AD-765 514

HIGH ENERGY LASER WINDOWS

R. W. Rice

Naval Research Laboratory

Prepared for:

Advanced Research Projects Agency

1 July 1972

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

High Energy Laser Windows

Semi-Annual Report No. 2
For period ending 30 June 1973

Sponsored by
Advanced Research Projects Agency
ARPA Order 2031

NAVAL RESEARCH LABORATORY
Washington, D.C. 20375

R

ARPA Order
2031

Program Code
3D10

Principal Investigator:
R. W. Rice
(202)767-2131

Contractor:
U. S. Naval Research Laboratory

Effective Date of Contract:
1 July 1972

Contract Expiration Date:
30 June 1973

Amount of Contract:
$200K

[illegible] 755716

Forward and Acknowledgments

This semi-annual technical report summarizes work performed by personnel of the U. S. Naval Research Laboratory, Washington, D.C. 20375, under ARPA Order 2031. The program was coordinated by Mr. R. Rice and Dr. P. Becher and monitored by Dr. C. M. Stickley of ARPA. The report covers the period 1 January 1973 through 30 June 1973.

The following members of the NRL technical staff are acknowledged for their contributions to this program: O. Imber, F. W. von Batchelder and J. G. Allard in the crystal growth and analysis, F. J. Bartoli for the use of CO_2 laser, and J. R. Spann in the high power CO_2 laser testing. Members of various laboratories are also acknowledged for their contributions, especially R. C. Pastor and colleagues of Hughes Research Laboratory for discussion of the "RAP" crystal growth process, B. G. Koepke and R. J. Stokes of Honeywell Research Center for discussions of their forging and strength results, and J. R. Hardy of University of Nebraska, T. C. McGill of California Institute of Technology, D. L. Mills of University of California, Irvine, and M. Sparks of Xonics Corporation, for their discussion of absorption theory.

TABLE OF CONTENTS

1.0 INTRODUCTION AND SUMMARY

The goal of this program is to improve the mechanical properties of, and reduce the absorption in, alkali halides for laser window use. With KCl as a model material, higher yield strengths and fracture toughness have been achieved by forging crystals to obtain fine grained polycrystalline bodies supplemented by alloying or irradiation. Very low absorption has resulted from improved crystal growth processes and finishing operations. The mechanisms of absorption are being studied both theoretically and experimentally as a guide to further reducing absorption. Advances in these areas are presented and discussed in this report.

Adaptation of the reactive atmosphere process (RAP) of crystal growth has been an important step in achieving the lowest absorption coefficient to date for KCl ($1.5 \times 10^{-4} cm^{-1}$). This is within a factor of two of the expected intrinsic absorption level. "RAP" growth has also been successful in reducing the absorption coefficient in Sr^{+2} doped (20 ppma) KCl (to $2.5 \times 10^{-4} cm^{-1}$), significantly below previous levels. Differential scanning calorimetry has shown that the $SrCl_2$-KCl compound formed during alloy crystal growth is very hygroscopic while the similar barium compound is not.

Forgings of low absorption crystals were shown to have the same strength as, but much lower absorption than, previous forgings of high absorption crystals. Studies of Sr^{+2} doped KCl have shown a dependence of recrystallization and strengthening behavior on Sr^{+2} content. Several of the benefits (i.e., elimination of cracking and edge tearing) of forging with constraining rings have been verified, while γ-irradiation of KCl crystals prior to forging has shown promise for obtaining a homogeneously fine grain size.

The polycrystalline KCl produced by press forging, besides having improved yield strength (5000 psi), also has a factor of ten greater fracture energy than crystals do. Fracture energies and yield strengths of KCl crystals have also been shown to be increased by a factor of two to four by either γ-irradiation or strontium alloying.

Chemical polishing has been further improved, especially for press forged materials where absorption coefficients as low as $6 \times 10^{-4} cm^{-1}$ have now been achieved. Such improved polishing was also an important factor in achieving the low absorption coefficient noted earlier for RAP grown KCl crystals.

A high temperature calorimetric technique was developed to study absorption as a function of temperature. Such measurements did not show nearly as great a temperature dependence of absorption as was predicted by previous theories. These results have therefore led to considerable re-evaluation of theoretical predictions. High temperature calorimetric studies show that absorption can sometimes be permanently reduced by annealing.

Further lowering of absorption in halides will be sought through theoretical and experimental investigations of absorption mechanisms which will draw heavily on high temperature absorption and emittance studies. Efforts to achieve yield stresses greater than 6000 psi by forging, alloying, and irradiation will continue, guided by studies of strengthening mechanisms of divalently alloyed polycrystalline KCl. Further high power laser testing of single crystal and polycrystal windows will be used to study failure modes and degradation during 10.6μm irradiation.

2.0 MATERIALS PREPARATION

2.1. Crystal Growth and Analysis, P. H. Klein

2.1.1. Purification and Crystal Growth

Halogen-bearing atmospheres have been found effective in purification of potassium chloride. Two methods have been used, both of which are variants of the techniques of Capelletti, Fano and Scalvini (1) and of Pastor (2). The first method has been abandoned because of the outstanding success of the second.

In the first method, reagent-grade KCl was zone-refined in glassy carbon boats under a gettered-argon atmosphere which contained carbon tetrachloride vapors and gaseous hydrogen chloride. Hydrogen chloride was admitted to the system after temperatures above 650°C had been reached, CCl_4 being allowed in only during premelting passes at lower temperatures. It was hoped that the cracking of CCl_4 to carbon and chlorine (most evident above 700°C) would thereby be diminished, so that contamination of the purified KCl by carbon granules could be eliminated. Although the over-all impurity content of the resulting KCl bars was of the order of 5-10 parts per million atomic (ppmA), carbon specks could frequently be seen.

Following the zone-refining procedure, pieces from the central portions of bars were placed in platinum crucibles and remelted under gettered argon in an A. D. Little-type MP crystal-growing furnace. Crystals measuring about one inch in diameter and three inches long were pulled from these melts by the Czochralski method. All crystals prepared by this refine-and-pull sequence showed definite, uniform Tyndall scattering when probed with a helium-neon laser. Typical (calorimetrically-measured) absorption coefficients at 10.6 micrometers were in the 0.002-0.01 cm^{-1} range.

The second method - and that currently used exclusively - combines purification and Bridgman growth into a single-vessel, single-apparatus process. Similar to the reactive atmosphere process ("RAP") of Pastor at Hughes Research Laboratories (2), purification is effected by exposure of KCl to carbon tetrachloride vapors in an argon carrier. Reagent-grade KCl, contained in a Vycor Bridgman crucible (approximately 2.5 cm in diameter and 15 cm long), is placed within a vertical ceramic tube through which the RAP gases are flowing. The tube is centered in a movable furnace. By positioning the furnace, the charge is heated from room temperature to 300°C, held there for about an hour, and allowed to cool to room temperature. This cycling fosters replacement of the air confined within the powder by the reactive atmosphere. After one or two cycles at 300°C and another one or two at 600°C, the furnace temperature is raised to 820-830°C for two to three hours to assure complete melting of the KCl. At the end of this time, the furnace is elevated at a rate of 2.8 mm/h.

A typical Bridgman crystal is shown in Fig. 1, just as removed from the crucible. Without exception, crystals slide from the crucible when it is inverted. Rows of facets, similar to that shown in the photograph, are evident on all specimens, and show fourfold (in <100> and <110> crystals) or threefold rotation symmetry (in <111> crystals).

Under crossed polarizers, as-grown crystals exhibit some birefringence, but this could not be associated with any local strains. If a crystal is set down on a hard surface, some strain birefringence is sometimes detected at the point of initial contact. If crystals are shaped and cleaned of excess material by washing with water, and are chemically etched to produce flat surfaces, no other birefringence is introduced. Tyndall scattering was not detected using a He-Ne laser beam. A few, isolated carbon particles, generally found within a millimeter of the surfaces, are evidence of complete cracking of the CCl_4 vapor.

Unalloyed crystals processed in this manner have calorimetrically determined absorption coefficients at 10.6 micrometers of 0.00015-0.00018 cm^{-1}. With 60 ppmA of strontium added to the charge (yielding a boule containing 15-45 ppmA of Sr), the measured absorption coefficient was 0.00024 cm^{-1}.

The small absorption coefficients determined for Bridgman-grown, reactive-atmosphere-processed crystals are attributable partly to damage-free handling, but are principally the result of removing absorbing impurities. Chief among these is the hydroxyl ion, although the conditions of the process foster volatilization of transition-metal ions and heavy halogens. The fact that low-cost, reagent-quality material can be upgraded in one step, to the point at which its absorption is very nearly the lowest measured for KCl of any quality, commends the process to further use. With minor modifications, it is planned to use the method for preparation of pure and alloyed crystals for the purposes of this program.

2.1.2. Alloy Studies

Divalent additives for strengthening of potassium chloride have been investigated further, with the aim of determining which of these pose fewest handling problems. As reported previously, strontium exsolution sets an upper limit to the amount of this element which can be incorporated in potassium chloride crystals. Nevertheless, it was deemed useful to study the hygroscopicity of potassium-strontium chloride (K_2SrCl_4) and its barium analog (K_2BaCl_4) and to compare the results with those obtained for potassium lead chloride (KPb_2Cl_5).

Figure 2 is a composite of three differential scanning calorimeter (DSC) traces, all obtained with the same batch of K_2SrCl_4. Curve I shows a slight enhancement of the rate of heat absorption near 400°K, suggesting loss of the last remnants of water, despite anhydrous conditions of preparation and storage. However, as shown by Curve II, allowing the sample used for Curve I to stand for 18 hours in room air results in sufficient water pickup to produce a marked "pip" near 410-420°K. An exaggeration of this pickup takes place when fragments of the K_2SrCl_4 melt are allowed to stand in air before calorimetry. Curve III is the result, and evolution of water is visible from about 340°K to above 450°K. Figure 3 shows similar behavior for an alloy of 2 mol percent $SrCl_2$ in KCl. Hygroscopicity is evident even at this dilution.

That K_2SrCl_4 is unstable to atmospheric moisture was corroborated by x-ray powder patterns. Fresh material, stored under anhydrous conditions, gave a powder pattern distinct from those of its constituents. However, upon standing in air overnight, the pattern was altered to a mixture of the patterns of KCl, $SrCl_2$, and the hydrates of $SrCl_2$. (It is noteworthy that Schmalzreid's x-ray data (3) for K_2SrCl_4 correspond to the latter mixture, and not the pattern of the fresh, presumably anhydrous, compound. Schmalzreid makes no mention of hygroscopicity.)

In contrast to the ease with which strontium-bearing crystals of potassium chloride may be hydrated, Fig. 4 shows the stability of K_2BaCl_4, the compound on the potassium-rich side of the potassium-barium-chloride composition diagram (3). It is clear that hydration is much less of a problem than is the case with K_2SrCl_4. Differential scanning calorimetry of potassium lead chloride leads to a similar composite figure. Both the lead and the barium compounds give distinct x-ray powder patterns which do not change with exposure of the sample to room air. All the facts suggest that barium or lead are more suitable than is strontium as stable additives to potassium chloride. It will require that strengths of alloyed crystals produced under CCl_4 vapor be measured before the value of these additives can finally be determined.

1. R. Capelletti, V. Fano, and M. Scalvini, "Purification and Growth of Alkali Halides," Ric. Sci. 38, 886-890 (1968); ibid., "Hydrochloric Acid and Chlorine Purification of Raw Powders for Crystal Growth of KCl," J. Crystal Growth 5, 73-74 (1969).
2. R. C. Pastor and M. Braunstein, "Halide Window Materials Technology," Technical Report No. AFWL-TR-72-38, March, 1972, p. 20-25.
3. H. Schmalzreid, "Reactions Between Solid Halides (Reaktionen Zwischen Festen Halogeniden)," Z. Phys. Chem. 33, 129-142 (1962).

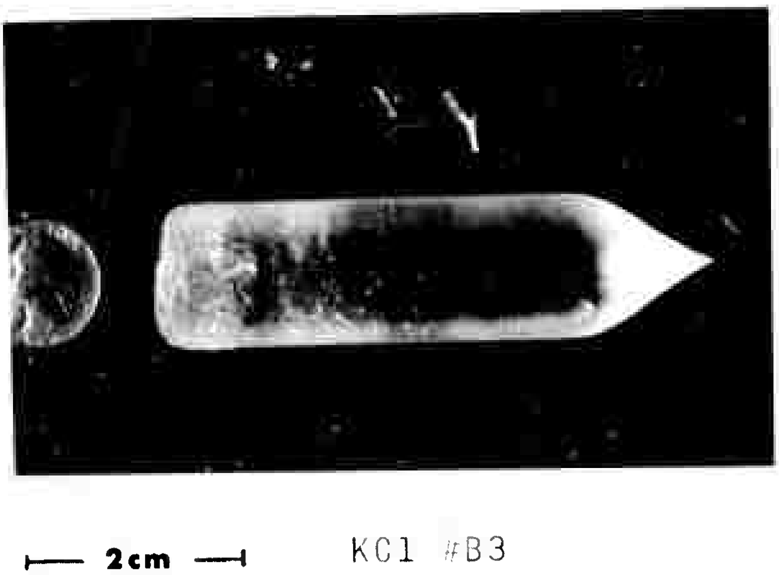

Fig. 1. Potassium chloride crystal as removed from Bridgman-growth crucible. A row of facets can be seen along the lower edge of the crystal.

