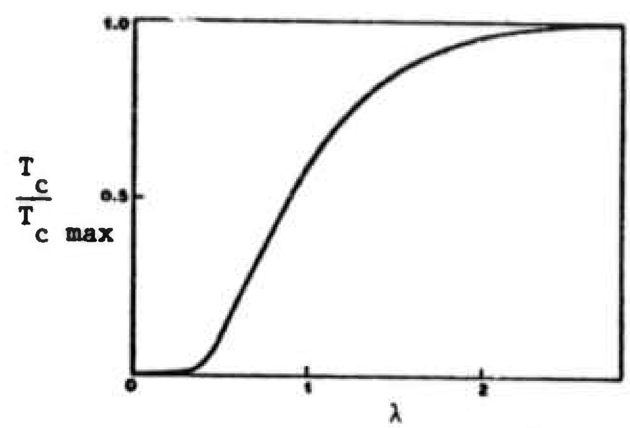

Fig. 2 -- Fraction of maximum possible temperature associated with coupling constant of the superconductor [A39].

Some predictions of this method compared with observations are summarized in Table 2. For lead and the niobium-tin compounds, superconducting temperatures approaching the maximum predicted have been attained. But observed transition temperatures have fallen far below the maximum in substances containing V_3Si, the material for which the highest transition temperature was predicted. Reliance on McMillan's method is based on the direct assumption, among others, that the coupling can be increased in the type of material selected and that the product of the electronic-lattice parameters mentioned is effectively constant. The properties involved directly affect the structure of the material. For example, the evident failure of the prediction for V_3Si may be a result of lattice instability which arises from excessively strong coupling when phonon frequencies favoring higher temperature superconductivity are present. The instability causes a change

Table 2

MAXIMUM PREDICTED SUPERCONDUCTING TEMPERATURE [A39]

Pure substance	T_c (°K)			Observed coupling coefficient
	Observed for pure substance	Predicted maximum	Highest observed	
Pb	7.2	9.2	9.1[a]	1.3
Nb	9.5	22	10.8[b]	0.82
V_3Si	17.1	40	---[c]	0.82
Nb_3Sn	18.1	28	21 [d]	---

[a]For pure Pb in Pb-Bi.

[b]For pure Nb in Zr-Nb.

[c]All alloying causes reduction in T_c.

[d]For Nb_3Sn in Nb_3Al-Nb_3Ge.

in the crystal structure. The reorganized, stable structure presents again only a normal phonon system and is thus likely to display only normal (low) superconducting temperature.

D. EXCITON SUPERCONDUCTIVITY -- ONE-DIMENSIONAL SUPERCONDUCTORS

1. Electron-Exciton Interaction

W. A. Little of Stanford University suggested in 1964 an alternative, novel mechanism for obtaining an attractive electron interaction leading to condensation of electron pairs in the superconducting state [A28]. In place of the electron-lattice-ion interaction of the BCS model for normal superconducting metals, Little proposed the interaction of electrons in a long chain with polarizable structures attached at regular intervals. Although the process is entirely analogous to that depicted in the usual metal superconductor, the interaction with the polarizable group in the new materials would be similar to a higher-energy optical excitation, hence the designation of *exciton* in place of *phonon* coupling. In place of the lattice-ion vibration frequencies, relatively high optical frequencies and therefore much higher energies, would be involved, leading directly to much higher superconducting temperatures.

The first model proposed for a material providing such an electron condensation was that of a long conjugated organic polymer with alternate single and double bonds (in the role of the central electron carrier) with positive-charged, polarizable dye side-chains attached regularly along the chain (Fig. 3).

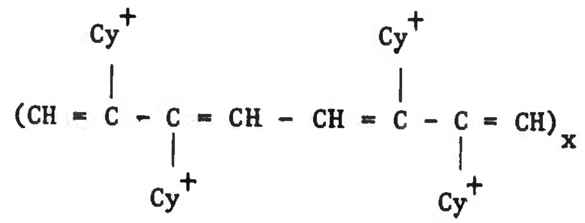

Fig. 3 -- Model of exciton-process superconductor

The parameters of the BCS temperature equation were estimated for this structure: the energy level of the electron-electron interaction $\hbar\omega$ given by the side chain, from the spectroscopic transition of the selected cyanine dye (600 nm), 2 eV; V, the electron attractive interaction (the net force of the side-chain induced attraction, -3.5 eV, less the Coulomb repulsion, 1.5 eV), -2 eV; N(0), the density of states of one spin at the Fermi surface, 0.2; or combining the latter two parameters, which were estimated for a structural unit of one bond (i.e., two atoms of the chain), 0.4 for g, the electron coupling. These provide an estimate of 2200 K for the transition temperature!

The variation of the transition temperature with (isotopic mass)$^{-1/2}$ in phonon-coupled superconductors may be used for a further qualitative approximation. If the coupling is induced in effect by the oscillation of an electron in the polarizable side chain rather than by the oscillation of a heavy lattice ion, the transition temperature may be greater by a factor $(M_{ion}/M_e)^{1/2} \approx 300$ to 400 times that of the usual phonon-coupled substances. The effective oscillation frequency, that is, the

Debye temperature-equivalent in the BCS equation for T_c would be 30,000 K.

Atherton concluded that such a filamental superconductor would have a very large critical current, estimated at 2×10^9 A cm^{-2}, more than 10^3 times that of a conventional superconductor, because of its restricted coherence length [A4]. In the usual superconductor, the coherence length may be of the order of 10,000 Å. The estimate was derived simply from the product of the density of the superelectrons (two paired electrons in a cube) the volume of which is equal to the coherence length -- 30 Å -- cubed and their velocity (from the 10 eV bandwidth, 2×10^8 cm/sec).

Little's theory predicted an electron interaction that had not been recognized in existing superconductors and led to the search for new types of superconducting materials. Also following on Little's predictions, a number of the basic aspects of superconductivity theory were subjected to more detailed analysis. However, experimental work on organic materials modeled on structures suggested by Little's theory lagged for several years, possibly a direct outcome of the theoretical activity by other investigators, the results of which were, as a rule, initially negative with respect to the concept of HTS. The work illustrated the difficulty of quantum physics of the solid state in which incorrect solutions were obtained through inadequate care in definition of problems.

2. Long-Range Order and Fluctuations in Limited-Dimension Structures

One of the first aspects of the exciton superconductivity theory to come under critical scrutiny was the one-dimensional structure, that is, the linear molecular chain bearing the electrons, in which electron pair condensation to the superconducting state was proposed. Both the Ginzburg-Landau description of superconducting electrons ruled by a density function -- known as the order parameter -- and the BCS wave function's "off-diagonal long-range order" (ODLRO) presented requirements for the formation of the condensed superconducting phase. The additional order required by superconductivity appeared possible only in three dimensions. The failure of the linear structure to provide the dimensional requirements of the order parameter in the Ginzburg-Landau model and of the Fermi surface in the BCS model has been noted by Abrikosov and by Schrieffer.

Ferrell found that fluctuations of the compressional modes of the electron gas in terms of the Gor'kov function

$$F(x) = \Delta \left\langle e^{i\phi(x)} \right\rangle$$

(with the modulus and phase for the superconducting Green's function) are infinitely large in one-dimensional geometry and prevent the appearance of the necessary long-range order [A15]. F(x) must have some nonzero value for superconductivity. DeWames, Lehman, and Wolfram pointed out that the zero value of F(x) deduced by Ferrell occurs at the limit of a very large system with an infinite number of electrons [A12]. A real macromolecule of the type which would be considered according to Little's proposal, with perhaps 10^5 electrons, need not be a large system by this criterion. Finite systems do not give a zero value of the Gor'kov function, although both the compressional modes and increased system size cause a reduction of the T_c estimated by Little.

One-dimensional systems had been investigated prior to Little's work, in connection with solid-state properties, including superconductivity. In a succession of studies with results curiously analogous to those just discussed, fermions in a one-dimensional ground state with pair interaction were studied with the Dirac Hamiltonian [A34]. The exact solution exhibited no discontinuity in momentum distribution at the Fermi surface, but did show an infinite slope there. Mattis and Lieb, however, noted that this solution was incorrect because of a difficulty in the solution of the Hamiltonian [A36]. The difficulty is to be found in the marked difference between a solution for a very large number of particles, for which the density operator commutators reasonably vanish, and the result for an infinitely large number, which are correctly considered for the case of a filled Dirac particle sea. In the latter situation the commutators do not vanish, and a new solution must be found. In the new solution a sharp Fermi surface occurs, but only for a weak interaction. A sufficiently strong interaction can eradicate the Fermi surface, although it always exists according to the perturbation theory. Mattis and Lieb also found that the electron-phonon interaction provided an exactly diagonalizable Hamiltonian in the model, and the normal modes in this case gave no phase transition. The absence of a phase transition was taken as proof that the one-dimensional metal cannot be a superconductor.

The absence of ODLRO in one-dimensional systems and, by extension, probably also in two-dimensional, was found by Rice to result from thermodynamic fluctuations in the phase of the Ginzburg-Landau order parameter [A44], supporting Ferrell's conclusion. Hohenberg proved rigorously the absence of long-range order in both one- and two-dimensional systems of bosons or fermions by using the Bogolyubov inequality [A22].

The Soviet investigators Bychkov, Gor'kov, and Dzyaloshinskiy examined the effect of dimensionality on the appearance of superconductivity at greater length [S15, S16]. They disagreed with the conclusions of Ferrell and Rice on the exclusion of superconductivity by fluctuations on the grounds that both the pair-wave function of the superconductivity gap for T = 0 and the Ginzburg-Landau equation were not applicable to the one-dimensional case. The fluctuation displacement of ions in the linear lattice was found to be large only at very high temperature or at large separation distance not affecting the electron order. The electron fluctuations were not small. They complicated the calculation for the one-dimension structure, but did not destroy the superconducting gap. A Peierls doubling of the lattice density vibrations was found accompanying the pair condensation into superconductivity, so that the superconducting Fermi sea consisted of particle quartets containing two electrons and two holes.

Little responded to the difficulties presented to the one-dimensional superconductor by fluctuations and requirement for long-range order with a study of current decay in a superconducting loop [A29]. Fluctuations in amplitude and phase of the Ginzburg-Landau order parameter destroy superconductivity by reducing the parameter to zero at some point in the loop. The time-averaged resistance from temperature fluctuations in the loop (part of the time it is superconducting, part of the time normal with ordinary resistance), according to standard fluctuation theory in Landau-Lifshitz, provides an estimate of the lifetime of the current at temperatures below the T_c of the bulk material and approaching 0 K. There is a uniform decrease in resistance, not a sharp one, with decrease in temperature. Thus, without the sharp discontinuity characteristic of a true phase transition in three dimensions, persistent currents may occur in one- or two-dimensional systems. In view of the absence of order in these limited-dimension structures, Little suggested that ODLRO may be a sufficient but not necessary condition for superconductivity.

Little's conclusion was supported by a similar analysis, also based on the Ginzburg-Landau equation, by Langer and Ambegaokar [A27], describing a resistive transition in narrow superconductors from large and improbable current fluctuations. Langer and Ambegaokar, however, reiterated the question of whether a local order parameter, as needed for use of the Ginzburg-Landau equation, can exist in one dimension.