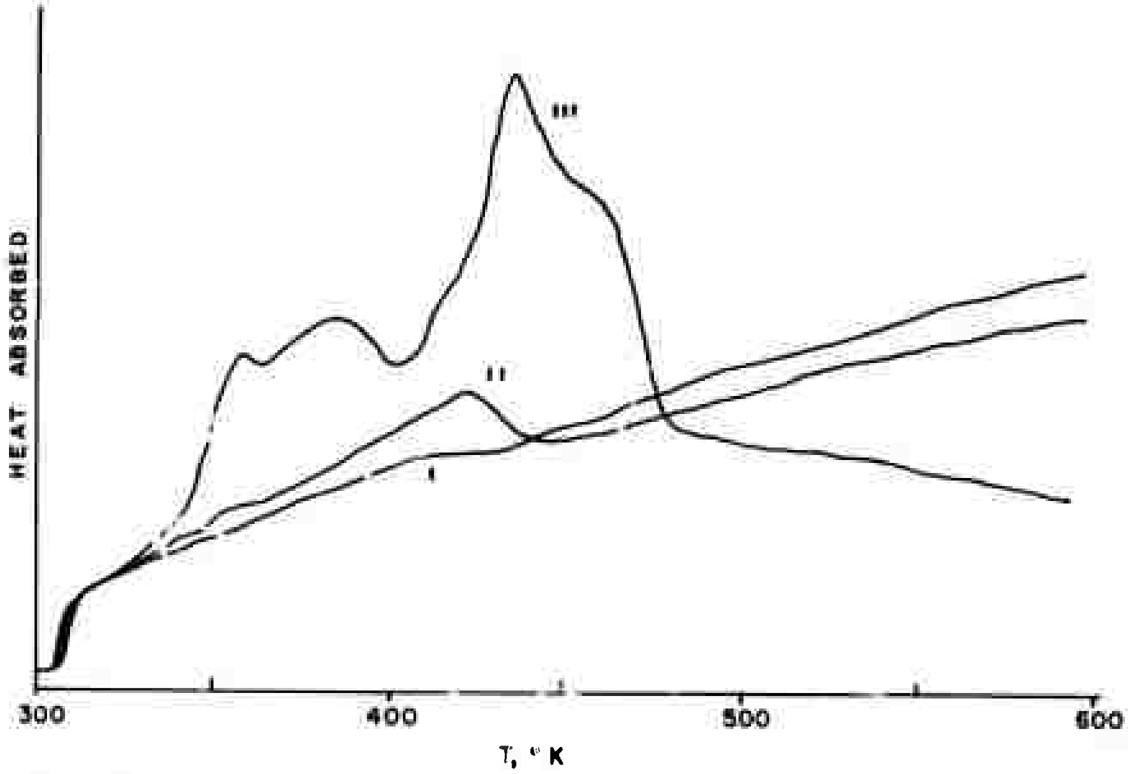

Fig. 2. Composite differential scanning calorimetric (DSC) trace for K_2SrCl_4. (I) Sample removed from crucible and run under anhydrous conditions. (II) Same sample, now allowed to stand in room air for 18 hours after Run 1. (III) Sample taken from crucible allowed to stand an additional 18 hours in room air prior to DSC run.

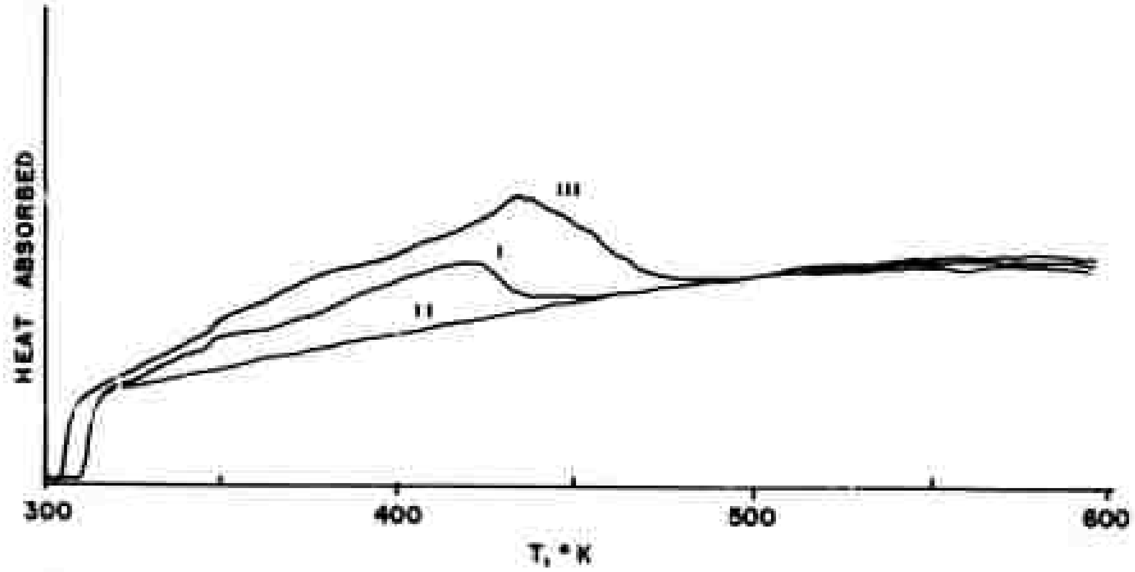

Fig. 3. Composite DSC trace for KCl containing 2 mol percent $SrCl_2$. (I) Sample run after removal from crucible, with no special precautions against hydration. (II) Sample from curve (I), left in anhydrous atmosphere for 20 hours and rerun. (III) Same sample, removed from anhydrous environment for 18 hours and again rerun.

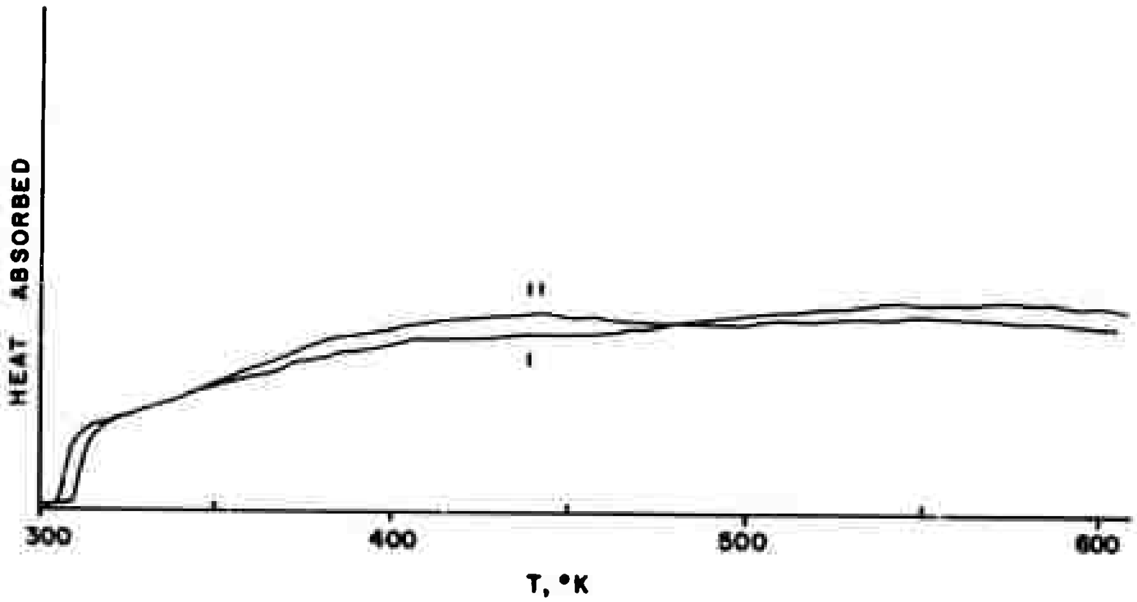

Fig. 4. Composite DSC trace for K_2BaCl_4. (I) Sample removed from crucible and run. (II) Same sample, allowed to stand in room air for 20 hours and rerun.

2.2. Press Forging, P. F. Becher and R. W. Rice

2.2.1. Introduction

Recent work has centered on forging alloyed (≦200 ppma $SrCl_2$) or γ-irradiated KCl crystals, constrained forging using the copper sleeve technique per Bernal G. et al (1) and Anderson et al (2), and further microstructural analysis. The unconstrained forging techniques employed have been described in detail previously (3). A new forging apparatus for 6-1/2" diameter forgings using platen heating is now operational. Initial studies of new alloys or material, however, still are being undertaken with the original forging system (4). The machining and preparation of subsequent mechanical test samples and laser windows have been previously described (3).

2.2.2. Results

Previous results had shown that KCl-0.1 m/o $SrCl_2$ crystals could be forged at a slightly higher temperature (200-260°C) range than that for unalloyed KCl crystal (125-200°C) (3). These Sr-doped crystals (0.1 m/o) have now been successfully forged (unconstrained) at temperatures as low as 175°C. Forging at 175°C results in a partially recrystallized structure (Fig. 1) as compared to the fully recrystallized microstructure at 260°C (see Fig. 6, ref. 3). The recrystallized grains appear to nucleate within slip bands (lying at 45° to vertical axis) and at their intersections (Fig. 1), giving a crosshatched pattern consisting of small recrystallized grains surrounding large "unrecrystallized" regions (center Fig. 1). As previously discussed (3), alloying is expected to increase the recrystallization temperature and this apparently is the case for KCl-$SrCl_2$. In addition, the recrystallized grains are ~5μm in size for the 260°C forging; thus alloying may be limiting grain growth.

With the addition of only 200 pma $SrCl_2$ to KCl, it was discovered that the forging temperature had to be raised over 300°C to achieve sufficient plasticity. This is felt to be a result of solid solution hardening limiting cross-slip at temperatures in the neighborhood of 200°C. The microstructure consisted of an average grain size of 10-15μm and was apparently fully recrystallized (Fig. 2). Thus the Sr addition appears to be limiting grain growth at the 330°C forging temperature used for the 200 ppma Sr-KCl crystal.

Subsequent forging studies investigated the use of a constraining ring as initially discussed by Bernal G. et al (1) and Anderson et al (2). The technique was modified slightly to be used with available square cross section crystals by fitting the crystals in a copper ring whose height would just equal the deformed, equi-cross section crystal. As shown by Bernal G. et al (1) and Anderson et al (2), the constraining sleeve eliminates cracking and edge tearing at lower forging temperatures. However, one must take care in the mounting and handling of these forgings after the sleeve is removed from the forging. High residual strains are present, particularly in low temperature forgings (125°C), so the forgings are subject to thermal and mechanical shock. Besides the elimination of edge tearing or cracking during or after forging, this technique also has the advantage that a nearly circular window is obtained even from a square crystal as compared to unconstrained forgings (Fig. 3). However, the strengths of these forgings is consistent with unconstrained forgings, not greater, as seen by Bernal G. et al (1) and Anderson et al (2). Although there appears to be some greater homogeniety of grain size in constrained forgings, the strengthening previously observed is felt to be a difference in either purity, texture, or residual strain.

A preliminary investigation of forging irradiated crystals was initiated to see if irradiation damage would increase the density of grain nuceli and thus refine and homogenize grain size. Success requires forging at conditions which avoid annealing out this damage (i.e., below the 150-200°C forging range generally used). A γ-irradiated (Co^{60} source, 10^7R dose) KCl crystal was forged using a constraining ring to a height reduction of 63% at 185°C (due to a failure of temperature control).

Though exceeding the intended 150°C limit may have resulted in considerable defect annealing, the resultant forging had a very homogeneous grain size (6-8μm) throughout. Also samples from this forging had a somewhat higher (~1000 psi) yield strength than comparable unirradiated crystal forgings from the same crystal stock. Thus, these initial results of improved microstructure and strength are encouraging, but further work to substantiate these is needed.