Aslamazov and Larkin of the Landau Institute of Theoretical Physics studied fluctuations of electron pairing in superconductors above the critical temperature with Green's function in the Ginzburg-Landau theory [S7]. They concluded that as the temperature decreased to the superconducting transition, the conductivity of metals in the normal state increased, as did the specific heat and sound absorption. The effect was enhanced in two dimensions (films) and in one (crystal whiskers), especially with impurities.

Zavadovskiy of the Landau Institute also examined the effect of impurities in the one-dimensional case [S47], using the method of Bychkov, Gor'kov, and Dzyaloshinskiy. According to Zavadovskiy, in the linear structure electrons move from point to point along only one path, and the potential introduced by an impurity is considered to depend on the straight-line distance. Impurities do not affect the transition temperature or excitation spectrum of possible superconducting states because the electron phase shifts that they cause cancel each other. This is entirely different from the case in three dimensions.

Dzyaloshinskiy and Kats suggested a physical model of a metal which circumvents the fluctuation difficulties presented by one-dimensional filaments [S18]. They pointed out that there are not appropriate excitonic states (that is, electronic excitations in the optical region) in a close-packed normal metal, but that a material made of conducting filaments separated by less than ten atomic distances may permit the desired excitations. If so, such a substance would be a high-field superconductor of the second kind. Conductivity along the filaments would be normal in character; in the transverse direction it would be small or nonexistent. Yet the long-wave fluctuations in the electron density remain approximately the same as in a normal metal because of the long range Coulomb interaction between chains, and thus they do not destroy superconductivity. Dzyaloshinskiy and Larkin found that with different weak electron interactions this type of unidimensional filamentary system may be either antiferromagnetic, metallic, or superconducting [S19]. However, experimental evidence was cited indicating that some substances that may possess the structure under consideration have strong interactions [S41]. This work will be discussed later.

Balkarey and Khomskiy of the Lebedev Physics Institute noted that, in view of the limitations placed on the coupling constant because of lattice instability (~ 1/2), the additional coupling of electrons by nonphonon mechanisms is extremely limited when the normal phonon coupling is present [S8]. Thus a high transition temperature is only possible in substances with weak phonon interaction.

3. Electron Screening and Interaction

The new exciton mechanism presented for HTS was also criticized on grounds that it would fail to give the necessary electron-attractive force for the formation of the electron-pair superconducting state described by the BCS theory. A few authors discussed this view from different aspects. L. V. Keldysh of the Lebedev Physics Institute concluded that the interaction of the electrons with the polarized side chains is much greater than the excitation energy concerned [S35]. This causes a structural instability that would result in rearrangement into a state, other than superconductivity. Paulus of Cambridge University stated that the rapid relaxation of the side-chain polarization in Little's exciton mechanism is unlike the slow ion-lattice motion in the phonon process in effecting electron pairing [A42]. In the exciton mechanism the second electron must be very close to the first to experience the attractive interaction before relaxation occurs, and there is no opportunity for screening as it occurs in the time retardation of phonon coupling. If an attractive interaction is desired, one must forego screening in this case. In the absence of screening, the excitonic attraction was found to be inadequate to give an attractive electron interaction and pairing in the proposed conjugated polymer chain. Kuper reached the same conclusion by considering Mott screening of electrons, as in a metal cylinder with a 1-Å radius [A26].

McCubbin also pointed out the difficulty in obtaining an attractive force sufficient to overcome the electron repulsion, using estimates particularly for the organic molecule of Little's model [A37, A38]. He ascribed this largely to the attempt to utilize conduction electrons on the carbon chain and suggested instead a structure with conduction along a path connected to the side chains [A37]. The TCNQ complexes were discussed for this use, and McCubbin was evidently the first to propose in the literature the study of the organic complexing substance TCNQ (Fig. 4) as a potential superconductor.

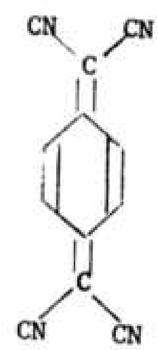

Fig. 4 -- Tetracyanoquinodimethane (TCNQ)

Consideration of the side-chain structure in more detail, with simple Hückel molecular orbitals, led Salem to present conceptually simple modifications that provided sufficiently strong interaction for electron attraction [A45]. An attractive interaction was obtained despite the conclusion of previous investigators that this would be impossible. In more complete self-consistent-field molecular orbital studies, Little found that there was screening of an inserted test charge in appropriate organic structure models [A21, A30, A32]. Zavadovskiy noted an unpublished result of Gor'kov and Dzyaloshinskiy to the effect that the Coulomb interaction was screened, based on the neutrality of the complete boson assembly [S47]. It is not clear whether this was shown explicitly for one-dimensional systems or only in the general case. Further studies of screening in filamentary structures noted that Kuper's result from consideration of a narrow cylinder is inadequate to describe a bulk material [A7, A11]. As in the Dzyaloshinskiy-Kats work on fluctuations in a material of parallel one-dimensional conductors [S18], interchain effects were significant in producing the requisite screening. Numerical parameters were obtained for typical platinum complex compounds [A11].

The more general problem of the appearance of superconductivity in a normal superconductor of only one dimension is itself a complex subject and one that has been investigated by several scientists. Tucker and Halperin studied fluctuations of the electrical conductivity with the time-dependent Ginzburg-Landau theory, using the Hartree-Fock approximation for the interaction [A49]. They found, in agreement with an earlier result, that an instability was predicted near the critical temperature, which should occur at lower currents in dirtier samples.

4. Chemical Synthesis of One-Dimensional Structures

Chemical substances with the complete structure indicated by Little in his first suggestion of the exciton superconductor (that is, the conjugated polymer molecule with dye side groups of Fig. 3) are unknown. Examples of the dye fragment alone number in the hundreds, if not thousands, with a range of excitation levels for selection. Methods of connecting such a group directly to the structure of the central chain have not come to light. Long conjugated molecules resembling the chain itself, but much shorter than a true high polymer, are well-known in such natural materials as lycopene (the color principle in a tomato) and carotenes, as well as in molecules synthesized in the laboratory (the natural compounds have also been prepared synthetically). Chemical methods of making a simple conjugated chain of moderate length are well in hand.

Almost coincident with the appearance of Little's paper proposing the superconducting polymer was the publication of Pen'kovskiy's review with 185 references of Soviet work on conjugated compounds [S40]. This was a field of special interest to Soviet chemists, and several polymer compounds with conjugated (alternating) double bonds had been reported from well-known, apparently simple reactions. The presumed structures were based on inference from the expected path of the reactions used, however, rather than direct study of the products. It was evident in several cases, from the few properties of these products described, that the supposed conjugated system was not present but that other molecular structures were formed. Conjugated polymer structures are, in fact, rare, and careful study of any specific material of interest for Little's polymer would be required.

Preliminary synthetic studies have been reported toward Little's proposed structure [A31]. Wiley suggested that an unspecified new polymerization of acetylene compounds would provide such a substance [A50]. Preparation of the desired material did not succeed, however, and interest in this specific structure seems to have disappeared. Little's associates have recently studied routes to polyatomic metal molecules. Synthesis of the unknown long polymers of directly linked metal atoms is also difficult.

It is not possible to predict which methods of synthesis might succeed. The complex structure of the minimum unit of the first proposed carbon polymer indicates, however, that synthesis of the basic unit followed by linking or polymerization of several units would not be successful. The structure of the basic unit would probably interfere chemically in the polymerization. Most of the methods being investigated apparently intended to use this strategy. An alternate approach would be to begin with the major polymer structure, for example, the conjugated chain, and to prepare the desired product by chemical reaction with the major structure already in existence. This method, while also difficult, is well known and has been used in preparation of a number of materials. Finally, there are reasonable paths to conjugated polymer structures with dye or other side chains to provide materials of the type Little suggested initially.

Bulayevskiy studied the states of long conjugated molecules with the Double- and Triple-Interactions approximation in the Pariser-Parr-Pople

Hamiltonian [S14]. He pointed out that the first strong transition above the ground state approaches a lower limiting value of ~2 eV in progressively larger cyclic conjugated polyenes, a value derived by Longuet-Higgins and Salem from spectra measured by Sondheimer. This gap is somewhat larger than the limit of 0.67 eV cited by Little as required for a transition temperature of several hundred degrees [A28]. Little has pointed out, on the other hand, that conjugated structures are known with absorption bands below 1 eV, as in the pentacarbocyanines.

E. EXCITON SUPERCONDUCTIVITY -- TWO-DIMENSIONAL SUPERCONDUCTORS

1. Thin Film Structures

Six months before the publication of Little's paper on the high-temperature organic superconductor in 1964, there appeared a suggestion by Ginzburg and Kirzhnits that electrons on a crystal surface may condense into the superconducting state [S22]. This process would produce a two-dimensional, planar superconductor that would cause significant surface conductivity, even though conditions in the internal region of the crystal might be unsuitable to give an electron-electron attraction. With the appearance of Little's theory, Ginzburg quickly took up the exciton mechanism with its promise of increased transition temperatures as being particularly applicable to two-dimensional systems.

It is evident that two-dimensional systems do not present such formidable difficulties as one-dimensional linear polymers in the matter of fluctuations, screening, or the possibility of an attractive interaction, all of which were compounded in the wholly new type of superconductor Little presented. Ginzburg, indeed, became the chief advocate of the exciton mechanism -- exchange of energy between electrons in a thin metal film through a polarization wave excited in dielectric layers attached to the metal. He published a dozen papers and reviews in which he discussed, at some length and with considerable skill, the major questions involved in this approach to hoped-for high-temperature superconductors [S23, S32]. The most complete discussion of the subject is found in "The Problem of High-Temperature Superconductivity. II," which appeared in *Uspekhi* in 1970 [S27]. In addition to this, his colleagues at the Lebedev Physics Institute contributed publications on a number of theoretical studies of the problems involved. Ginzburg's research conferences at the Lebedev Institute discussed subjects in this field thoroughly, and the influence of his seminar group was acknowledged in publications by several Soviet workers investigating exciton superconductivity.

Ginzburg's physical models were modified gradually to provide more favorable structures for exciton superconductivity. Directly after the appearance of Little's initial paper, he suggested the addition of a monomolecular dielectric film to the crystal surface he had first considered, in order to favor the desired electron-exciton interaction [S23]. The use of donors and acceptors in semiconductors was proposed as a means of influencing the number of electrons at the surface. Ginzburg pointed out that in a one- or two-dimensional system -- unlike in a conventional three-dimensional bulk superconductor -- any small attraction produces two-particle states, possibly making electron degeneracy unnecessary for superconductivity in the restricted-dimension systems. The difficulty of obtaining more than a microscopic superconducting region near the surface because of a rapid decrease in interaction with distance was considered. In addition, the damping of excitons in the metal phase requires that this layer be thin to insure small attenuation of excitons while providing a large screening radius in the nonmetallic coating. In view of these factors, a system consisting of a metal film 10 to 20 Å thick, coated on both surfaces with a semiconductor of dielectric constant 1 to 30 (Fig. 5), was proposed [S24, S25, S27, S32]. An electron concentration of 10^{18} to 10^{23} cm^{-3} in the metal is desired, and the exciton energy in the dielectric should be 0.03 to 3 eV with a bandwidth of 0.1 to 0.3 eV.