2.2.3. Microstructural Defects

Examination of as-forged KCl has revealed two important microstructural features. One is the presence of voids in the forged KCl bodies. These are present as negative crystals and are primarily located at or near the grain boundaries of grains undergoing exaggerated growth (Fig. 4). The size of these voids has an upper limit of about 1-2 μm; thus they probably will not interfere with transmission at 10.6μm. However, their presence at grain interfaces can act as a source of mechanical weakness. As a result of the non-homogeneous distribution, it is difficult to establish a void density. However, an upper limit of $\sim 1\text{x}10^3$ voids per cm of boundary length has been observed in the case of exaggerated grain growth. Examination of fine grained materials indicated that void densities were much lower if at all detectable. However, as shown in Fig. 5, dark field microscopy of relief polished samples exhibit light scattering at the boundaries. This is expected from surface boundaries which exhibit a surface groove due to the water-alcohol etching action at the boundary. However, one can focus into the interior along some of these boundaries and still observe light scattering. This could result either from voids or from absorption due to the diffusion of the polishing fluid along the boundary. The latter would result in increasing the surface absorption. Presently, Auger analysis is being undertaken with similar large grain samples to determine if chemistry of the boundaries has been altered in the surface region.

Future studies will center on the influence of alloy additions on recrystallization during forging and the distribution of the alloy constituent within press forged KCl. As a result of the detection of microvoids in some forgings, their source and elimination will also be sought. KCl forgings from high purity crystals having lower absorption have shown similar strength and forging behavior to those from less pure, higher absorption KCl crystals. Thus as the reduction of the absorption of forging is enhanced by employing the highest optical quality single crystals (5), further studies will concentrate on such crystals which are now grown at NRL (6).

1. E. Bernal G.,B.G.Koepke, R. J. Stokes and R. H. Anderson, "Preparation and Characterization of Polycrystalline Halides for Use in High Power Lasers," QTR No. 3, ARPA Order No. AO2172, Honeywell Research Center, 1973.

2. R. H. Anderson, B. G. Koepke, E. Bernal G., and R. J. Stokes, "Preparation of High Strength KCl by Hot Pressing," J. Am. Ceram. Soc. 56, 287 (1973).

3. P. F. Becher and R. W. Rice, "Press Forging Studies" in High Energy Laser Windows, Semi-annual Report No. 1, ARPA Order No. 2031, U. S. Naval Research Laboratory, Dec. 1972.

4. P. F. Becher and R. W. Rice, "Press Forging Studies" in High Energy Laser Windows, Semi-annual Report No.1, ARPA Order No. 2031, U. S. Naval Research Laboratory, June 1972.

5. M. Hass, F. W. Patten, J. A. Harrington and J. W. Davisson, "Absorption Measurements" in High Energy Laser Windows, Semi-annual Report No. 1, ARPA Order No. 2031, U. S. Naval Research Laboratory, Dec. 1972.

6. P. H. Klein, "Crystal Growth and Analysis," see this report, Section 2.1.

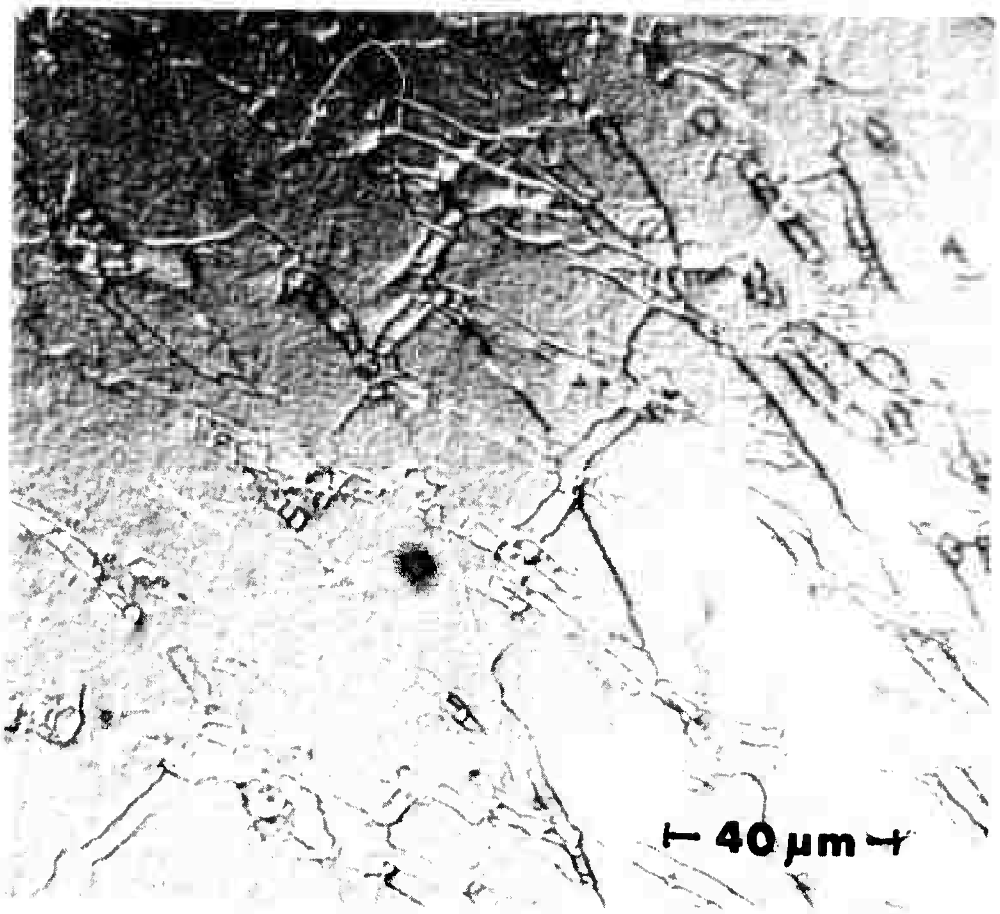

Fig. 1. Microstructure of KCl - 0.1 m/o $SrCl_2$ sample as forged at 175°C to 66% height reduction.

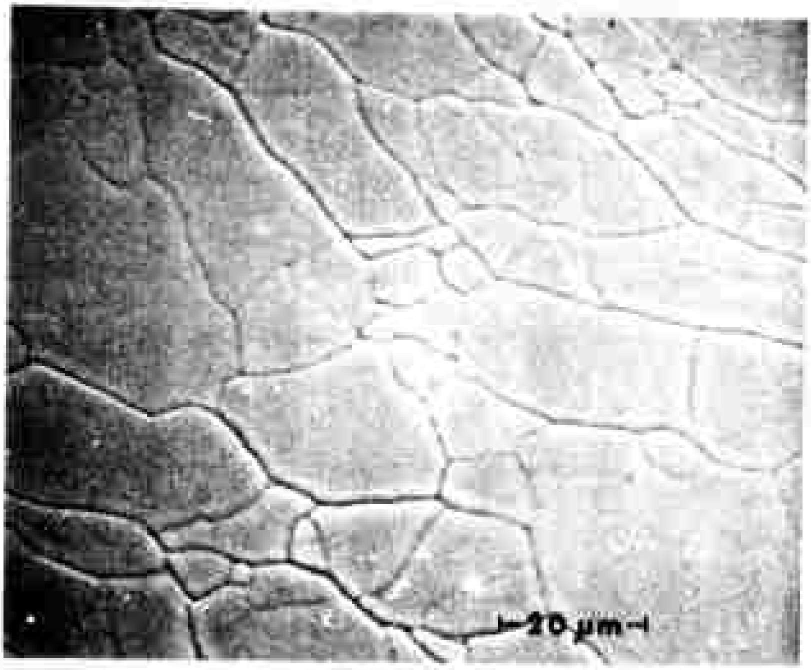

Fig. 2. Fully "recrystallized" grains in KCl-200 ppma $SrCl_2$ forging after 70% height reduction at 330°C.

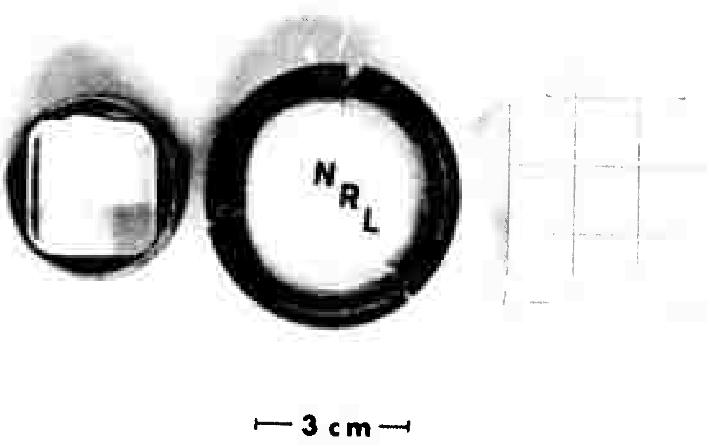

Fig. 3. Comparison shape and cracking for constrained and unconstrained forgings. a. <100> single crystal with copper sleeve. b. After forging in 70% height reduction at 125°C. c. Unconstrained crystal forging processed at 150°C to 70% strain. (Note copper ring has been cut after forging.)

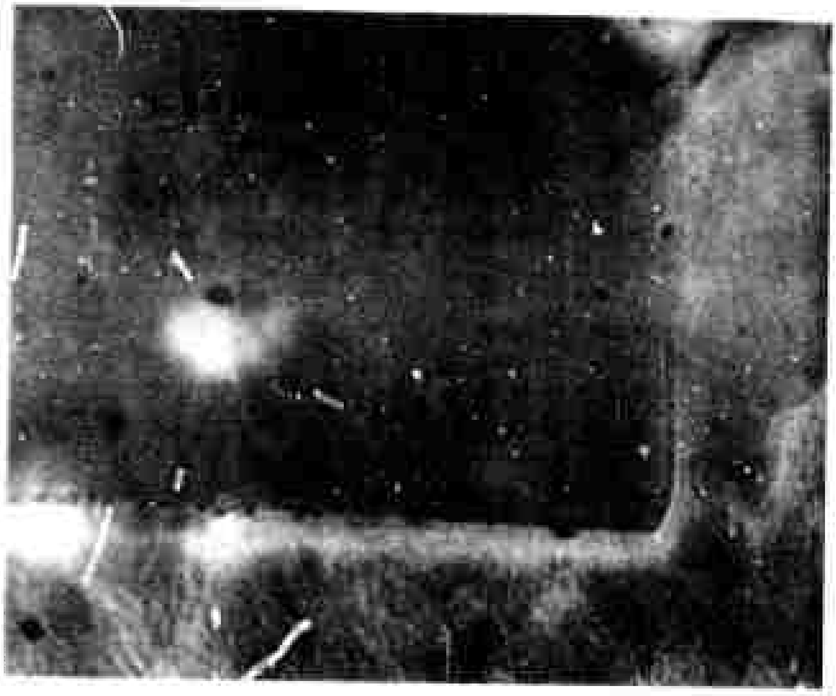

Fig. 4. Microvoids accumulation along grain boundary which is associated with exaggerated grain growth in KCl.

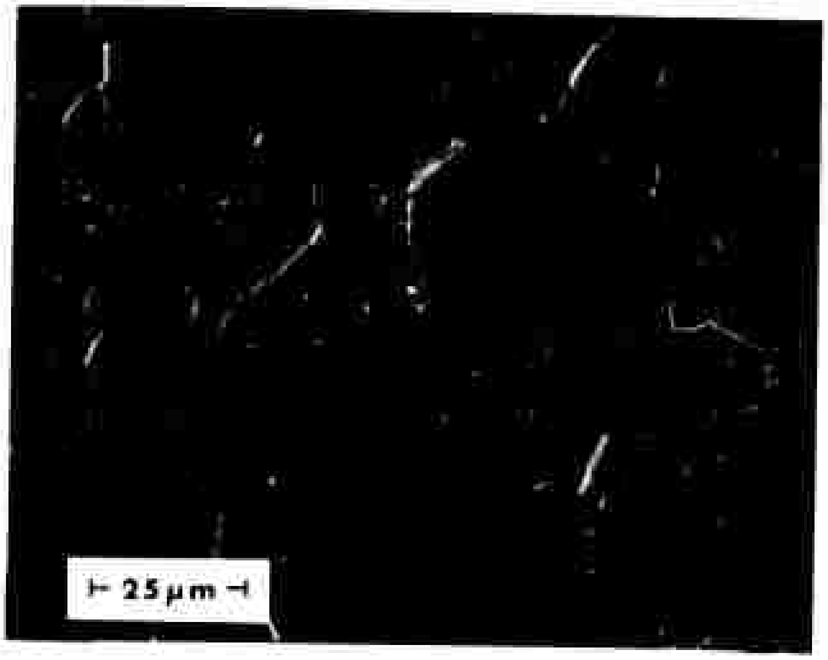

Fig. 5. Light scattering from surface and subsurface grain boundaries in water-alcohol polished KCl forging.