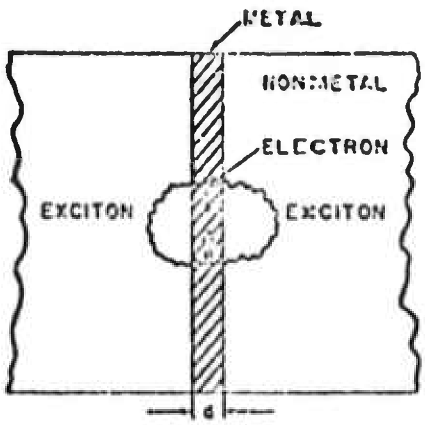

Fig. 5 -- Model of thin-film exciton superconductor

Fluctuations, which are not a problem in bulk superconductors, become more significant with substances of limited dimensions. In a film the transition temperature decreases as the Green's function of the particle interaction diverges with the logarithm of the dimension; in a filament the divergence is linear. Ginzburg and Kirzhnits estimated that fluctuations were negligible in a thin 10-Å film, but that they were not so in a single filament of the same diameter; a similar relative advantage for a film is expected in the screening problem [S24].

Considering the difficulty presented by the preparation of a material that meets all the specifications given and the qualitative estimates on which they were based, Ginzburg repeatedly urged experimental study of all possible high-temperature systems: the organic filaments, three-dimensional substances in which excitons might be favored (Ginzburg suggested transition metals with selected impurities for this purpose), and sandwich structures, which he concluded were most favorable. *In contrast to the response to exciton theories from solid-state experimentalists in the United States, leading Soviet workers urged the consideration of new materials and the search for systems exhibiting such new mechanisms of superconductivity* [S3, S9].

The theoretical study of the parameters of the thin-layer system has continued during the decade since this type of structure was suggested in 1964. Kirzhnits and Maksimov of the Lebedev Physics Institute, using the method that Gor'kov applied to the microscopic derivation of the G-L theory from the BCS theory (1958), found that (1) the logarithm of the critical temperature of such a superconductor was proportional to the film thickness by a linear function and (2) the thermodynamic properties, as well as the excitation spectrum, were all quite similar to those of a bulk superconductor [S36]. When the value of a parameter exhibits some variation through the film, a mean value gives the equivalence for the uniform system.

Zharkov and Uspenskiy of the Lebedev Physics Institute examined film-electron interaction with the high-frequency excitations of the dielectric coating using the "jellium" uniform-medium model of the superconducting film and the time-dependent electric-field potential [S48]. The strong screening of the electron interaction by conduction electrons in the metal layer markedly limits the effective region for the exciton mechanism, which occurs within a narrow layer with the approximate thickness of the screening length, 5 to 10 Å, according to these authors. In thin superconducting films the transition temperature varies exponentially with the ratio of the screening length to the film thickness, an independent result similar to that of Kirzhnits and Maksimov [S36]. The effect of the dielectric coating on the film T_c is negligible when this ratio is small, that is, when the film is much thicker than the screening distance. To obtain a large increase in the superconducting temperature, therefore, the dielectric must be suitable, the superconducting film must be thin, and the screening length must be large. A doped semiconductor with a low effective mass of carriers was cited as an example of a material meeting the latter requirement. Yet, fulfillment of these characteristics presents some difficulty for significant increase in T_c.

The study of fluctuations of electron density and the phase of the order parameter for a layer system showed an angle-dependent gap [S34]. Thus, the electron fluctuations have three-dimensional character, supporting the previous conclusion of Dzyaloshinskiy and Kats that, unlike in the case of one-dimensional systems, the fluctuations do not destroy the superconducting state. The phase fluctuations give a temperature range in which there is a two-dimensional transition to superconductivity. The shift of the transition temperature with fluctuations of the order parameter has been examined [S39].

A number of studies have been made in other problems of superconductivity which present some interest for the layer structure. Aronov and Gurevich of the Ioffe Physicotechnical Institute found that tunneling from a superconducting film coated on both sides with a dielectric layer should increase T_c, since there is a decrease in both the number and distribution of superconducting excitations [S6]. However, the superconducting film thickness considered specifically was almost one thousand times that of interest in Ginzburg's model. Further, two semiconductors were placed in contact with the opposite dielectric layers, one a p- and the other an n-type material. Tunneling in this case resulted in quasi-particles moving into the p-material and holes into the n-material. Phonons compensated for these losses by producing excitation-hole pairs, but the total exciton concentration decreased. Junction and tunneling processes have been studied extensively in superconductors separated by thin dielectric and semiconducting films and, finally, in three-layer systems, all superconducting [S33]. Fluctuations of the order parameter occurred from proximity effects; corrections for the phases became negligible when the layers were much thicker than the coherence length involved.

2. Granular Structures

On the basis of experimental results suggested in the literature, Ginzburg noted the applicability of his exciton theory to substances with a granular rather than layered structure [S27-S32]. He concluded, in a long note devoted to this subject that experimental difficulties in preparing sufficiently thin metal films for the layered structure might be circumvented by a material containing small spheres or flakes embedded in the dielectric [S29]. To minimize fluctuations, the volume of the granules should not be exceedingly small, yet the depth to which the effect of the dielectric reaches into the particles must be not too much smaller than their radius or thickness. To obtain an appreciable exciton mechanism, excitons in the dielectric with frequencies much smaller than the limit given by the Fermi surface of the metal must not be attenuated excessively at wave numbers near those of the Fermi surface. Ginzburg recommended that the dielectric matrix of this type of material utilize semiconductors with marked exciton bands below

1 to 2 eV, considerably below the metallic Fermi energy. These also are difficult requirements.

Hurault considered a system of small metal crystallites coated with a dielectric and calculated the change in transition temperature that would occur from the Ginzburg excitonic mechanism. This was compared to the effect of an increase in phonons at the surface [A23]. He found that for small crystals whose dimension could be approximated by an average radius R the exciton process gave a variation of log T_c with R^{-2}, whereas the phonon process resulted in a dependence on R^{-1}. In both cases, for weak coupling in which the constant g is at most 0.25, the critical temperature would be below 20 K. Ginzburg disagreed with this conclusion, however, on the basis of Khirzhnits's calculation for the temperature showing that there was a direct dependence on the excitation frequency for appropriate dielectric constants [S27]. Evidently, Hurault's solution for the gap equations with the jellium model was incorrect. The relationship given by Khirzhnits showed that a high transition temperature could result from a sufficiently large frequency of the polarization wave. Ovchinnikov recently derived a quantitative method for calculating the change in T_c with grain size, with specific results given for bismuth and gallium [S39]. The change was linear with the reciprocal of the grain dimension.

3. Allender-Bray-Bardeen Film Structure

Allender, Bray, and Bardeen of the University of Illinois made an extended, detailed study, in 1973, of an exciton superconductivity mechanism occurring in a physical model similar to the one suggested by Ginzburg, that is, a thin metal layer on a semiconductor surface [A1]. The electron-exciton interaction arises from valence bond polarization, resulting in an attractive interaction directly analogous to the conventional BCS phonon mechanism of superconductivity. Thus, an exciton coupling constant similar to the interaction constants of interest in normal superconductors may be considered. To obtain high transition temperatures a high concentration of mobile carriers is needed. If, instead of the metal layer, the method of doping the semiconductor is used to provide this concentration, the semiconductor gap is covered over, eradicating one of the requirements for the exciton process. Electrons near the Fermi surface tunnel approximately 5 Å into the semiconductor. The space charge of the electrons from the metal bends the semiconductor band. It would be desirable for the bending to be approximately one-half or less of the average gap. Thus, the number of electrons in the dielectric should not be excessive, although some compensation might be gained by doping the semiconductor with a p-type impurity. In many semiconductors the plasma frequencies are in good agreement with the density of valence electrons, permitting use of the approximation of the jellium model, a free-electron metal with gaps introduced to provide the semiconducting or insulating property.

The requirements for the exciton interaction are favored by semiconductors with an average gap frequency that is small compared to the plasma frequency. Ge, InSb, and PbTe are promising narrow gap materials of this type. The energy of the Fermi surface of the metal should be near the center of the semiconductor gap at the metal-semiconductor interface to aid penetration. Matching of the work functions of the metal and the semiconductor within about one-half the gap energy (probably ~ 1 eV) avoids severe bending of the semiconductor band with accompanying loss of tunneling. The number of electrons crossing the interface per unit area is

$$\sigma = \gamma N(0) E_g D,$$

where N(0) is the density of states at the Fermi level for electrons of one spin in the metal, $\gamma N(0) E_g$ is the corresponding electron concentration at the interface with energy from $-1/2\ E_g$ to 0 of the semiconductor gap E_g, and D is the penetration depth.

The electron-exciton coupling constant is given by

$$\lambda_{ex} \approx \mu - N(0)V = ab\mu\ \omega_p^2/E_g^2,$$

where μ is the product of the density of states and an average screened Coulomb interaction (with energies up to the magnitude of the Fermi energy above the Fermi level itself), a is a factor (1/3 to 1/5) that includes screening, b is the fraction of time an electron is found in the semiconductor, and ω_p is the electron plasma frequency in the superconductor. The following values would favor substantial transition temperatures in the metal film: $b \sim 0.2$, $\mu \sim 1/3$ to $1/2$, $\omega_p \sim 10$ eV, and $\omega_g \sim 2$ eV, and would result in λ_{ex} of 0.2 to 0.5. The question of larger coupling constants is of interest, as they lead to very high T_c's, for example, 800 K for the unrealistic case of λ_{ex} about 1.4. In general, λ_{ex} should be 0.5 or less, but just as in phonon coupling, larger values that might otherwise be associated with structural instability are possible in localized fields or with the occurrence of umklapp processes which modify the momentum exchange.

To solve the gap equation and obtain estimates of transition temperatures for superconductivity, Allender, Bray, and Bardeen used McMillan's linear equation with a Lorentzian function for the phonon state density. Numerical computer solutions were made with iterations until the parameters in the gap equation converged. The exciton kernel for the gap equation was simply written in the same form as the phonon kernel. The Lorentzian is a good approximation for the peak in the exciton spectrum, if not for a real phonon spectrum. The results for the exciton mechanism operating alone showed that T_c's no higher than those found with the phonon mechanism were obtained for reasonable values of the parameters. Considerable increases in T_c occurred, on the other hand, when both exciton and phonon processes were effective. For example, in typical cases, a T_c of 40 K was found with the general parameter values cited above and with phonon coupling approximately 0.4 and exciton ~ 0.5; approximately 60 K was obtained with phonon coupling 0.57 and exciton 0.5. The authors stated their conviction that the exciton mechanism had a firm basis in theory, and while announcing an experimental program to produce a material favorable to its occurrence, emphasized the difficulty of preparing systems with the desired parameters.

Even before the publication of the Allender-Bray-Bardeen paper, a critical evaluation by Phillips of Bell Laboratories appeared with the conclusion that, because of covalent instability, this approach could provide no increase in T_c of pure metals with a transition temperature already greater than 5 K [A43]. Phillips argued that homogeneous metals with high T_c, such as Pb, NbN, and Nb_3Sn, were close to lattice instability and that this condition limited the maximum T_c attainable to about 25 K.

A high density of surface states is characteristic of the gap materials Ge, InSb, and PbTe, which have attracted interest, and Phillips said that the covalent instability limiting T_c was probably associated with the presence of surface states. He considered unlikely the approach to an increase of excitonic coupling λ_{ex} above the stability limit of ~ 0.5 by intensifying local fields within the unit cell (favoring umklapp energy transfer processes). This conclusion results from a comparison of the regions of possible local field nonuniformity in phonon vs. exciton interaction. The ion core from which phonon exchange arises is relatively small, possibly 10 percent of the volume of an atomic cell of the material. On the other hand, Phillips estimated the region of the exciton interaction, that is, the valence bond polarization, to be the length of an atomic radius or about two-thirds the volume of the atomic cell. Thus, the local field can be much greater near the ion than over the region involved in excitonic coupling, and the corresponding increase of phonon coupling above the stability limit of a uniform field can be much greater than with the excitonic interaction. From experimental results already found with some layered materials, which will be discussed in the following section on experimental work, Phillips concluded that the optimum parameters for such a system have already been studied and found to be ineffective for the increase in T_c sought by Bardeen and his associates, in part because the parameter values anticipated are not accessible.