2.3. Surface Finishing, J. W. Davisson

2.3.1. Introduction

The objective of this work has been to develop high quality low loss surface finishes for alkali halide laser windows. Existing methods of preparing laser windows leave scratches from abrasive materials used in finishing which may serve as sites for atmospheric degradation or as absorbing centers for the high power laser beam. In this work, a chemical polishing technique for alkali halides is described which can serve to remove the scratches and abrasive particles inherent in any of the mechanical finishing techniques. Methods for chemical polishing of both single crystals and press-forged materials have been described (1). By suitably controlling the chemical polishing conditions, it may be possible to achieve excellent quality surfaces with minimum deterioration in the optical figure.

In the course of carrying out this work in conjunction with simultaneous absorption measurements, it became evident that the importance of finishing the materials transcended the initial requirement of achieving a high quality surface. A strong connection between the nature of the entire finishing operation and the resulting absorption of single crystals was noted and this has important implications for deducing the optical absorption coefficient of starting single crystal materials. In the case of press forged materials, a connection was also noted between the absorption coefficient and the processing operation. While it might be assumed that some absorbing centers can be introduced by finishing operations and that the presence of dislocations introduced in the finishing operation can be noted, the mechanism of such absorption has not yet been established.

In this work, a method of finishing single crystals with a minimum of absorbing centers introduced during the polishing process is described. Essentially damage-free end faces of a boule can be prepared and the absorption coefficients of such crystals have been measured. This is followed by a study of the dislocation damage and the elastic stress introduced in single crystal alkali halide material by the mechanical actions of lapping and polishing, and of the changes that occur when the specimen is waxed to a base. Corresponding techniques have been developed for press forged KCl and the absorption coefficients have been studied. However, there are small, but important, differences in the experimental techniques for forged and single crystal materials.

2.3.2. Fabrication of High Quality Damage-Free Faces on KCl Boules

In this section, a method of preparing end faces for studying the optical absorption of crystal boules is described. The starting material consists of the raw boule. Since cleaving and cutting operations have been observed, both at NRL and Hughes-Malibu (2), to result in increased absorption, such operations are avoided in the procedure which has been developed.

The sequence of operations is shown pictorially in Fig. 1 and an extended description is given below.

(a) Preparation of wheel: Lapping has been carried out on a rotating wheel with a 6" disc of Politex Poromeric* which is rotated at 60 rpm. Water is added and the excess is removed from the rim with a paper towel. The removal of excess water is required to prevent undercutting of the crystal in the lapping operation.

(b) Lapping: The boule is pressed gently against the polishing wheel so that removal of material is effectively achieved through the wiping action of a wet cloth. A spirit level on the opposite face serves to keep the two end faces reasonably parallel. The wheel must be recharged with water several times if considerable lapping is necessary.

(c) Lapping (intermediate wipe): In the course of lapping, it is helpful to wipe the wet face of the boule with a soft tissue. The use of an alcohol wash at this time is not recommended. The lapping operation is continued until the desired size is reached.

(d) Chemical Polishing: The boule is then chemically polished by immersion in concentrated HCl. As shown in the figure, the boule is suspended from platinum wire. The length of time is not critical and periods from one minute to one hour may be employed. As indicated in the previous report (1), a dissolution rate of less than 0.1 μm/sec in concentrated HCl (unagitated) for KCl can be expected.

(e) Washing: The crystal is then washed with absolute ethanol. Deliberate, but not excessive, speed is used to wash the two end faces of the boule. It should be noted

---

* Geoscience Instruments Corp., Mt. Vernon, N.Y.

that the alcohol used for washing is kept in a glass container. A plastic wash bottle should not be used as it is slightly soluble in ethanol and hence leaves a residue on evaporation.

(f) Drying: The crystal is dried by draining from the bottom edge of the boule while blowing a jet of inert gas. At NRL, a spray can of Microduster (Texwipe Co.) has been used. The remaining liquid is blotted with tissue. The absorption coefficient of crystals does not change after standing a few days in a dessicator in moderately dry air.

A few general comments can be made. Cleanliness at each stage of the operation is essential. While the procedures as described have been consistently successful at NRL, some difficulty may be encountered at first in removing some of the surface film after the drying operation. Some practice in removing the excess liquid may be necessary.

Crystals prepared in this way have yielded absorption coefficients as low as 0.00015 cm^{-1}, in which the absorption coefficient is obtained by dividing the total absorption by the length, i.e., no correction for surface absorption whatsoever has been introduced (a correction might decrease the absorption even further). It should be noted that these low loss crystals can be very sensitive to the nature of the treatment. Even gentle cutting of a crystal using a cotton string can affect the absorption. This and previous evidence suggests that certain types of absorbing centers are introduced on finishing. It is not yet known whether these absorbing centers are present near the surface or are distributed through the bulk. Sometimes such centers can be annealed out.

In conclusion, a method for preparing single crystals which minimizes the introduction of absorbing centers has been described. The method is not very involved and might be further simplified. In the interim, it can be recommended as a means of preparing single crystal KCl for absorption studies.

Finally, a comment about commercial polishing procedures. In the past, most commercial finishes have tended to leave small scratches on the crystals, which presumably could be removed by chemical polishing of the type described. Very recently, NRL has received single crystal KCl polished by Janos Optical Corporation*. Preliminary

---

* Janos Optical Corp., Newfane, Vt.

examination of these indicates that both flatness and excellent quality surfaces on single crystal KCl have been achieved. It is not known at this time when any absorbing centers have been introduced in this finishing process.

2.3.3. Damage and Mechanical Processing Techniques

In the usual methods of finishing crystals, abrasive lapping operations are generally employed. Such operations tend to produce damage which may extend to some depth in the material. In the previous section, it was shown how to finish crystals to minimize such damage. Unfortunately, the techniques developed in the previous section have not been developed to the point of producing flatness over large areas. Consequently, it is believed that mechanical processing will be required to obtain the necessary flatness and that a final chemical polish might be used to remove a small layer of surface material. However, the mechanical processing may introduce dislocations into the bulk material which may affect the absorption.

In this section, the dislocations introduced in mechanical processing have been studied. The primary tool of this investigation involves the technique of etching wherein dislocations can be directly observed. In addition, the presence of internal stress at any surface location both as to sign and relative magnitude can be evaluated by observing the asymmetry in the indentation dislocation rosette patterns (5).

Dislocation etching studies on the transverse cleavage face of NaCl specimens (1 cm^2 x 3 mm) having one face polished showed that the mechanical operations of lapping and polishing (1) produced a well defined damaged surface layer about 30 microns thick. Dislocation rosettes formed on these transverse faces showed no stress trend relative to the side of the sample that had been polished. The stress distribution was instead apparently controlled by the grain wall structure of the crystal and by its thermal history. The crystal immediately beneath the damaged layer usually showed the presence of a weak tensile stress, but larger stresses of either sign existed in other locations. The samples, with polished face down, were then waxed to a base and removed therefrom to determine whether or not this operation causes dislocations to be emitted into the volume from the damaged layer. This study revealed that the emission was negligible when either soft wax (MP 60°C) or hard wax (MP 180°C) was used. The damaged layer was unmodified when soft wax was used, but extensive recovery of the damage occurred with the hard wax. However, dislocation emission from isolated sources, such as from indentations, occurred in the latter case. It is suggested that dislocation emission did not occur from the damaged layer because the stress in this region was relieved by dislocation annihilation; whereas emission occurred at isolated sites because the stress could not be relieved by dislocation annihilation, since the positive and negative dislocations were spatially separated.

2.3.4. Production of High Quality Surfaces in Forged KCl.

The production of high quality surfaces on forged KCl has presented some problems. Mechanical processing techniques so far at NRL have resulted in surfaces containing obvious scratches. While it is believed that additional effort in this area might result in significant improvements in such mechanical finishes, it was felt that adaptation of chemical polishing techniques developed for single crystals might be applicable to forged materials. This has proven to be the case, except that the polishing time is much more critical for forged materials. By use of such techniques, it has been possible to prepare forgings having an absorption coefficient as low as 0.0006 cm^{-1}, or within a factor or two of the starting single crystal. In addition, the absorption coefficient is reasonably uniform across the face of the crystal and the nonuniformity, which was a source of difficulty earlier, is no longer a problem.

The production of forgings having absorption coefficients within a factor or two of the starting single crystal might even be considered remarkable in view of the sensitivity of the starting single crystal to mechanical damage. Here it might be added that the starting single crystals were prepared in such a way as to minimize introduction of absorbing centers.

By use of the above procedures, forging of crystals having an absorption coefficient of 0.0003 cm^{-1} has been used to obtain polycrystalline bodies having an absorption coefficient of 0.0006 cm^{-1}. Here, these statements require some qualification. First, it has not yet been clearly established whether the absorption coefficient of the starting material is as low as it might be, or whether even the gentle finishing procedures have introduced some absorbing centers. Second, the absorption coefficient of forged materials as a function of length has not yet been obtained.

Finally, there are a few comments on some superficial observations of the optical transmission of these materials. In the case of single crystal materials, the optical transmission of a helium:neon laser beam is excellent. While some small amount of scattering does occur at the crystal surfaces, no internal scattering can be observed. On the other hand, in the case of forged materials, some internal scattering is plainly evident. In addition, the surfaces of the forged material scatter much more than single crystal material. Furthermore, there is noticeable degradation in the beam after traversal of the forged material. Consequently, while the absorption of the forged material is low, the beam quality is far from that which is required. Although the beam quality at 10.6 μm is apt to be much better than in the visible red of the helium:neon laser, it could stand great improvement. Furthermore, it has not been established whether this degradation is due to surface or bulk effects. Since absorbing centers can be easily introduced merely by cleaving or cutting the crystal, it would not be unexpected to find that the forging might even have an absorption coefficient smaller than the starting single crystal. Presumably, there is some factor in the forging process, possibly the temperature, which precludes the formation of absorbing centers.

The preparation of high quality forged surfaces can be carried out in the same way as for single crystals. However, the polishing time must be determined somewhat empirically, but about twenty-five seconds seems optimum. The effect is shown in the photomicrographs of Fig. 2. Here the scratched surface of the original piece is shown. When a small amount of polishing action takes place, these scratches enlarge. If the polishing action is allowed to proceed too far, the grain structure is revealed and the surface is degraded. When the optimum time is employed, a good surface seems to emerge with some grain structure becoming evident.

A corresponding effect on the optical properties seems to be noted. The absorption coefficient of mechanically finished surfaces seems to be consistently higher than chemically polished surfaces. However, this is probably a function of the starting mechanical polish which could very well be improved. With chemical polishing, the lowest absorption coefficients occur when the optimum polishing time is employed.

1. J. W. Davisson, "Chemical Polishing High Energy Laser Windows," Semiannual Reports 1 and 2, ARPA Order 2031, Naval Research Laboratory, Washington, D.C., June and December (1972)

2. R. C. Pastor and M. Braunstein, "Halide Window Material Technology," Interim Report 3, AFWL-TR-72-38, Contract F29601-71-C-0101, Hughes Research Laboratories, Malibu, Calif. July 1972

3. W. H. Vaughan and J. W. Davisson, "Dislocation Motion Associated with Indentations," Acta. Met. <u>6</u>, 554 (1958)

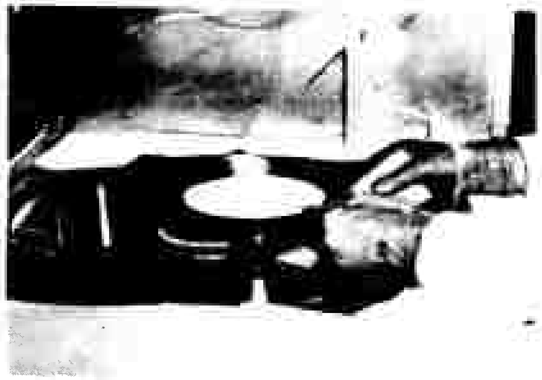

Fig. 1(a) Preparation of wheel. Excess water is removed with tissue.

Fig. 1(b) Lapping

Fig. 1(c) Lapping (intermediate wipe) .

Fig. 1(d) Chemical polishing. Sample is about to be immersed.

Fig. 1(e) Washing in jet of ethanol .

Fig. 1(f) Drying by blotting and gas jet.

Fig. 2(a) - Initial Mechanical polish of forging

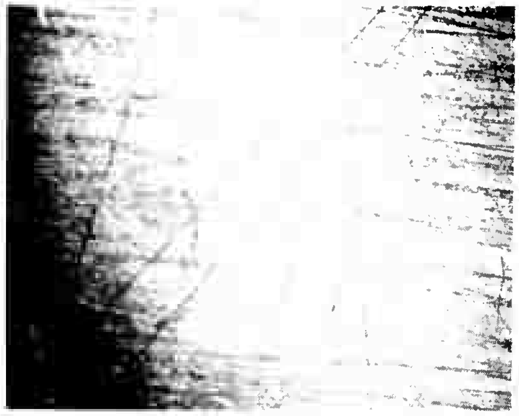

Fig. 2(b) - Insufficient chemical polish of forging (10 sec)

Fig. 2(c) - Optimum chemical polish of forging (25 sec)

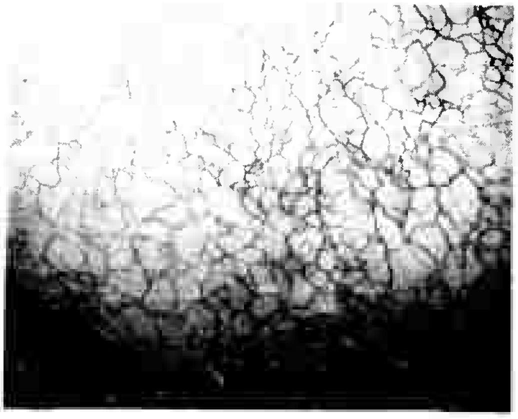

Fig. 2(d) - Excessive chemical polish of forging (40 sec)

3.0 MECHANICAL PROPERTIES

3.1. Yield Strength of Alkali Halides, P. F. Becher and R. W. Rice

The yield strengths of KCl have been increased by over an order of magnitude (to 5000 psi) by press forging to obtain fine grained polycrystalline KCl. However, advances beyond this to desired levels of 6000 to 8000 psi mean that additional strengthening methods are necessary. In order to more effectively select and apply such methods, alloying and irradiation experiments have been conducted and previous work reviewed. These are both evaluated in terms of lattice effects in single crystals (individual polycrystal grains) and grain boundary effects in polycrystals.

3.1.1. Results and Discussion

KCl Single Crystals

Alloying experiments included divalent Sr doping over levels which cover primarily solute Sr^{+2} (additions of 200 ppma) to precipitation (1000 ppma Sr^{+2} additions), as well as monovalent alloys (KCl-KBr). Irradiation with a Co^{60} γ source was at a dose rate of $3x10^4$ rotengens/min to levels of 10^6R and 10^8R without exposure to light until after testing to avoid bleaching effects.

As shown in Table I, both alloying and γ-irradiation substantially improve the yield strength of KCl. Chin et al (1) have found that annealing can result in a decrease in yield strength in Sr-doped KCl crystals and they note this occurred in the temperature region where Debes and Frohlich (2) observed precipitation. This suggests that the strength loss in both their annealed KCl and our 1000 ppma Sr^{+2} KCl is associated with either a decrease in dislocation interaction centers or over-ageing precipitate strains. In contrast to this, Chin et al (1) also report divalent solution hardening of halides with yield stresses following a half-power dependence on dopant levels up to 2230 ppma Sr^{+2} in rapidly cooled crystals. This points out the importance of crystal processing, such as faster cooling, which promotes retention of solutes in the lattice. However, rapid cooling may present problems of thermal shock or segregation in large KCl crystals.

Monovalent alloy results (Table I) are consistent with previous studies showing that substantial monovalent alloying is required to obtain significant strengthening. Stoloff et al (3) found that additions of 6.9 M/o KBr were required to obtain a yield strength of only 900 psi in KCl crystals. The present crystals with 50 M/o KBr addition exhibited fracture strengths greater than 4000 psi, while Arbel (4) has found strengths of 15,000 psi in KCl-50 m/o NaCl which was polycrystalline. No yielding was detected in his crystals, which apparently had some second phase precipitation as was true in our crystals.

Finally, γ-irradiation substantially raised the yield point of KCl (Table I). The dependence of yield strength on irradiation level is similar to that previously observed (5,6,7). As was reported by Sibley and Sonder (5), bleaching, which alters the irradiation damage, was found to lower the yield stress.

Alloying (1,3,8) and irradiation (5,6,7) hardening appear to result in substantial hardening of alkali halides by increasing the lattice resistance to dislocation motion or by limiting dislocation sources. In precipitation hardening, precipitate size and chemistry must be carefully controlled to avoid degrading optical as well as mechanical behavior. Hydroxyl contamination appears to foster precipitation in the KCl-Sr alloys (2) and these precipitates of K_2SrCl_4 or a similar compound are highly deliquescent and can increase absorption levels (9,10).

The single crystal results thus illustrate that the lattice resistance to dislocation motion is most effectively increased by divalent solution hardening. Irradiational hardening, although successful in substantially raising the yield stress, suffers from bleaching effects. On the other hand, monovalent alloys require large dopant additions to achieve comparable strengthening and can exhibit brittle fracture without any prior plastic deformation. Thus the following study of polycrystalline KCl has been concerned with divalent dopants.

Polycrystalline KCl

Our previous findings have demonstrated the strengthening effects obtained in press forged KCl (11), which have been confirmed by others (12,13,14). Subsequently, it was shown that press forged Sr-doped KCl offered an additional means of strengthening (11) over that achieved in pure polycrystalline KCl. These results are consistent with the Hall-Petch equation (i.e., $\sigma_y = \sigma_o + kd^{-1/2}$) in Fig. 1. Note that 1, the slope (or k term) is greater for the 1000 ppma Sr-doped KCl and 2, the identical results for the non-doped KCl with forgings of either commercial crystals or very pure crystals. The latter is very encouraging, as previously one had to be concerned with the strengthening effects induced by tramp impurities in the commercial crystals used.

The additional strengthening obtained with the Sr doping in the form of an increased grain size dependence of strength (i.e. increased k) has not been confirmed by other investigators (13,14). Thus, press forged KCl with 200 ppma Sr was tested and the results are shown in Fig. 1. The limited data for this material indicates additional strengthening but due only to an increase in the single crystal yield stress (i.e., σ_o) and not k (Table II). As discussed in the single crystal results, the decrease in yield stress with Sr^{+2} levels of 1000 ppm versus 200 ppma Sr crystals can be related to precipitates and associated strains. However, this same material in polycrystalline form exhibits a k value nearly 70% greater than the undoped KCl or KCl-200 ppma Sr^{+2}.

Although further study is required, it is felt that the increase in k for 1000 ppma Sr^{+2} KCl forgings may be due to chemical strengthening of the boundaries. This is based on the fact that any increase in k reflects an increase in the boundary resistance to dislocation motion, and chemistry can affect the boundary's effectiveness in blocking slip. This is shown, for example, by the value of k being dependent upon grain boundary segregation of a solute in iron (15). It has also been shown that k can be influenced by strain ageing, again suggesting that impurities can influence the boundary resistance (or k) (16). Leipold has shown that the amount of impurity segregation to grain boundaries in MgO is dependent on purity and cooling rate (17). Thus strengthening (i.e., increase in k) for 1000 ppma Sr forgings is felt to be a result of chemically altered grain boundaries. The absence of a change in k for 200 ppma Sr forging results suggests that such changes are concentration-dependent as would be expected.

3.1.2. Summary

Although there are several techniques for strengthening single crystals, one cannot expect this to extend directly to polycrystalline bodies. As shown in the last report (11), increasing the single crystal yield strength increases the Petch plot intercept, σ_o. However, the strengthening mechanism technique (irradiation, alloying, etc.) must increase or maintain the value of k as well as increase σ_o. Any change in k reflects a change in the resistance of the grain boundary to either glide or generation of dislocations. Changing k by alloying requires that grain boundaries be altered, either structurally (18, 19) or chemically.

The dependence of the yield stress in AgCl on grain size (i.e., on k) has been reported to be sensitive to test temperature and related slip mode changes (20). At temperatures high enough for sufficient cross slip and number of slip systems to operate so wavy slip occurs in AgCl, there is no detectable grain size dependence of the yield stress. However, at lower temperatures where slip is limited to planar glide of dislocations, yield strength has a substantial grain size dependence. This suggests that limiting cross slip and the number of slip systems and hence wavy slip by alloying can improve the boundary resistance.

Thus further work is necessary to fully resolve how both the dopant and its distribution affect the lattice or grain boundary resistance to slip to strengthen polycrystalline materials such as KCl. Efforts will continue in studying polycrystalline alloys to resolve these questions in order to gain insight into strengthening mechanisms and raise the yield stress of KCl to the 6000-8000 psi level.

1. G. Y. Chin, L. G. VanUitert, M. L. Green, G. J. Zydzik, and T. Y. Kometani, "Strengthening of Alkali Halides by Divalent Ion Additions," J. Am. Ceram. Soc., to be published.

2. M. Debes and F. Frohlich, "Aggregation and Precipitation Processes in Sr Doped KCl Crystals Studied by Conductivity and Density Measurements," Crystal Lattice Defects 2, 55-57 (1971).

3. N. S. Stoloff, D. K. Lezins and T. L. Johnston, "Effect of Temperature on the Deformation of KCl-KBr Alloys," J. Appl. Phys. 34, 3315-3322 (1963).

4. A. Arbel, "Deformation Properties of a Polycrystalline KCl-NaCl Alloy," J. Am. Ceram. Soc. 50, 114 (1967).

5. W. A. Sibley and E. Sonder, "Hardening of KCl by Electron and Gamma Irradiation," J. Appl. Phys. 34, 2366-2370 (1963).

6. K. Akimoto and W. A. Sibley, "Hardening of Potassium Chloride Single Crystals by Quenching and Irradiation," J. Appl. Phys. 34, 1767-1770 (1963).

7. J. S. Nadeau, "Hardening of Potassium Chloride by Color Centers," J. Appl. Phys. 34, 2248-2253 (1963).

8. R. J. Stokes and C. H. Li, "The Sodium Chloride-Silver Chloride Alloy System," Acta Metall. 10, 535-542 (1962).

9. P. H. Klein, Semi-Annual Report No. 1, ARPA Order No. 2031, U. S. Naval Research Laboratory, Dec. 1972.

10. P. H. Klein, Annual Report 1, ARPA Order No. 2031, U. S. Naval Research Laboratory, June 1973.

11. P. F. Becher and R. W. Rice, "Press Forging Studies" in Semi-Annual Report No. 1, ARPA Order No. 2031, U. S. Naval Research Laboratory, June 1972.

12. E. Bernal G., B. G. Koepke, R. J. Stokes and R. H. Anderson, "Preparation and Characterization of Polycrystalline Halides for Use on High Power Lasers," QTR No. 3, ARPA Order No. A02172, Honeywell Research Center (1973).

13. J. R. Fenter and W. B. Harrison, "Development and Characterization of Polycrystalline Alkali Halides for Use as Infrared Laser Windows," Am. Ceram. Soc. Bull. 52, 372 (1973).

14. B. W. Harrison, G. Hendrickson and J. Starling, "Halide Material Processing for High-Power, Infrared Laser Windows," Interim Report No. 2, Contract No. F-33615-72-C-2019, Honeywell Corporation (1973).

15. R. W. Armstrong, "The Influence of Polycrystal Grain Size on Mechanical Properties," p. 101-146 in Advances in Materials Research 4, H. Herman (editor), Interscience Pub., New York (1970).

16. D. V. Wilson and B. Russell, "Stress Induced Ordering and Strain-Ageing in Low Carbon Steels," Acta Metall. 7, 628-631 (1959).

17. M. H. Leipold, "Addenda to Impurity Distribution in MgO," J. Am. Ceram. Soc. 50, 628-629 (1967).

18. C. J. Ball, "The Texture and Mechanical Properties of Iron," J. Iron Steel Inst. 191, 232-236 (1959).

19. D. J. Abson and J. J. Jonas, "The Hall-Petch Relation and High Temperature Subgrains," Metal Sci. J. 4, 24-28 (1970).

20. R. D. Carnahan, T. L. Johnston, R. J. Stokes and C. H. Li, "Effect of Grain Size on the Deformation of Polycrystalline Silver Chloride at Various Temperatures," Trans. AIME 221, 45-49 (1961).