4. Alternate Methods of Favoring Exciton Interaction

The possibility of an electron interaction similar to those invoked by Little, Ginzburg, and Bardeen occurring in a three-dimensional system and resulting in high T_c was proposed by Geylikman [S20, S21]. Two models of such a system were suggested: (1) a pure transition metal or an ordered bimetallic alloy (or compound) containing comparable concentrations of the two components with overlapping unfilled bands (e.g., s and d or s and f) and (2) an ordered alloy of a metal with a nonmetal in comparable concentrations in which electrons of the upper unfilled shell of the nonmetal are strongly bound and not free carriers in the alloy. The interaction in the first type of material may be depicted as that between electrons in the one band with charge-density fluctuations of electrons in the other. A favorable situation occurs when the d- or f-band is significantly narrower than the s-band it overlaps, and when the s-electrons are weakly bound, but those of the d- or f-band strongly bound. The expression for the transition temperature (at vanishing energy gap) is the same form as the conventional BCS equation with the addition of a few terms in the coupling constant representing the effect of the respective bands on the density of states. When this electron coupling process predominates (over phonon coupling), a critical temperature of 10^2 to 10^3 K is obtained if the difference in energy from the Fermi surface to the top of the d-band is 0.3 to 1 eV. Geylikman pointed out that, although it would be possible in principle, this effect could not be significant in pure transition metals, since all have transition temperatures closer to 10 K than to 100 K. The search must, therefore, extend to alloys, which present difficulties because their electronic spectra and electron-wave functions are unknown. In the alternative metal-nonmetal system, the electron attraction is the result of Coulomb interaction between the metallic conducting electrons and those of the nonmetal. The upper shell of the nonmetal is unfilled, and the tightly bound electrons in the lower levels are those that provide the coupling interaction in the electrons of the metal. In this material, the gap is the energy difference from the highest filled level of the nonmetal to the nearest unfilled level. This is much smaller than in the previous model, so that the T_c will be much lower than in the case of the overlapping bands. Geylikman made the interesting deduction that these entirely electronic interactions cannot generate lattice instability, since the pairing does not involve the lattice structure element, unlike phonon interaction in which the lattice ions participate. Additional studies have been made of the electron interactions which can provide attractive interactions, such as the s-d electrons in a Fermi liquid [S17]. Electromagnetic sound waves with large phase velocities are possible, and the Coulomb interaction can lead to high critical temperatures of 100 K.

A means of favoring interband pairing of electrons to give high transition temperatures (~ 100 K) for superconductivity was suggested by the use of laser excitation to populate an unfilled band heavily with a selected state [A25]. An ultrasonic source could similarly provide phonon-level energies. Blazhin and Selivanenko proposed the laser irradiation to produce polarization and a resultant increase of electron condensation into Cooper pairs in highly-doped semiconductors with already high equilibrium concentration of electrons relatively unchanged by the light ([S11]; a review of this work appeared in a previous Rand report [A24]).

In considering a nonequilibrium system of excitons that might be formed by a laser in this way, however, Bulayevskiy, Kopayev, and Kukharenko of the Lebedev Physics Institute found that the attraction between conduction electrons becomes comparable to the screened Coulomb repulsion only at an exciton concentration so great that the average distance between excitons is comparable to their radius [S13]. This results in the destruction of the virtual particles, indicating that in an ordinary system there will be no effective interaction through excitons. Metallic systems damp possible excitons, so that excitations of the desired energy must be sought in semiconductors. When common semiconductors are doped to obtain high conduction electron concentrations, the exciton spectra disappear; this is true at the concentrations in those doped semiconductors that have exhibited superconductivity. In MoS_2 and WSe_2, however, exciton spectra of 1 to 2 eV energy remain with electron concentrations as high as 10^{20} to 10^{21} cm^{-3}. These exciton energies are much larger than the Fermi energy of the conduction electrons, so that Coulomb repulsion is still too great for any exciton mechanism. But in layer compounds it appears that excitons can exist with conduction electron concentration at larger than the usual critical value, indicating that the destruction expected in an isotropic material will not occur in layer compounds. The laser excitation may thus be effective only in the layer systems.

Kirzhnits and Kopayev examined the characteristics of a superconducting state from an inverted population, such as one that might be generated by a laser pulse [S37]. They suggested that a high density of populated states could produce superconductivity, even in a substance in which the coupling constant alone corresponded to electron repulsion. Extended lifetimes of the population inversion (up to 10^{-5} sec) may occur with a sufficiently narrow dielectric gap and a separation of the boundaries of the bands (between the initial ground state and the upper state into which the excitation drives the electrons). The critical temperature may be high, depending on the chemical potential or the magnitude of the population inversion.

F. SPECTROSCOPIC MANIFESTATION OF EXCITON PROCESSES

Agranovich, Mal'shukov, and Mekhtiyev of the Institute of Spectroscopy of the USSR Academy of Sciences particularly considered the spectroscopic properties of organic compounds in contact with metals involved in exciton superconductivity [S1, S2]. Their theoretical investigation dealt with, for example, a layer structure or an alloy in which the metal was doped with the organic molecule. Experimental spectroscopic information on such systems is as yet unavailable. With reasonable values of the ionization potential and electron affinity of the organic substance compared to the work function of the metal, only neutral species need be considered in both ground and excited states, and there is no contribution of electrons from the organic to the metallic conduction bands. Nevertheless, characteristic spectral processes will occur in electron-exciton interactions: (1) renormalization of the intermolecular contribution to the exciton energy and (2) quenching of excitons by the metal through radiationless transfer into the kinetic energy of the free electrons. In addition to absorption lines derived from excitation of the organic material, there would be expected lines from simultaneous excitation of both the organic compound and the metal. The authors pointed out the use of infrared and Raman spectroscopy to find possible vibrational effects, beyond the direct results in the electronic spectra that would be involved. The high-frequency boundary of the absorption band was defined by absorption to the exciton level and by low frequency excitation of the metal itself. Absorption in this region, when the superconducting state exists, contributes to the exciton energy and disrupts increasing numbers of the Cooper pairs. The possibility of aiding electron pairing by laser excitation and the accompanying negative effect of exciton destruction with disruption of pairs were discussed. Exciton breakdown may be negligible if radiative, rather than radiationless, decay is the major process. All these conclusions were obtained for an isotropic metal-organic system. When parameters of reasonable magnitude for a layer structure, such as those given previously, were considered, screening was weak, with concomitant exciton quenching as severe as that in a homogeneous solid.

III. EXPERIMENTAL STUDIES ON EXCITON AND OTHER MECHANISMS OF HIGH-TEMPERATURE SUPERCONDUCTIVITY

Experimental data on the occurrence of superconductivity by the exciton process is practically nonexistent. Although considerable work has been done with interface effects, layer structures, and films in connection with the Josephson effect and a number of interesting electronic devices, little information applicable to the question of one- and two-dimensional superconductivity has resulted. Evidence of this paucity of data is the absence of specific citations to the exciton process in the large literature in the field of superconductivity. Several investigators, however, have reported on studies of films and layer structures following (and possibly inspired by) Ginzburg's proposal of increased transition temperature to be expected in suitable systems of this type, and some have referred specifically to his suggestion. There have been several papers concerning superconductivity in granular systems and a few on the characteristics of one-dimensional materials. Recently, exceedingly interesting data that demonstrate (in support of all the preceding theoretical analysis) the possibility of the sought-after high-temperature effects have become available for a one-dimensional system. Investigation of one-dimensional substances is evidently limited, considering the lapse of time since their study was initially proposed, but it appears that this lack may be remedied by the interest generated by the favorable results that will be discussed later in this section. Work with layer -- or sandwich -- structures has not been much more extensive than that with one-dimensional substances, but *it appears that an appreciable increase will now follow the investigation of Bardeen and his colleagues.*

An evaluation of the available experimental studies is presented in this section. An indispensible, comprehensive review of the chemical synthesis of the substances that have been studied, based on 197 references, was published in the USSR December 1972 by Yagubskiy and Khidekel' of the Institute of Chemical Physics [S46].

A. TWO-DIMENSIONAL LAYER STRUCTURES

Naugle investigated the effect of thin films of germanium deposited by condensation at 4 K on metal surfaces [A41]. Films 10 to 100 Å thick on tin decreased the T_c of the metal by up to 0.07 K for the thickest coating. This was attributed to the removal of electrons from the metal with the production of a contact potential at the interface. Films of approximately 10 Å on thallium, on the other hand, increased the T_c of a 235-Å layer of that metal by 0.11 K. Had the change been due to electron removal, each germanium atom in the one- or two-layer coating would have been required to accept from 1.5 to 3 electrons. Naugle suggested, instead, that the additional exciton interaction advanced by Ginzburg might account for the sharply peaked T_c of thallium with a coating of one monolayer or more of germanium.

Chopra briefly reviewed work with films and layers involving increased T_c, attributed by Strongin and by Abeles, who investigated aluminum films, to surface superconductivity with a high BCS coupling constant, as suggested by Ginzburg [A9]. Annealing of vapor-quenched films decreased T_c, and tungsten films formed by sputtering exhibited increasing T_c with smaller crystallite size (determined by electron diffraction). Chopra discarded the explanation of these effects based on a surface electron interaction of the type suggested by Ginzburg in favor of one in which the great stresses implicit in extremely small grains stabilize a metastable phase with higher T_c. This could result from both greater Debye frequency and greater electron coupling in the BCS theory.

Simultaneous deposition of aluminum and TCNQ films on a quartz crystal at 4 K gave a material with a maximum T_c of 5.24 K [A18]. Gamble and McConnell interpreted the effect in this case (evidently misinterpreting Chopra's explanation for the enhancement in aluminum and tungsten films) as one of disorder. Annealing of the codeposited aluminum-TCNQ layers reduced the transition temperature to 0.72 of its initial value, regardless of the composition of the film.

Thin films were prepared by Alekseyevskiy on a mica substrate by flash evaporation with a pulsed neodymium glass laser of a fused alloy of 50 percent germanium and 50 percent gold [S4]. The starting alloy was not superconducting down to 1.4 K. Films deposited at either liquid nitrogen or liquid helium temperatures showed a superconducting transition at about 2.7 K. After these films were allowed to anneal at room temperature, the transition temperature fell to 1.8 K, approximately the same as in the case of similar alloys prepared by rapid cooling by previous investigators. Alekseyevskiy ascribed the higher T_c to a new modification of the alloy and noted that the effect may have resulted from nonequilibrium and a large electron-phonon interaction.

Layer compounds that are probably two-dimensional superconductors were prepared by adding pyridine to niobium disulfide, tantalum disulfide, tantalum diselenide, and palladium ditelluride (Table 3) to form the intercalated metal dichalcogenides [A19]. The metal compound occurred in layers approximately 6 Å thick, with the pyridine entering between the planes of the metal atoms, first reported as separated by 12 Å. This distance would result if the flat pyridine molecules were perpendicular to the layer of the metal compound. It is now generally accepted that the pyridine molecules lie flat against the metal, providing in this conformation the strongest interaction. The compound produced contained one pyridine molecule per two molecules of the original metal compound. The insertion of the organic molecule caused an increase of T_c in the majority of substances shown in Table 3.

Table 3

T_c CHANGE ON INTERCALATION OF METAL DICHALCOGENIDES

Compound	T_c (°K)
NbS_2	6
$NbS_2 \cdot Py_{1/2}$	4
TaS_2	0.7
$TaS_2 \cdot Py_{1/2}$	3.5
$TaSe_2$	0.2
$TaSe_2 \cdot Py_{1/2}$	1.5
$PdTe_2$	1.45
$PdTe_2 \cdot Py_{1/2}$	1.65

Further increase in the separation between the metallic layers by the insertion of more of the organic material gave only a small further change in T_c. The investigators, Gebalie and his associates, concluded that the observed superconductivity occurred in the two-dimensional metallic layers, unless there was some coupling through the organic layer that is not very sensitive to the distance [A19]. Otherwise, the superconductivity was considered to be of the usual BCS type. Thus, they preferred not to enlist Ginzburg's interaction machanism to explain the effects, partially on the grounds that similar increases were found with different organic molecules. Geballe's explanation is adequate to account for superconductivity in these systems, but not for the changes in T_c. If conventional superconductivity alone were involved, it could be argued, for example, that T_c's should decrease in the thin metallic layers because of the effect of fluctuations.

Phillips of Bell Laboratories examined these effects on T_c from intercalation to see if the presumed additional interaction contributed by the organic layer might be increased to give considerably higher T_c by means of the processes suggested by Ginzburg and Bardeen [A43]. The coupling constants λ^*_{ph} and λ^*_{ex} for the respective phonon and exciton interactions in the layer system may be given in terms of the fraction of time an electron near the Fermi surface spends in the metal f_1 and in the semiconductor (or organic layer) f_2. Thus,

$$\lambda^*_{ph} = \frac{f_1\lambda_{ph}}{1 + f_1\lambda_{ph}} \text{ and } \lambda^*_{ex} = \frac{f_2\lambda_{ex}}{1 + f_2\lambda_{ex}}$$

This, in the Allender-Bray-Bardeen work [A1], led to

$$T_c = 0.7\omega_D \exp(-1/g),$$

and

$$g = \lambda^*_{ph} + (\lambda^*_{ex} - \mu)[1 - (\lambda^*_{ex} - \mu) \ln (\omega_g/\omega_D)]^{-1}$$

Using the data from Table 3 for TaS_2 and NbS_2, with the curious exception that 0.8 K and 3.3 K were substituted for those given by the original investigators for TaS_2, Phillips obtained $\mu = 0.1$, $\lambda_{ex} = 0.3$, and $f_2 \leq 0.2$ by numerical fitting to the equations. He concluded that this value of f_2 would probably be the maximum obtainable because it is produced by π-bonding between the metal compound and the organic layer, a condition that would presumably permit the electron to spend the larger portion of time in that layer. While Bardeen and his colleagues anticipated the use of substances to obtain $f_2 = 0.2$, Phillips considered that 0.1 would be a realistic upper limit for other materials in which π-bonding might not occur. He pointed out that the depression of T_c on intercalation of NbS_2 indicates that in substances where the T_c was already high, i.e., greater than 5 K, the introduction of excitonic interaction is actually a disadvantage.

There are a number of extremely doubtful, if not wholly incorrect aspects in Phillips's arguments. It appears possible to improve π-bonding in the intercalated compounds with appropriate ring structures that would provide favorable values of f_2. Phillips's consideration of exciton interaction in the intercalated materials is also doubtful. Geballe and coworkers stated that they believed such mechanisms were not present [A19], and it appears that the energy levels presented by these systems do not meet the requirements for effective electron-exciton interaction.

The question of the significance of the exciton mechanisms in these layered materials was examined further by Bulayevskiy and Kukharenko [S12]. They concluded that this process could not occur in the pyridine-containing complexes because the excitation energy of pyridine is approximately 5 eV. In fact, energies limited to 0.1 to 1 eV would be needed to meet the requirements of excitation below the Fermi energy of the conduction electrons and the plasmon energy, and to provide rapid (logarithmic) screening of the Coulomb repulsions. The phonon mechanism is thus much more significant in the pyridine-layer compounds and exerts the sole effect in determining T_c. The low excitation level desired in the organic layer is attainable only in large molecules; the Soviet authors suggested large planar molecules longer than 9 Å with more than 30 π electrons in the conjugation system. Even with such a material, the relative contribution of the exciton process is 0.03 if the planes of the organic and the conduction system are parallel. When the large molecules are perpendicular to the conduction plane, the exciton process increases only to approximately 0.1. In the experimentally studied dichalcogenides, the van der Waals interactions, which are responsible for the existence of the complexes, strongly localize any excitons. Similarly, the low-frequency excitons have insufficient oscillator strength for the dielectric constant of the layered substance to contribute significantly to superconductivity. Bulayevskiy and Kukharenko suggested strongly-delocalizing electrons to reach lower energies by using semiconducting layers (in place of the insulator pyridine).

The transition temperatures of increasingly thin layers of niobium diselenide were examined by Frindt of Simon Fraser University in Canada to determine possible dimensional effects in the metallic layer alone for a compound of the type utilized in the intercalated layer materials [A17]. The T_c for a thick or bulk sample is 7 K, decreasing as crystal thickness falls below six molecular layers. Temperatures were measured for three, four, and five molecular layers, and these extrapolated linearly to a value of 3.8 K predicted for a single layer. The critical temperatures found by Gamble et al. for niobium disulfide intercalated with aniline ($\sim$ 4 K) and tantalum disulfide intercalated with stearamide ($\sim$ 3.1 K) are close to the extrapolated value [A19]. Frindt concluded that the result supported the picture of the widely separated layers in intercalated material as two-dimensional conduction systems. In contrast to the appreciable broadening noted with intercalation, the 80 per cent width of the transition did not increase significantly in the thinner layers of $NbSe_2$ in this study.

A simple empirical method of predicting the transition temperature as a function of the number of layers in such systems was developed by Antoniewicz and Fredericks [A2]. It is based on the linear relationship of the energy gap with the transition temperature given by the Ginzburg-Landau theory and Josephson coupling, assuming that the energy states are not changed by the structure. The variation of T_c with pressure is also linear in this method.

Alekseyevskiy of the Institute of Physics Problems, in reviewing progress in superconducting materials, took particular note of those that evidenced two-dimensional aspects [S3]. He pointed out that C_8M compounds (in which M may be K, Rb, or Cs) can be regarded as quasi-two-dimensional superconductors, as shown by the stratified crystal structure and the marked anisotropy of conductivity. This is the opposite conclusion from the one given by Matthias of Bell Laboratories and the University of California (San Diego), who prepared and investigated these compounds. In addition to the C_8M compounds, Matthias was able to prepare $C_{16}M$ by changing the relative amounts of the reagents. The latter is a series of compounds with the same layer structure but one in which the metal layers are separated by two layers of carbon rather than one. This series, in which exchange between metal layers is impossible, is not superconducting, and Matthias concluded that the absence of superconductivity in this case showed that two-dimensional superconductivity was impossible. Alekseyevskiy suggested rather that the distinction between the two types of compounds and the reason for superconductivity in the one and its absence in the other resulted from differences in their phonon spectra. The transition temperature of the C_8M compounds varied from a few hundredths of a degree up to a maximum of 0.55 K for C_8K. Alekseyevskiy also discussed silver fluoride, Ag_2F, an anisotropic superconductor with a layer structure of fluorine atoms separated by layers of silver two atoms thick.

Another series of layer compounds with superconducting properties was obtained in the alkali metal intercalates of molybdenum disulfide (Li, Na, K, Rb, and Cs in MoS_2) [A46]. Molybdenum disulfide exhibits a layered structure and promising exciton spectra, even in the presence of high electron concentrations, and is thus of particular interest to the study of the Ginzburg theory. Intercalation produced superconductors from the initial nonsuperconducting material, with the T_c varying from 3.7 to 6.3 K along the series of metals listed. The superconductivity, however, displayed no anisotropy. Intercalation evidently produced more symmetrical substances. In addition, the excitons of MoS_2 were disrupted in the new structures. The appearance of superconductivity was credited to electron transfer from the intercalated metal to an empty MoS_2 band, accompanied by an increase in electron density and in the density of states at the Fermi surface. The intercalates are more three-dimensional in nature, reflecting coupling of the layers by the intercalated metal.

A study of film properties made by evaporating aluminum and germanium simultaneously, done by Fontaine and Meunier of the Laboratory of Physics of Solids in Orsay, France, supported the presence of a granular structure in the resulting material [A16]. Electron microscopy and limited X-ray studies were consistent with the formation of small aluminum crystallites ~ 20 Å in diameter in a matrix of amorphous germanium, even though these were not clearly visible. Transition temperatures of the crystallites increased by 2.6 K above the 4 K of the pure metal, reaching 6.6 K. A critical resistivity of approximately 10^{-2} ohm.cm, above which superconductivity was suppressed, was derived from experimental measurements in agreement with that reported for granular aluminum in silica. This parameter and the estimated crystallite size are in accord with the intervention of expected superconducting fluctuations. The investigators concluded that the enhancement occurred through a surface process consisting of an increased electron interaction through the exchange of a polarization wave in the dielectric between electrons of the metal. However, in view of Ginzburg's anticipation of extremely high temperature by such a process, Hurault's proposal of a quadratic variation in the attractive coupling with the surface-to-volume ratio was used to derive grain size in the films studied. The size calculated in this way was in agreement with the other estimates.

Ginzburg commented that germanium evidently does not provide the states needed in the dielectric medium to provide a large enhancement to T_c through the exciton process [S29]. A favorable dielectric matrix should exhibit distinct exciton levels of 1 to 2 eV or less, much below the Fermi level of the metal, with strong oscillator strength.

Recently, transition temperatures of 30 Å-thick aluminum and lead epitaxial films were compared with disordered films prepared by the usual rapid cryogenic condensation at the Brookhaven National Laboratory and the University of Illinois [A47]. The ordered films gave a T_c near that of bulk material and lower than those of the disordered films. The authors concluded that microscopic disorder, not film thickness, accounts for the enhancement of T_c in cryogenic films. Commenting on the study presumably dealing with aluminum crystallites in germanium, they concluded, after obtaining the same T_c enhancement in aluminum and germanium films that the effect is one of disorder, rather than an intrinsic electronic mechanism. They did not, however, actually provide any further data on either electronic properties or the structure of aluminum-germanium systems. And comparison of a "nonepitaxial" film of aluminum with the highly-ordered epitaxial material, both grown under the same conditions and both 30 Å thick, gave the same T_c for both, although the transition of the latter was much sharper and its resistance one-tenth that of the former. This result, conceivably, could lead to the interpretation that disorder has no effect on T_c. In fact, disorder has been credited with reduction in T_c by some authors. It should be noted that the T_c of niobium diselenide decreased appreciably from the normal bulk value in the work of Frindt only when film thickness decreased below 30 Å [A17]. This study indicates the significance of detailed examination of a film's physical structure for investigations of superconductive transitions, a significance also implied in the difficult dimensional requirements suggested by both Ginzburg and Bardeen. Low-energy-electron diffraction was utilized in observing the growth of epitaxial aluminum in this case.