TABLE I

YIELD STRENGTH OF ALKALI HALIDE CRYSTALS

Crystal	Yield Stress*		Fracture Stress*	
	MN/m^2	(psi)	MN/m^2	(psi)
KCl	2.1-4.4	(300-625)	31.2	(4460)
KCl + 10^6R γ-irrad.	7.2	(1030)	9.6	(1390)
KCl + 10^8R γ-irrad.	12.1	(1730)	14.0	(2000)
KCl + 200 ppma $SrCl_2$	7.8	(1120)	15.4	(2200)
KCl + 1000 ppma $SrCl_2$	5.1	(730	16.1	(2300)
KCl - 50 m/o KBr	-	-	30.0	(4290)
KBr + <1 m/o KCl	4.1	(585)	15.4	(2210)

* Proportional limit for {100} tensile surface, <100> tensile axis, water polished bars tested in three point bending, tensile surface strain = $5 \times 10^{-6} s^{-1}$ in 50% R.H. at 22°C.

TABLE II

PETCH EQUATION PARAMETERS FOR POLYCRYSTALLINE KCl

$(\sigma_y = \sigma_o + kd^{-1/2})$

Crystal	σ_o		k	
	MN/m^2	(psi)	$MN/m^{3/2}$	$(psi\text{-}in^{1/2})$
KCl	3.5	(500)	5×10^{-2}	(44)
KCl - 200 ppma $SrCl_2$	7.8	(1120)	5×10^{-2}	(44)
KCl - 1000 ppma $SrCl_2$	5.1	(730)	8.3×10^{-2}	(73)

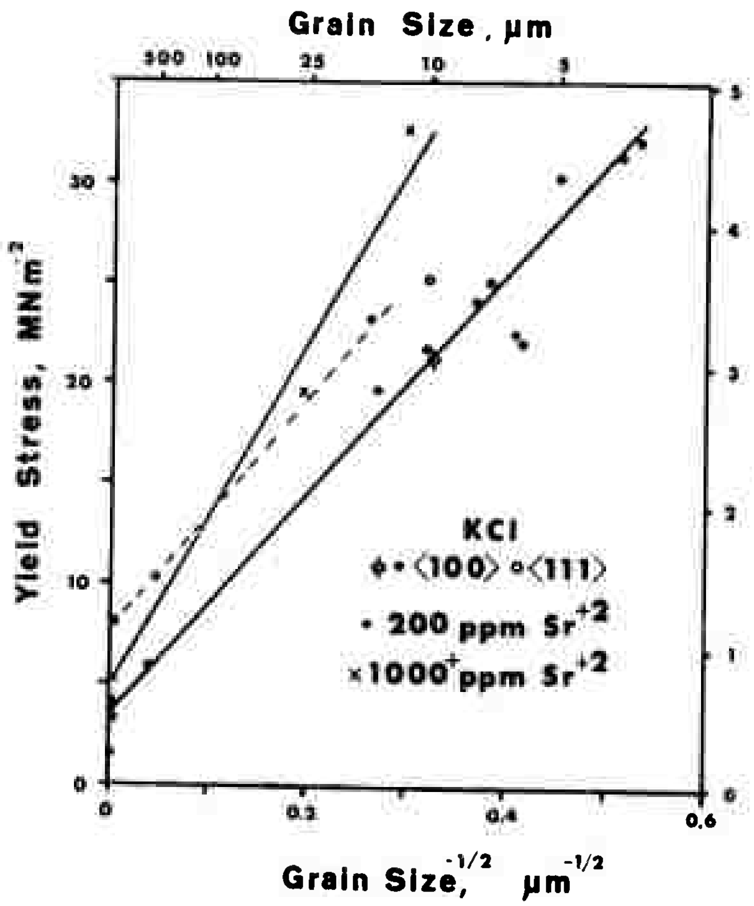

Fig. 1. Effect of grain size and alloying on the yield strength of polycrystalline KCl. (Note: Φ is a forging of crystal with low absorption.)

3.2. Fracture Energies, S. W. Freiman

Effort during this period was concentrated on determining the effects of gamma irradiation and Sr doping on the fracture toughness of both single crystal and press forged KCl.

3.2.1. Experimental Procedure

The gamma irradiation of pure KCl specimens (Harshaw) was carried out at 25°C in a Co-60 source at a dose rate of 3×10^4 R/min until dosages of 10^6 and 10^8R were achieved. Single crystals of KCl containing 150-200 ppma of Sr^{+2} were grown by the technique described in (1). Fracture energy specimens were cleaved from these crystals along {100} planes. The crack propagation direction was along <100> except for KCl-200 ppma Sr^{+2} crystals, where it lay just off the <100>. Specimens were prepared for testing by attaching aluminum loading arms to the tops of the specimens with epoxy (air-cured at 25°C for 3 to 4 hours). To prevent optical bleaching, irradiated specimens were prepared and tested in a darkened room using only a microscope light to illuminate the crack during testing. Those specimens having a dosage of 10^6R bleached in an hour or two in room light, but no detectable difference in coloring could be seen in those having a dose of 10^8R after two or three weeks.

The technique used to measure the fracture energies (γ) of these materials was essentially that described in the previous report (2). In the present case, however, loading was achieved by a dead weight rather than a closed loop system. Weights were gradually added to the system until visual observation of the crack indicated that propagation had taken place. In some cases, crack arrest did not occur; the crack propagated rapidly through the specimen when the critical load was applied. Since 20 grams were added at one time, the results are estimated to be accurate within ± 10%. The expression used to calculate γ is the same as before,

$$\gamma = \mathcal{G}/2 = \frac{M^2}{2EIt} \tag{1}$$

All tests were carried out in air at 25°C and approximately 40% relative humidity.

3.2.2. Results and Discussion

The results of the fracture energy measurements presented in Table 1 indicate that both irradiation and doping cause an increase in the fracture toughness of KCl single crystals. A value of γ for an undoped, unirradiated specimen (K18) is given for comparison. This value is slightly higher than that reported previously (2), probably because the smaller value of specimen half-width used here allowed more plastic deformation to take place in the specimen arms. The value of γ for the press forged, irradiated specimen (K11) is in the range of those measured for the unirradiated press forged KCl.

These results might be somewhat unexpected considering those obtained by Wiederhorn et al on NaCl (3). They showed no effect of irradiation up to 3.38×10^7R or doping with Ca^{+2} up to 700 ppm on the fracture energy of NaCl. One explanation for the apparent difference in behavior is that, in all cases but one, his measurements were made on very thin samples ($\approx$ 0.5 mm = 0.02 in) (4). For the unirradiated, undoped material, the yield stress is so low ($\approx$100 psi) (5), that since the plastic zone size is larger than the specimen thickness, the specimen is in a state of plane stress. As one irradiates or dopes the NaCl, its yield stress rises (5). At a dosage of 3×10^7R, the yield stress is approximately 500 psi so that the plastic zone size is 25 times smaller, leading to a stress state intermediate between plane strain and plane stress.

In metals, such a change in the stress state would be expected to give rise to a decrease in the measured fracture energy because of plastic zone-specimen size effects (6). In the case of most alkali halides, the room temperature plastic deformation involves fewer independent slip systems and thus not the same general ductility found in the cubic metals. Nevertheless, it is felt that the increase in measured fracture energy which would occur upon irradiation or doping of alkali halides was masked in Wiederhorn's thin samples by similar plastic zone effects. Support for this specimen size effect is given by the increase in fracture energy which Wiederhorn et al observed in one thicker specimen of NaCl upon irradiation (4), as well as by the large γ's which we measured in thin KCl specimens (2). The photograph of the KCl specimen in Fig. 1, which was taken under polarized light, shows the type of slip system acting at the crack tip. This system is the same as that shown by Wiederhorn (3) for NaCl in a state of plane strain.

Gross and Gutshall (7) also observed an increase in the fracture energy of NaCl with an increase in F-center concentrations, but they did not report specimen sizes. Bhattacharya and Zwicker (8), however, measured a decrease in the fracture energy of KCl with Co-60 irradiation at 300°K, and an increase in γ at 155°K. Their specimens were relatively thin, $\approx$0.04", but measured fracture energies were 115 ergs/cm^2 and less, much smaller than those determined in this study for the same size specimens.

No complete explanation for the differences in results of the various investigators can be given at present. It appears, however, that the way in which the crack front interacts with the slip planes in the crystals is paramount in determining fracture toughness. Normally, one would expect that a decrease in plastic deformation such as occurs upon irradiation or doping would lead to lower fracture energies, since less strain energy is used up in plastic flow. However, it appears that the limited slip systems in halides can result in focusing dislocations at the crack tip such that they aid crack growth (3,7) and reduce fracture energy. In this case, impeding the motion of these dislocations, e.g. by irradiation or doping, would increase the fracture energy.

The high fracture energy of forged KCl may be due primarily to its polycrystalline character which forces the crack to follow a more tortuous path. However, the higher fracture energy might also be due to the impeding of dislocation motion by the grain boundaries, consistent with the effects found in single crystals.

Theoretical estimates of the thermodynamic surface energy of the {100} face of KCl range from 56 to 318 ergs/cm^2 (9), and measurements of the thermodynamic surface energy generally fall in this range. Thus, the fracture energies reported for Sr-doped and irradiated KCl in Table 1 are substantially above thermodynamic surface energies. However, fracture energies of materials usually exceed thermodynamic surface energies. A common example is that of polycrystalline ceramics, of which press forged KCl is a typical example. Consideration of the roughness of a polycrystalline fracture surface fails to account for the total fracture energy. Even in such simple, homogeneous, brittle materials as glasses, fracture energies exceed thermodynamic surface energies by several-fold (10). Thus obtaining fracture energies for unalloyed and unirradiated crystals which are in the range of thermodynamic surface energies may simply be fortuitous.

If slip-assisted crack growth does take place in KCl, then one might expect to measure values of fracture energy which are lower than the surface energy. However, other factors such as environmental effects probably affect fracture energies, and hence make separation of variables more difficult.

In the future, the mechanisms which determine surface energy will be studied. Tests will be conducted at low temperatures and in inert atmosphere to determine the influence of environment on fracture toughness. Other work, such as photoelastic and etch pit studies, is needed to determine how the slip systems vary with irradiation and how these systems interact with the crack.

1. P. H. Klein, "Crystal Growth and Analysis" in Semiannual Report No. 1, ARPA Order 2031, U. S. Naval Research Laboratory (1972).
2. P. F. Becher and S. W. Freiman, "Strength and Fracture of Single and Polycrystalline KCl," ibid.
3. S. M. Wiederhorn, R. L. Moses, and B. L. Bean, "Plastic Deformation and the Fracture Surface Energy of Sodium Chloride," J. Am. Ceram. Soc. 53(1), 18 (1970).
4. S. M. Wiederhorn, private communication.
5. J. S. Nadeau, "Radiation Hardening in Alkali-Halide Crystals," J. Appl. Phys. 35(4), 1248 (1964).
6. A. S. Tetelman and A. J. McEvily, Jr., Fracture of Structural Materials, p. 132, John Wiley & Sons, New York (1967).
7. G. E. Gross and P. L. Gutshall, "Evidence of a Dislocation Feeding Mechanism for Crack Reinitiation in F-colored NaCl," Int. J. Fract. Mech. 1(2), 131 (1965).
8. T. K. Bhattacharya and E. F. Zwicker, "Ionizing Irradiation Effects on the Fracture Surface Energy of Potassium Chloride," J. Appl. Phys. 37(2), 771 (1966).
9. Jules J. Duga, "Surface Energies of Ceramic Materials," DCIC Report 69-2, June 1969.
10. S. M. Wiederhorn, "Fracture Surface Energy of Glass," J. Am. Ceram. Soc. 52(2), 99 (1969).

Table 1. FRACTURE ENERGIES OF IRRADIATED AND Sr^{+2} DOPED KCl

Specimen No.	Condition	Specimen Dimensions (in.)			γ ergs/cm^2	Observations
		w	t	h		
K13	Single Xl; radiation dosage = 10^6R	0.150	0.150	0.135	380	A little plastic deformation of arms.
K14	"	0.138	0.138	0.123	330	Same behavior as K13.
K15	Single Xl; radiation dosage = 10^8R	0.140	0.140	0.130	>1000	No bending of arms; fracture occurred $\perp$ to crack.
K16	"	0.170	0.170	0.133	>1000	Same behavior as K15.
K17	"	0.250	0.250	0.145	1050	No bending; crack propagated down specimen.
K18	Unirradiated KCl single Xl	0.20	0.20	0.125	300	Quite a lot of plastic deformation in arms.
K19	Press forged KCl; radiation dosage = 10^6R	0.085	0.042	0.250	>2600	Fracture occurred $\perp$ to crack.
K20	Single Xl KCl doped with ≈ 200 ppma Sr^{+2}	0.250	0.250	0.226	790	No bending of arms.
K21	"	0.243	0.243	0.133	>520	Fracture occurred $\perp$ to crack.