B. ONE-DIMENSIONAL LINEAR STRUCTURES

The corresponding experimental work dealing with linear systems, which might be said to fall under Little's original proposal for excitonic superconductivity in one dimension, has been relatively limited. In accordance with the more liberal attitude toward all possible approaches, and despite their generally better grasp of the essential theoretical difficulties, *Soviet physicists fostered an earlier and larger initial experimental effort than that in the United States on potential one-dimensional superconductors*. Studies done by commerical organizations, such as DuPont, the results of which are not generally available, are not considered here. Ginzburg, the leader of a large group with considerable influence, is probably in large measure responsible for the greater Soviet activity.

In considering, on the one hand, the obstacle of fluctuations preventing superconductivity in a narrow linear system that might otherwise be favorable for the exciton mechanism and, on the other hand, the absence of exciton (electronically excited) states of appropriate energy in close-packed metals, Dzyaloshinskiy and Kats pointed out that TCNQ complexes might supply a structure of ordered, loose-packed chains in which the feared fluctuations would be no more significant than in a normal metal because of long-range Coulomb interaction between chains [S18] In such quasi-one-dimensional materials there can be metallic conductivity along but not across the chains; conductivity is nonexistent in the transverse direction. Dzyaloshinskiy and Larkin also cited the TCNQ complexes as an example of the ordered multiple-thread system in which varying electron interaction can result in either a metal, a superconductor, or an antiferromagnetic insulator [S19]. Experimental attention was thus directed to TCNQ materials, particularly for the study of superconductivity, rather early in the Soviet program.

Preparation of a series of TCNQ complexes with cyanine and cyanine-type dyes was reported with measurement of absorption spectra, resistivity, electron paramagnetic resonance, and magnetic susceptibility [A33, S45].

The conductivity mechanism of the TCNQ-phenazine complex was investigated in some detail by means of conductivity, paramagnetic susceptibility, and optical spectroscopy [S41]. The initial work by Kepler of DuPont, where these materials were discovered and first studied in 1963, led to the conclusion that their conductivity is metallic, electrons being in a degenerate, free-gas state. Several of the complexes exhibited relative temperature-independence of magnetic susceptibility, and the carrier concentration was one spin per molecule. In contradiction to this result, the paramagnetic susceptibility measured by Shchegolev and his associates at room temperature was much too low for this spin concentration, indicating that the spin sources are strongly coupled, not degenerate. The variation of the susceptibility with temperature suggested additional contributions at temperatures above the liquid helium region. On the other hand, the mobility of carriers in a single crystal derived from conductivity measurements was nearly exponentially dependent on the reciprocal of the temperature, which is also not in accord with a hopping mechanism. With the two major mechanisms of conductivity thus excluded, as they occasionally are in organic-molecule systems, no conclusive explanation of the observed behavior is available. The presence of potential barriers from defects in the linear conducting chain was tentatively proposed to account for the conductivity characteristics. Dzyaloshinskiy and Larkin pointed out that the increasing magnetic susceptibility observed with decrease in temperatures (below 50 K) in this work is a symptom of a strong interaction rather than the weak one desired as favorable to an exciton process [S19].

In pursuing the properties desired for a model structure fulfilling the criteria presented by Little for a linear excitonic superconductor, Yeremenko, Khidekel', Fedumin, and Yagubskiy of the Institute of Chemical Physics prepared a TCNQ complex with tetrathiotetracene (Fig. 6) [S44].

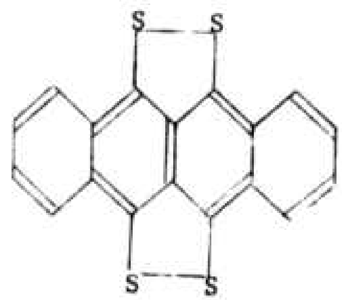

Fig. 6 -- Tetrathiotetracene (TTT)

The role of this new cation in the complex was to provide the high polarizability that Little had discussed as the means for producing the exciton interaction in his linear structure. These investigators reported that the TTT cation-radical in the complex absorbed at 1000 to 1300 nm in the infrared, i.e., in the region of the 1200 nm indicated as favorable by Little [A31]. Its position in the experimental complex, on the other hand, may have differed from the one visualized by Little. A resistivity of 12 ohm.cm at 293 K and an activation energy of conductivity of 0.03 eV (80 to 293 K) were reported for the complex.

The square-planar complex of platinum $K_2Pt(CN)_4Br_{0.3} \cdot 2.3\ H_2O$ is a highly conducting chain (3.5×10^2/ohm.cm) very much like the TCNQ complexes in structure and behavior [A40, S10]. This material has also been examined for its possibilities with respect to the one-dimensional superconductor.

An extensive review of TCNQ complexes and square-planar metal complexes of interest as linear conducting chains was published recently by Shchegolev [S42]. The comprehensive discussion covered the available crystal structures, direct current conductivity, magnetic properties, thermoelectric properties, and conductivity and dielectric constant at microwave frequencies. The high anisotropy of the electrical conductivity in these materials indicates that they may be considered unidimensional with respect to this property. Although metallic character would be expected according to band theory, the temperature dependence of the conductivity indicates an activation. Shchegolev concluded then that all are semiconductors that would become nonconducting at low temperature. He summarized the properties that would make the band description inappropriate: lattice disorder, electron-electron interaction through the structure, and the intervention of polarons. These can account for the apparent electron localization in the usual TCNQ complexes. The disorder and interaction effects prevent degeneracy of the electron gas into a metallic system by presenting energy differences to the electron at different sites. The complexes of intermediate conductivity are largely under the influence of electron-electron interaction. Conductivity occurs by electrons in the band states, with negligible thermally activated hopping. In the highly conducting complexes, on the other hand, the influence of lattice disorder or electron interaction has decreased, and electron-phonon interaction predominates. Conductivity now takes on the hopping characteristic. These complexes also have very high dielectric permeability associated with an almost uniform energy level for electrons at different sites during polarization. Shchegolev adduced the possibility that it is the one-dimensional structure which prevents occurrence of the metallic state in such cases.

A complete review -- comparable in scope to the Shchegolev review cited above -- of chemical structures considered for excitonic superconductivity has been given by Yagubskiy and Khidekel' [S46].

Continuing study of the TCNQ complexes to clarify the electronic processes and to obtain increasingly metallic behavior has led most recently to the discovery of the complex with the greatest reported conductivity [A10, A14]: the TCNQ complex with tetrathiofulvalene (TTF), the maximum observed conductivity of which was 1.47 x 10^4/ohm.cm at 66 K (Fig. 7). The sulfur compound was selected for consideration

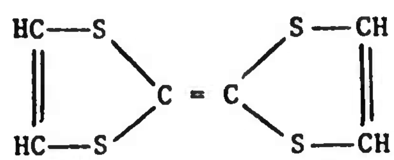

Fig. 7 -- Tetrathiofulvalene (TTF)

on the basis of its high cation polarizability and small size. The room temperature conductivity of the complex is 1.837 x 10^3/ohm.cm, and the carrier density is 5 x 10^{21} cm^{-3}, approximately 1/20 that of copper metal at the same temperature. Hegger and Garito, with other collaborators at University of Pennsylvania, reported a sharp maximum in conductivity of greater than 10^6/ohm.cm at 58 K (Fig. 8) in only three of a total of seventy crystals examined. Eventually, six examples showing the extreme peak were reported. No quantitative measure of the difference between these and the remainder of the crystals, aside from the electronic property, was reported. The intense peak in the conductivity was interpreted as due to a superconducting fluctuation, which, at lower temperatures, gives way to an insulating ground state because of the intervention of the Peierls lattice-doubling instability.

The occurrence of the extremely high conductivity peak was not confirmed in measurements at Johns Hopkins and Bell Laboratories with independently prepared TTF-TCNQ single crystals. Investigators at

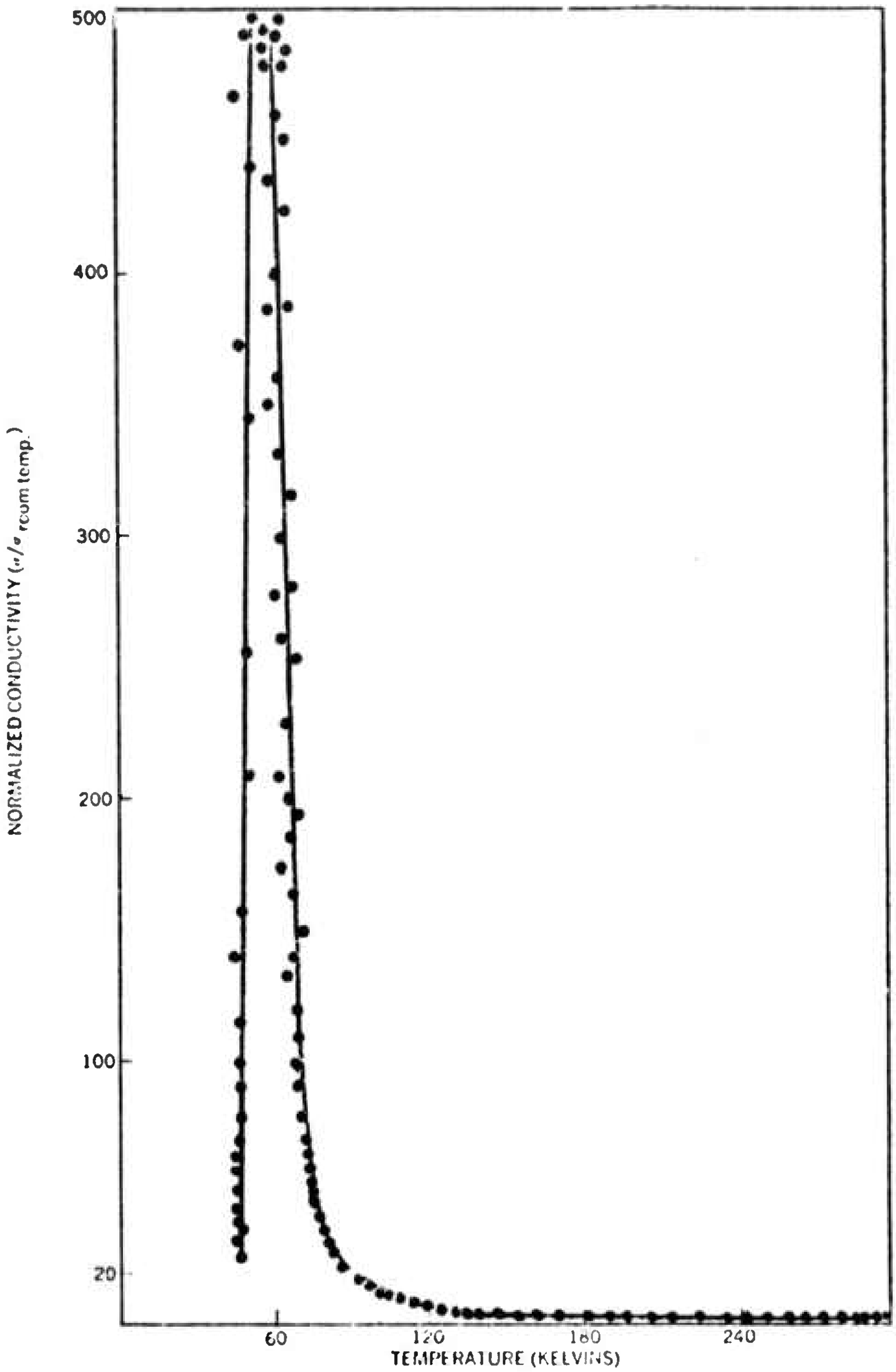

Fig. 8 -- Variation of conductivity with temperature of TTF-TCNQ

these laboratories attributed the unusual conductivity to experimental difficulty with the probes used at the University of Pennsylvania [A48]. Nevertheless, this complex is metallic above 60 K and by far the best organic conductor known.