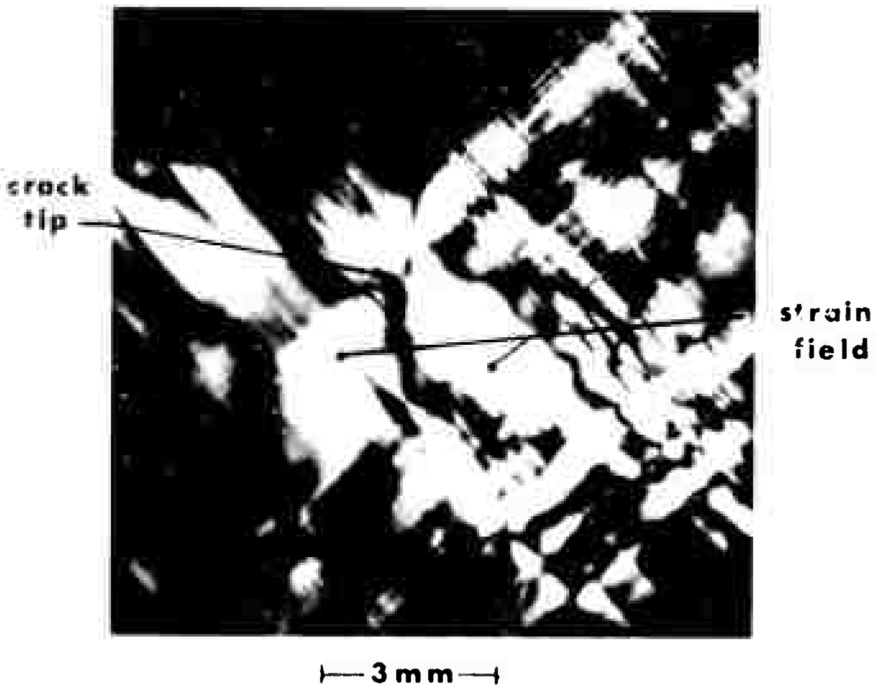

Fig. 1. Strain birefringence pattern associated with crack tip in KCl crystal fracture energy specimen. Crack motion on (100) was in [100] (from top towards bottom on vertical axis of figure).

3.3. Laser Test, P. F. Becher and R. W. Rice

Preliminary testing of KCl windows has been undertaken with a moderately high power CO_2 laser facility. Prior to testing, the commercial KCl crystal (4.7 cm x 4.7 cm) and forged KCl (4.2 cm diameter) samples were chemically polished in concentrated HCl, as described by Davisson (1). It was noted that due to surface "fogging," the polycrystalline sample was not as transparent as the single crystal. The absorption coefficient of the parent crystal used for the forging was lower than the KCl crystal irradiated ($\sim 5x10^{-4}cm^{-1}$, compared to $\sim 2x10^{-3}cm^{-1}$). However, as a result of the poorer surface finish of the forging, the total absorption is probably comparable in the single crystal and polycrystal windows, which were 4 cm and 2 cm thick, respectively. The post-irradiation absorption values are to be measured in subsequent examinations.

Both samples were irradiated with a 0.7 cm diameter, 4.7 KW beam at near normal incidence giving a power density of 12.7 KW/cm^2. These first tests only involved exposure of a window for ~5 s., which is the limit of the laser capability. Plane polarized transmitted light photography taken just off the normal axis of the window was used to examine the strain patterns developed during irradiation.

Although analysis of these tests is not complete, the initial results are presented. The KCl crystal survived the 11 KW/cm^2 irradiation with no visible crack formation or degradation of the sample, though the residual strain pattern developed during irradiation remained indicative of plastic deformation (Fig. 1a). In contrast, the strain pattern of the unirradiated crystal shows some limited and random strain birefirengence. On the other hand, the polycrystalline sample failed by formation of a cleavage-type crack along the approximate window diameter after 1 sec. of exposure, as shown in Fig. 1b. The crack is similar to a {100} cleavage crack in crystals being nearly planar and lies such that it parallels the {100} in the original crystal as a result of the preferred orientation in the forging.

As seen in Fig. 2, this sample was in a highly strained condition prior to testing, although it had been annealed (100°C, 1 h) after machining but prior to polishing. These residual strains and some surface and interior cracks detected prior to irradiation and the likely high surface absorption, are seen as important factors in the failure of this polycrystal window. High-speed motion pictures and crack branching indicate that failure originated from a crack at the window edge well out of the beam area. After the first crack appeared, the mounting adhesive on a portion of the window periphery decomposed, indicating considerable heating (200-300°C) and further cracks developed. The adhesive charring probably results from absorption of the irradiation reflected from the initial crack. However, the continued crack development is attributed to absorption in the window. Also the strain birefringence patterns within the window illustrated that {100} cleavage type crack propagation is preceded by a 45° strain pattern (see tip of vertical crack, just above center, Fig. 1b). These strain patterns are consistent with slip on {110} planes and are of the same type observed in our fracture energy test specimens. While a more strain- and crack-free forging was not available, these tests clearly show the need for high quality windows and the utility of actual laser testing for determining window failure modes.

Plexiglas burn patterns of the transmitted beam were made during the entire exposure of both windows. The fact that these burn patterns were the same as those with no sample suggests that the polycrystalline window did not cause substantial beam divergence or scattering in these tests. Analysis of the irradiation strain patterns, post-irradiation examination, and subsequent temperature mapping during testing should provide useful information on microstructure and mechanical stability of the window.

1. J. W. Davisson, "Chemical Polishing" in Semiannual Report No. 1, ARPA Order 2031, U. S. Naval Research Laboratory, Washington, D.C., December 1972.

Fig. 1. Strain patterns after 5 sec. exposure to 12.7 KW/cm^2 CO_2 laser beam (~0.7 cm diameter)

a. KCl single crystal

b. KCl press forging

<100> direction vertical both samples

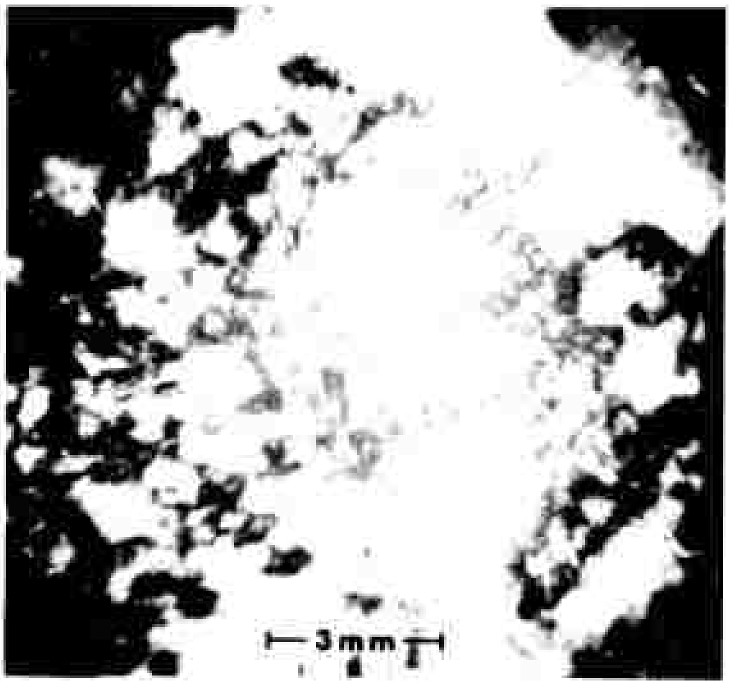

Fig. 2. Residual strain pattern in KCl forging prior to laser irradiation.

4.0 ABSORPTION MECHANISMS

The study of absorption mechanisms during this reporting period has centered on the temperature dependence of absorption. First, some comments are presented on the previously developed theory of the temperature dependence of absorption in light of experimental results. Second, the development and evaluation of a high temperature calorimetric technique is described. While this was developed for fundamental investigations, it became evident that this technique would also have important application in the study of effects of annealing on absorption. Finally, the results on the temperature dependence of the absorption are given in the form of a manuscript submitted for publication. It is noted that this work showed that existing theoretical treatments were not adequate and has stimulated the development of several approaches in an attempt to reconcile experiment and theory. Basically, it appears that the temperature dependence of the lattice vibration frequencies and possibly anharmonic line broadening were not adequately included in earlier treatments.

4.1. Theory, H. B. Rosenstock

During this period, the theory of the temperature dependence of the absorption, described in the previous semiannual report (1), was prepared for publication. This theory employs a Debye model for the crystal, which provides a simple way of incorporating lattice dynamics and is probably quite adequate for describing the gross features of the temperature dependence. In addition to providing a prediction of the temperature dependence, it also can be employed to indicate that the frequency dependence will be approximately exponential if the crystal potential is expanded in a power series with one adjustable parameter.

In terms of agreement with experiment, this theory, as well as others, can serve to indicate that the observed exponential frequency dependence of the absorption can be explained with very few adjustable parameters. However, the observed temperature dependence appears to be lower than that using theories of this type where the temperature enters only as a Bose-Einstein population factor. Several attempts to incorporate other factors in the theory have been carried out elsewhere which involve temperature dependent lattice frequencies or anharmonic damping. By a judicious choice of parameters, the experimental data can be explained in this way. The theory suggests that temperature dependence would be substantially different, depending on whether the incoming light is initially coupled to an intrinsic or an impurity oscillator. Thus, experiments with crystals containing known quantities of impurities should provide a tool for establishing the mechanisms of absorption.

4.2. Experimental Techniques, J. A. Harrington

The determination of the temperature dependence of the absorption is important because it provides a check on one of the basic assumptions of the theory. If simple Bose-Einstein population factors are employed to predict the temperature dependence of the absorption, then large effects can be expected in the high temperature region. However, the experimental determination of such absorption coefficients using laser calorimetry in the high temperature region has not been reported previously. At the time these experiments were attempted, it was not clear whether these measurements would be possible, as small temperature differences in the range of tenths of a degree are measured. However, it was found that laser calorimetric techniques can be modified for high temperatures in the following way.

The special high temperature calorimeter, constructed for measurements of β from room temperature to within 50°K of the sample's melting point, consisted of a horizontal core furnace with an API controller. In order to have the good thermal stability required for calorimetry, the sample was placed in a large thermal mass (a 2" O.D. x 1" I.D. x 4" stainless steel cylinder with four asbestos support screws to hold the sample), which was in turn placed inside a stainless steel box to minimize convection currents. This entire assembly was then loaded into the furnace. Using this arrangement, it was possible to achieve an ambient temperature stable to within half a degree at 1000°K or to within a few tenths of a degree at 500°K.

To measure the small change in temperature produced by either laser or resistor (see below) heating at elevated temperatures, it was necessary to modify our usual method of thermalcouple attachment. In this case, 5 mil chromel-alumel thermocouples were imbedded in a small hole (No. 70) drilled in the crystal. Sauereisen cement was used to maintain good thermal contact between the crystal and thermocouple at high temperatures. The reference junction was similarly attached to the thermal mass.

The entire experimental setup for high temperature calorimetry is shown schematically in Fig. 1. In addition to the calorimeter described above, the setup includes our standard signal detection equipment: a Keithley microvolt meter and HP strip chart recorder for monitoring the differential temperature changes and a CRL laser power meter. The absorption coefficient was evaluated from the heating and cooling curve using a "three-slope" method (1).

Measurements of β as a function of temperature in NaF were not made calorimetrically because of the high value (0.6 cm^{-1}) of β at 10.6 μm (300°K). Instead, β as a function of temperature was measured optically simply by measuring the incident and transmitted laser power with the power meter.

In KCl, NaCl, and NaF, care was taken to insure that surface degradation at elevated temperatures was minimized. Since all measurements were made in air, surface effects at the highest temperatures could be a problem. Initially, the crystals were chemically polished (2). In the process of data taking, the temperature would occasionally be recycled to a lower value and β remeasured to check for surface absorption. In many cases, the value of β obtained on recycling was less than the original value, but this can be explained in terms of an annealing out of absorbing imperfection centers (see following paper). In any case, surface degradation did not affect the results except when the temperature was very near the melting point and at that point, data taking was terminated.

As a means of checking on the reliability of our high temperature calorimetric results, we replaced laser heating with electrical heating in KCl and measured the specific heat, Cp, as a function of temperature (1). Such a measurement of Cp and comparison against accepted values would provide a check of our apparatus. A resistor, fabricated using a porcelain core and 3 mil chromel wire, was imbedded and cemented with Sauereisen into a KCl crystal. The results of Cp as a function of temperature are given in Table 1. It can be seen that,while the agreement is not as good as one would desire, the measured values are not so different from the accepted values so as to lead us to seriously doubt the validity of our high temperature calorimetric measurements.