The crystal structure of analogous complexes appears favorable for the concept of Little's theory, with the TCNQ anions distributed around a central chain of TTF cations, all stacked in layers. It is the TTF that plays the role of the polarizable side chains of Little's model and the TCNQ the spine.

Previous studies in the University of Pennsylvania laboratory considered thoroughly the electron processes responsible for the transition from metal to insulator of a similar complex, NMP-TCNQ [A13]. In this case the cation is provided by N-methyl phenazine. The crystallographic structure data indicate that a quasi-one-dimensional system is involved. The transition from metal to insulator occurs when the temperature falls below 200 K. The polarizability of the cation was credited with a major role in the formation of the metal state, that is, the reduction of the Coulomb interaction to a sufficiently low value, 0.17 eV. The investigators estimated that without this effect the interaction would be as much as 1 eV, which with the bandwidth of 0.1 eV would exclude the metallic state. The metallic behavior in the NMP-TCNQ complex was interpreted as the first experimental proof of the major significance of polarizability. In a major twenty-five page paper discussing the molecular parameters affecting electron processes in an organic solid, these authors felt it necessary to point out as late as 1971 that the theoretical studies on the absence of long-range order in one dimension should not rule out research in unidimensional systems. They considered fulfillment of the requirements of Little's theory possible, but only under extremely specific and difficult conditions. It seemed unlikely that the overall interactions could be made attractive with the proper frequency dependence to give superconductivity. But improvement of the correlation to reduce Coulomb repulsion further was deemed quite possible, and they proposed the general approach of preparing complexes that would retain metallic character to lower temperature [A13]. The use of a smaller, more polarizable molecule for the TCNQ complex was advanced as the way to accomplish this. The validity of the approach has been demonstrated by the high conductivity of the TTF-TCNQ complex.

The electron-exciton interactions appropriate to TCNQ complexes were considered more specifically in further work by the same group [A8]. An attractive interaction, the strong-coupling version of Little's exciton process, was indeed derived, but with accompanying strong narrowing of the band. The attraction increases linearly while the bandwidth is decreasing exponentially, so that the desired attraction is to be found only with a very narrow band system. The requirements for an exciton process thus appeared to result in an insulator before a superconducting state could be attained. Reconsideration of this interaction in terms of the localized exciton with discrete energy levels, more appropriate to the process invoked in Little's model than to the continuous spectrum of the Einstein oscillator, gave appreciable bandwidth when there was strong interaction [A6]. The intervention of superconductivity is more favorable, and the insulating state that would result from band narrowing is less likely.

In two experimental studies published earlier than that of Heeger and his associates, observations that could be interpreted as fluctuations associated with one-dimensional superconductors were reported at high temperature. Geballe's study of the magnetic susceptibility of TaS_2 (pyridine)$_{1/2}$, the layered superconductor with a T_c of 3.7 K, discussed previously, exhibited apparent persistence of electron interaction at high temperature [A20]. The anisotropy of the layers (metallic TaS_2 6 Å thick, separated by ordered pyridine layers 6 Å thick, reported earlier as 12 Å) was evident in measurements made with the magnetic field applied parallel and then perpendicular to the layers. The susceptibility with field perpendicular to the layers increased slowly as temperature increased to the value observed with the field parallel to the layers and associated with the nonsuperconducting material. The anisotropy increased approximately with the reciprocal of the temperature. This possible evidence of a residue of superconducting electron correlation remained from above 35 K up to almost 50 K. In bulk lead such an effect has been reported up to

16 K, i.e., ~ 3 T_c. More recent measurements by the same investigators with different samples of the same material from other sources did not show the effect. Recent work indicates that a structural transformation involving a TaS_2 superlattice may have given the observed variation in the susceptibility.

In a second, similar observation, a persistent diamagnetic susceptibility exhibiting a possible superconducting fluctuation was reported by Alekseyevskiy and Krasnoperov in the higher temperature superconducting alloy $Nb_3Al_{0.75}Ge_{0.25}$ [S5]. The authors suggested that the alloy presents a one-dimensional structural aspect in the Nb chains, so that fluctuation phenomena from the superconducting transition should be discernible in related electron phenomena. As the temperature decreases below 300 K, the experimental magnetic susceptibility increases, reaching its maximum between 50 K and 19 K, where it drops precipitously. If the susceptibility is graphed as a function of 1/T, it may be separated into two components by extracting a linear portion readily given by the data down to 50 K.

The total susceptibility below 50 K can be formally represented by a diamagnetic susceptibility of increasing significance at lower temperature superimposed on this linear component. The diamagnetic component persists up to 50 K, although it is appreciable only up to approximately 30 to 35 K.

Bardeen has suggested [A5] that the fluctuation phenomenon reported by Coleman et al. in TTF-TCNQ [A10] arises from a mechanism for superconductivity in one dimension described by Fröhlich in 1954. Fröhlich's model is one of strong coupling of a single electron with a lattice vibration, and Bardeen favors this over BCS pairing. The model gives metallic conduction at high temperature, changing to semiconduction or insulation below a critical temperature. Superconductivity can occur when the lattice distortion moves with the electron as a lattice wave. Recent theoretical results reinforce doubts about the experimental work indicating large conductivity fluctuations in the TCNQ complex as reported by three groups: Patton and Sham of the University of California (San Diego); Anderson, Lee, and Rice of Bell Laboratories;

and Weger, Gutfreund, and Horovitz at Hebrew University [A48]. These recent results rule out true superconductivity because of the intervention of a number of phenomena, including the Peierls instability and the incapability of the current flow in the Fröhlich state.

IV. COMPARISON OF U.S. AND SOVIET RESEARCH ON ADVANCED HIGH-TEMPERATURE SUPERCONDUCTIVITY

This section will compare American and Soviet work in *high-temperature* superconductivity.* The contrasts that emerge from such a comparison originate in the differences in the planning and implementation of national research programs in each country. We will attempt to show (1) how governmental planning (or its absence) has influenced research in this field in each of the two countries and (2) how the nature of the specific studies has affected progress in this field.

Table 4 lists U.S. and Table 5 Soviet institutions and the scientists affiliated with them engaged in the investigation of *new mechanisms* in the search for a major increase in superconducting temperatures. Both institutions and scientists are named in descending order of the volume and significance of their activity. Open-source literature was the major source for their selection; reports given at the recent Gatlinburg Symposium [A48] were another basis for selection.

A. RESEARCH IN THE UNITED STATES

The United States has never had a coherent experimental study program on new, advanced concepts of high-temperature superconductivity. The significance of the field had been recognized by a few interested individuals in the academic world, and limited research had been supported by corporate R&D funding. The U.S. Government manifested its awareness of the issue in the form of tardy and austere research funding for a few scientists. Theoretical progress and recent optimistic data produced under these conditions provide an interesting example of the tenacity of individual investigators. Although the scientific odds against success remain high, interest in the field has spread to

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*The Soviet effort in the field of conventional superconductivity, materials, and engineering applications was discussed in general, in J. G. Beitchman and B. S. Deaver, *The Science and Technology of Superconductivity in Eurasian Communist Countries and Japan*, DIA, ST-CS 01-175-72, December 29, 1972.

Table 4

U.S. RESEARCH IN ADVANCED CONCEPTS OF SUPERCONDUCTIVITY

Institutions	Scientists
Stanford University	Little Geballe Gamble, DiSalvo, Klemm, Menth
University of Pennsylvania	Heeger, Garito Chaikin,[a] Coleman, Cohen, Sandman, Yamagishi Epstein, Etemad
Johns Hopkins University	Bloch Minot, Pearlstein, Farraris Cowan, Walatka
University of Illinois	Bardeen Allender, Bray Miller
University of California (San Diego)	Matthias Rice
Bell Telephone Laboratories	Hohenberg McMillan Phillips Halperin
Brookhaven National Laboratory	Strongin, Kammerer, Farrell
North American Aviation Science Center	DeWames, Lehman, Wolfram
Harvard	Tucker
I.B.M.	Mattis
Belfer Graduate School, Yeshiva University	Leib
Columbia University	Luttinger
University of California (Berkeley); University of Maryland	Ferrell
Cornell University	Ashcroft
California Institute of Technology Jet Propulsion Laboratory	Somoano, Rembaum, Hadek

[a]Now at U.C.L.A.

Table 5

SOVIET RESEARCH IN ADVANCED CONCEPTS OF SUPERCONDUCTIVITY

Institutions[a]	Scientists
Lebedev Physics Institute	Ginzburg Kirzhnits, Maksimov Bulayevskiy, Kukharenko, Kopayev Keldysh Blazhin, Selivanenko Balkarey, Khomskiy Zharkov, Uspenskiy
Landau Institute of Theoretical Physics	Bychkov, Gor'kov Dzyaloshinskiy, Larkin Kats Ovchinnikov Aslamazov Zavadovskiy
Institute of Chemical Physics	Shchegolev, Zvarykina Yagubskiy, Khidekel', Buravov, Lyubovskiy, Stryukov Berenblyum, Yakimov Yeremenko, Fedumin Kompaneyets, Romanova, Yampol'skiy
Moscow Physicotechnical Institute	Geylikman
Vavilov Institute of Physics Problems	Alekseyevskiy Zakosarenko, Tsebro, Krasnoperov
Physicotechnical Institute of Low Temperatures, AN UkSSR	Gorbonosov
Institute of Spectroscopy	Agranovich, Mekhtiyev, Mal'shukov
Ioffe Physicotechnical Institute	Aronov, Gurevich
Moscow Engineering Physics Institute	Demin

[a]All are institutes of the USSR Academy of Sciences, except for the Low Temperatures Institute, which is under the Academy of Sciences of the Ukrainian SSR.

experimental work, the resulta of which, while promising, are subject to some skepticism. But a national scientific leadership committed to space spectaculars and harnessing the atom must surely recognize -- eventually -- the benefits that would accrue from the development of room-temperature superconductivity.

W. A. Little of Stanford University, in 1964, advanced the entirely new concept of superconductivity that is the subject of this paper by proposing

1. a new (excitonic) mechanism by which superconductivity could occur
2. that superconductivity from this process -- as opposed to conventional superconductivity -- might be present at virtually unlimited high temperatures
3. that entirely novel substances, especially organic chemical structures, should be investigated for the occurrence of this new superconductive process

New physical mechanisms that might be involved in superconductivity had, of course, been adduced in some number both before and after Little's original paper [A28]; but the additional aspect of greatly increased temperatures and unusual materials to be considered exerted a major -- if delayed -- influence lacking in other work.

Little's firat paper was followed by further publications by him and by other researchers concerning the problem of the order parameter resulting from the limited dimensionality of the linear and planar systems. The conclusions were taken as ruling out any possiblity of superconductivity in the proposed systems, although these first studies were far from complete and were not based on the best available analytic descriptions. A generally negative aspect of the exciton theory evidently became widespread at this time (1964-1966), although Little pointed out that superconductivity could occur in a one-dimensional system in the absence of a conventional phase transition. Interest in the field remained alive only by virtue of a few analyses that favored the possibility of superconductivity in limited-dimension systems.

In 1966 a meeting on Electrical Conduction Properties of Polymers was held at the California Institute of Technology Jet Propulsion Laboratory. A discussion of the associated questions concluded with a perceptive statement -- confirmed by subsequent events -- by the chairman, D. D. Eley of the University of Nottingham (U.K.), *recommending that a strong experimental program would be timely and more effective than further theoretical contention.*

The thrust of Eley's recommendation was evidently blunted by influential but negative views in the United States, where work continued at a low level by only a few investigators. Most of the studies undertaken were further theoretical analyses of fragmentary, although interesting, aspects of the large problem. The effect of this adverse climate for experimental research in the field continued; and today, although to a lesser degree, it is still noticeable. In 1972 Heeger at the University of Pennsylvania reiterated Eley's 1966 comment and said the absence of long-range order should not be used as an argument against experimental study of one-dimensional systems in which valuable phenomena may occur.

A few years after the appearance of Little's initial publication, some investigation of organic chemical synthesis was undertaken. The study apparently lacked a clear chemical approach to the total synthesis of the actual structure proposed by Little, although specific routes had become available within less than half a year. Instead, a major effort was made to synthesize small molecular models of the subunit of Little's polymer, with limited success. A Conference on Organic Superconductors was held in Honolulu in 1969 under Little's aegis at which basic theoretical problems and chemical approaches to potential excitonic superconductors were reviewed [A31]. A number of experts in chemical synthesis were present to consider promising methods for preparing molecular structures with the desired characteristics. Ginzburg also attended and contributed an incisive discussion of the basic problems of excitonic theory.

A larger program, eventually involving twenty-five researchers, was initiated at Stanford in 1970 to study problems in both physics and chemistry of superconductors. The screening of Coulomb forces in organic molecules and the conductivity mechanism in a Krogmann (platinum) complex -- a potential base for the desired one-dimensional macromolecule -- were investigated on the physics side. In the synthetic approaches, Krogmann complexes, insertion of cyanine dyes into these square-planar metal complexes, and preparation of direct-linked metal-metal atom polymers were studied. However, the synthetic difficulties were evidently too great to permit appreciable progress toward the desired materials in three years of effort.

Little's activity has now covered almost a decade. Work at the other American centers that are most active now and that will probably continue so in the near future has a relatively short history.

The study of TCNQ complexes, which recently gave the greatest conductivity of an organic substance, has been under way at Johns Hopkins and the University of Pennsylvania for some three years. The group involved in this work at the University of Pennsylvania under the leadership of Heeger and Garito has increased to about ten.

The experimental studies of Bardeen and his associates at the University of Illinois have shifted direction within the past year. The previous theoretical calculations of Allender, Bray, and Bardeen are now being applied to experiments with materials in thin-film systems with rather well-defined specifications and dimensions.

Thus, notwithstanding the absence of appreciable planning or funding, there appears to be a relatively recent, well-founded -- if rather localized -- effort in this country with some prospect of considering organic substances and exciton processes for HTS and with some promise of discovering valuable candidate materials.

B. RESEARCH IN THE USSR

Soviet institutional interest in excitonic processes and systems of reduced dimensionality dates to the time that Ginzburg first combined the suggestion of an exciton mechanism with his proposal of surface superconducting states, directly on the appearance of Little's article in 1964. From that time on, the Soviet efforts in this field present an interesting contrast to those of the U.S. investigators.

The gap in leadership left by Landau's death was in fact filled to some extent by Ginzburg and Alekseyevskiy. Ginzburg, Landau's student and collaborator, has given HTS reasearch the hoped-for breadth and direction. His seminars in the field are legendary and have influenced a number of research studies. They also have doubtless stimulated large audiences. Although possibly open to criticism as an excessively vocal exponent of excitonic superconductivity, Ginzburg nevertheless remains a leading figure in this field, a distinction he shares with Little. Alekseyevskiy, an experimentalist of considerable accomplishment in work on metal superconductors, including the niobium materials with the highest presently known T_c's, has reviewed studies of one- and two-dimensional superconductors with interest and reported his own attempts to prepare Ginzburg's layer structure.

Ginzburg and Alekseyevskiy have become an influential factor in Soviet HTS research. Together -- with the help of Kapitsa and a large number of former Landau students, including Abrikosov and Dzyaloshinskiy -- they successfully influenced a major science policy decision of the Soviet Academy of Sciences: the establishment in 1970 of a permanent commission on superconductivity.

With the recognition of superconductivity as a significant national scientific endeavor and supported by a large, capable, and stable research community, the Soviet effort proceeds, one would expect, in a favorable climate. However, work in advanced concepts of HTS is approached by the Soviets with a great deal of care and caution, and up to now they have made no spectacular advances in the field.

Leadership in the emerging field continues to seesaw between the Americans and Soviets. For example, at the time that Heeger and Garito -- among those most active in the race for organic materials with metallic conductivity -- were defending the value of research on conductivity of one-dimensional TCNQ complexes, Soviet scientists had already been working on them for five years with the specific goal of superconductivity. Little, who visited the Soviet Union in October 1971, noted the confidence of these investigators that they would find superconductivity in a TCNQ system. He also commented on the number and awareness of researchers with interest in the field, based on the size of his enthusiastic audiences in the Soviet Union, which he described as three to five times the size of those in the United States.

Thus, at present it appears that the Soviet Union has a formidable understanding of the subject and a great potential for future advancement. Attention and effort devoted to high-temperature superconductivity has been steadily increasing in recent years.

C. SIGNIFICANT DIFFERENCES

A comparison of the American and Soviet efforts in HTS would be incomplete without some discussion of the basic institutional and programmatic differences that clearly exist between the two in this area. Generally speaking, the Soviet manpower input into HTS is greater than the American. The larger number of scientists in the USSR is in part a result of the organization of Soviet institutes, which are staffed with a more stable population of investigators than the universities in the United States. Soviet scientists generally do not leave the institutes with which they are affiliated, and additional members are gradually added to any given research project; on the other hand, the major work force in a U.S. university -- with the exception of a relatively few major figures -- may be expected to change completely during a five-year period.

The significance of the large number of Soviet scientists concerned with HTS is largely the result of Ginzburg's comment in 1968 that *insufficient attention was being devoted to HTS in view of its importance.* He rated HTS second in technological significance only to controlled thermonuclear reaction. Ginzburg is an ardent advocate of experimental work in the field, favoring consideration of all the proposed structures. He attributed the lack of adequate study in part to fashion in scientific endeavors, which he compared to the selection of the proper length for skirts. This comment may have been directed at Western programs which, particularly at that time, could only be described as small.

An unusual contrast exists in the publications from the two countries, particularly in the earlier years of research. Soviet papers concerning the difficult obstacle of long-range order generally admitted the possibility that some method might be found to solve the theoretical problem and urged the experimental study of all available suggestions. The U.S. papers were strongly negative -- some almost polemic in the manner commonly associated with Soviet publications in fields other than HTS.*

It is commonly said that Soviet work in general is entangled in theory and that this entanglement prevents practical developments. Kapitsa commented in support of this view that a reversal of the ratio of theoretical to experimental physicists in the Soviet Union would be desirable; he estimated a beneficial ratio to be three to fifty. In the area considered in this paper, there is no evidence of an unsatisfactory ratio. The validity of both the theoretical concepts of Soviet scientists in this field and their experimental approach have been supported by recent developments. Furthermore, the leading Soviet authorities in superconductivity -- both exciton (Ginzburg) and conventional (Alekseyevskiy) -- generally favor *new approaches*. And in contrast to comparable leaders in the United States, Alekseyevskiy, who made early contributions to the Nb-Al-Ge system, commented positively on the applicability of limited-dimension structures.

However, despite the fact that work in the USSR -- unlike that in the United States -- has been fairly consistent over the past decade, and despite other favorable aspects of the Soviet research -- systematic approach, steady research population, and strong theoretical understanding followed by experimentation -- *the major contributions of recent interest have been made by U.S. investigators.*

The significant events in HTS development may be selected, somewhat restrictedly, as follows:

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*One notable exception to this comparison, however, was to be found in the excellent paper by Hohenberg [A22] in which he used a method proposed by Bogolyubov to show the absence of long-range order in both one and two dimensions.

1. The suggestion of the exciton interaction for electron pairing by Little to produce superconductivity in a one-dimensional structure at greatly enhanced temperature.
2. The formal application of the exciton concept by Ginzburg to a planar -- or sandwich -- structure for obtaining HTS.
3. The numerical estimation by Bardeen and associates of favorable quantitative experimental parameters to provide exciton superconductivity in a thin-layer planar system.
4. The observation of unusually high conductivity in quasi-one-dimensional organic materials.

Three of the above contributions were made by U.S. researchers; only the second is a Soviet development. It should be noted that the fourth is not considered as a manifestation of an exciton process, but we take it to be a result related to the questions of restricted dimensionality and organic structures which arose from work in this area.

While the expected predominance of Soviet research in the field has thus been reversed, the current U.S. leadership is precarious. The occurrence of the above discoveries in the U.S. -- particularly the fourth -- was not planned or programmed, at least to the extent to which research is organized and coordinated in the USSR. Instead, it must be ascribed to such other factors as the superiority of U.S. research practices and the excellence of our investigators.

The prominence and number of the Soviet researchers currently active in HTS is sufficient evidence that more leadership leap-frogging can be expected in the near future. In the battle for world prestige in significant areas of science and, more important, technological leadership, the Soviets leave very little to chance. While the United States is currently challenging the 60 K mark, the Soviets are silently regrouping for the assault on still higher critical temperatures.

D. THE FUTURE OF HTS

It should be noted again that *there has yet to be a demonstration of the exciton process in a superconductor*. And, one might add, there is no guarantee that the mechanism will be effective or significant in any superconducting material. However, highly promising observations have been made, even in systems in which this mechanism is probably absent.

Low-temperature physics and solid-state theory have become powerful accessories for the materials scientist. A basic understanding of the physical processes of superconductivity came rather slowly after a long history of experimental work. More recently, the ability to deal with electronic properties of this special state has improved, to a considerable extent through the contribution of Soviet scientists. While theoretical methods have advanced, they are still not powerful enough to account quantitatively for all observed properties. However, knowledge of superconductivity seems sufficient for certain predictions, as in the case of the Josephson effect. The extension of this knowledge to the description of the electron-exciton interaction is somewhat more difficult but appears to have a reasonable basis.

An estimate of the potential significance of HTS to practical materials may be formed from the present status of superconductors in technology. Appreciable outlays are being made to develop advanced technological applications that rely on presently available superconductors, such as those used for magnetically levitated and propelled trains. Developments of this sort, which extend to preparation and test of prototype machinery and vehicles, call for large expenditures at an early stage. Material studies and research toward more or less conventional superconductors with higher T_c also command a reasonable effort. On the other hand, the attention devoted to the search for novel materials for the purpose of attaining a *major* increase of T_c has been insignificant for a considerable length of time, despite the impact a successful result would have.

It appears that in the past, experimental study of novel materials and the exciton mechanism of superconductivity in the United States developed more slowly than was desirable and was inadequately supported and directed in view of its potential. Valuable information and possibly guidance on favorable approaches to be considered can be obtained by close study of the Soviet open-source literature and of the continuing owrk in the Soviet Union. *The present level of effort there is approximately on a par with our own but involves a larger number of experienced investigators.*

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