Table 1

Specific Heat of KCl as a Function of Temperature

T (°K)	Cp Observed (J/gr · °K)	Cp Accepted (J/gr · °K)
298	0.583	0.6835
470	0.690	0.736
655	0.88	0.760

1. M. Hass and F. W. Patten, "Calorimetry" in Semiannual Report No. 1, ARPA Order No. 2031, U. S. Naval Research Laboratory, p. 49

2. J. W. Davisson, "Chemical Polishing" in Semiannual Report No. 1, ARPA Order No. 2031, U. S. Naval Research Laboratory, p. 23

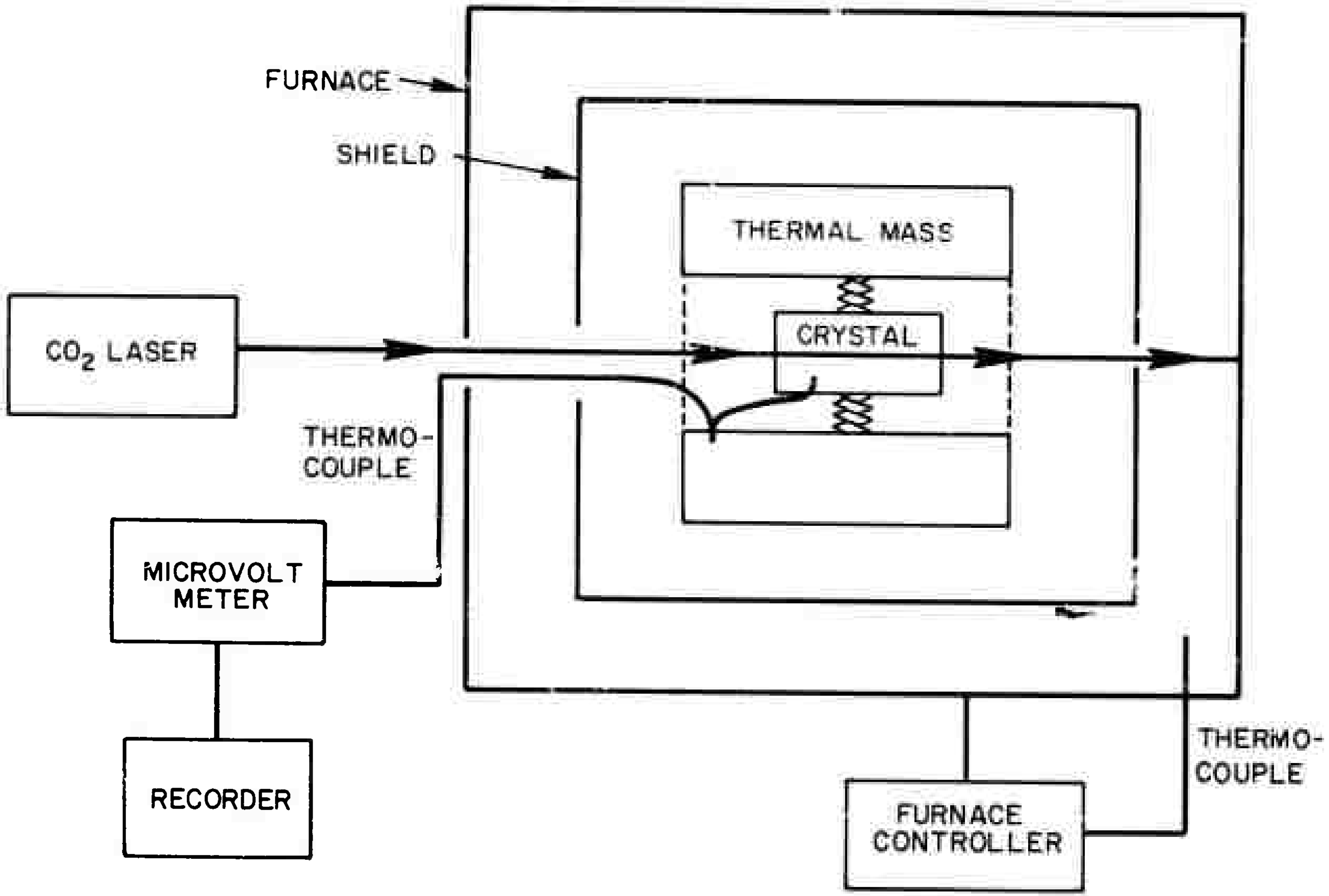

Fig. 1. High temperature calorimetry system.

4.3. Temperature Dependence of Multiphonon Absorption,

J. A. Harrington and M. Hass

The temperature dependence of multiphonon absorption in NaF, NaCl, and KCl was studied from room temperature to near the melting point at a wavelength of 10.6 μm. A large discrepancy between the experiment and that predicted using the usual expressions based upon temperature-dependent Bose-Einstein population factors and temperature-independent transition matrix elements was noted.

In this Letter, experimental measurements of the temperature dependence of the multiphonon lattice absorption in NaF, NaCl, and KCl are presented which differ markedly from that expected by application of the usual simple expressions based upon consideration of phonons as bosons. This suggests that there are some inadequacies in the approach which have not been evident in previous measurements. In earlier work (1,2), the simple expressions based upon Bose-Einstein population factors have appeared to be satisfactory to explain the temperature dependence of multiphonon absorption. However, practically all of the previous investigations in this area have involved lower order processes at lower temperatures. The present work is primarily concerned with higher order processes at higher temperatures in which the temperature dependence is expected to be much greater.

The usual expressions for the temperature dependence of multiphonon processes can be written in terms of the energies of the various phonons participating in the process. For higher order processes this can be quite complicated, but Sparks and Sham (3) pointed out that a T^{n-1} law would be expected to hold (if some average phonon frequency is assumed) in the high temperature limit where n is the number of phonons participating in the process. Similar results were obtained by Rosenstock (4) who employed a Debye spectrum for the crystal, and by Hardy and Agrawal (5) using an Einstein oscillator type model. Using this latter approach (5), the contribution to the multiphonon absorption coefficient, β, at high temperatures will be dominated by the contribution

$$(\bar{n} + 1)^n - (\bar{n})^n \qquad (1)$$

where $\bar{n}$ is the usual Bose-Einstein population factor

$$\bar{n} = [\exp(\hbar\bar{\omega}/kT) - 1]^{-1} \qquad (2)$$

and the transition matrix elements are assumed to be essentially temperature independent. After rearrangement, the coefficient β can be expressed as a function of temperature giving

$$\beta \propto \frac{1 - \exp(-n\hbar\bar{\omega}/kT)}{[1-\exp(-\hbar\bar{\omega}/kT)]^n} \qquad (3)$$

In the limit where $kT >> \hbar\bar{\omega}$, it can be seen that the temperature dependence of β will be given by

$$\beta \propto n(kT/\hbar\bar{\omega})^{n-1} \qquad (4)$$

so that β is proportional to T^{n-1}. Consequently, if measurements are carried out at a frequency high compared to a single phonon frequency, then the resulting multiphonon absorption would be expected to exhibit a very large temperature dependence at high temperatures. Any failure to exhibit a temperature dependence predicted by Eq. 4 could most likely be attributed to the failure of the assumption that the transition matrix element is temperature independent.

In order to test the applicability of Eq. 4, careful measurements of the absorption coefficient at 10.6 μm from 300°K to within 50°K of the melting point were obtained in single crystal NaF, NaCl, and KCl. In the case of NaCl and KCl, the absorption coefficients were small and were measured by calorimetric methods using a CO_2 laser source (6). In the case of NaF, simple transmission measurements with a laser and power meter were adequate. All measurements were carried out inside of a stabilized oven on samples whose surfaces were first mechanically, then chemically polished.

The experimental results for these compounds are shown in Figs. 1, 2, and 3, along with the temperature dependence predicted by Eq. 3 in which the parameters were selected in a way which will be discussed shortly. It can be seen that in the case of NaF and NaCl, the experimentally determined temperature dependence differs markedly from that given by Eq. 3. In the case of KCl, the absorption coefficient and its temperature dependence have been observed to vary markedly from sample to sample. In most cases, the temperature dependence below 600°K is essentially independent of temperature or even decreases with temperature. In the high temperature limit for one of our purer samples (obtained from Hughes Research Laboratory), the temperature dependence does increase more sharply at high temperatures as would be expected for intrinsic behavior.

These results might be interpreted in the following way. In the case of NaF and NaCl, the absorption is expected to be largely intrinsic based upon a semi-empirical extrapolation of the frequency dependence of the absorption (7). In the case of KCl, the observed absorption coefficient in all known samples is well above the extrapolated absorption coefficient (7) of about $8x10^{-5}cm^{-1}$ at 10.6 μm and thus is probably largely extrinsic in origin at room temperature. These extrinsic contributions could arise from impurities, surfaces, or some other imperfections. It has been predicted that the temperature dependence of the absorption associated with impurities will be less than that for the intrinsic case (4,5). This appears to be the case for KCl although there are some quantitative discrepancies. In the case of the Hughes KCl crystal where the absorption decreases with temperature in the low temperature region, it is believed that this is associated with some absorbing imperfection centers which are being annealed out. In the high temperature region above 500°K where the absorption increased markedly with temperature, it is not clear if this can be attributed to extrinsic or intrinsic processes.

It can be seen from Figs. 1, 2 and 3 that a plot of the log of the absorption coefficient as a function of the log of the temperature yields nearly a straight line, implying a power law dependence of the form given by Eq. 4. The experimentally determined exponential factors are listed in Table I along with the values expected using a mean single phonon frequency, $\bar{\omega}$. For simplicity, $\bar{\omega}$ was selected as the frequency closest to the transverse optic mode so that $n\bar{\omega} = 943\ cm^{-1}$ (10.6 μm) with n integral. The values are shown in Table I. Even though the way in which $\bar{\omega}$ and n have been chosen here is slightly different from that used by others (3,4,5), this different will not lead to any significant changes. In the case of NaF, the theoretical curves were adjusted in scale to fit the experimental results at room temperature. For KCl and NaCl, the theoretical curves were normalized to the extrapolated intrinsic room temperature values of $8x10^{-5}cm^{-1}$ and $1x10^{-3}cm^{-1}$, respectively, as given by Deutsch (7).

Table I

Comparison of Theoretical and Experimental Exponential Temperature Factors for Multiphonon Absorption at 10.6 μm

Crystal	$\bar{\omega}$ (cm^{-1})	n Theoretical	n Experimental
KCl	134.7	7	2.8[a]
NaCl	157.2	6	3.3
NaF	235.7	4	2.6

[a] Possibly limited by extrinsic processes

The large discrepancy between the experiment and that expected from the Bose-Einstein population factors seems quite remarkable. We are not aware of such discrepancies being reported elsewhere, although a similar analysis to that presented here has not been given. Some studies of the multiphonon absorption of alkali halides in the high temperature region have been reported by Barker (8). While a comparison of the type given here was not made, inspection of his curves suggests that the temperature dependence could not be satisfied using a simple expression of the form in Eq. 3.

While the agreement between the experiment and theory reported here might be improved somewhat by consideration of lower order processes involving only high energy phonons, good agreement would still not be obtained. This suggests that some other explanation be sought. The theory of higher order multiphonon absorption has been addressed by a number of investigators (3,4,5,9). These treatments have not yet been carried sufficiently far to yield temperature dependent predictions adequate to explain the present experimental results. However, very recent theoretical treatments by Sparks and Sham (10), Maradudin and Mills (11), and McGill (12) can provide good agreement with experiment even though each of these approaches is based upon very different starting physical assumptions.

In conclusion, it is believed that these studies of the multiphonon absorption have revealed a serious shortcoming in the usual approach employed to calculate the temperature dependence of multiphonon absorption. In addition, they provide a way of distinguishing intrinsic and extrinsic absorption in highly transparent materials as well as providing a tool for studying imperfection-induced absorption.

The authors are grateful to J. R. Hardy, T. C. McGill, D. L. Mills, H. B. Rosenstock and M. Sparks for stimulating discussions of the theory. They also thank J. W. Davisson for development of chemical polishing methods.

1. S. J. Fray, F. A. Johnson and R. Jones, Proc. Phys. Soc. (London) 76, 939 (1960).

2. W. G. Spitzer in Semiconductors and Semimetals, Vol. 3, edited by R. K. Willardson and A. C. Beer, (Academic Press, New York, 1967), p. 21.

3. M. Sparks and L. J. Sham, Solid State Commun. 11, 1451 (1972).

4. H. B. Rosenstock, Bull. Am. Phys. Soc. 18, 674 (1973).

5. J. R. Hardy and B. S. Agrawal, Appl. Phys. Letters 22, 236 (1973).

6. C. A. Klein and R. I. Rudko, Appl. Phys. Letters 13, 129 (1968).

7. F. A. Horrigan and T. F. Deutsch, Research in Optical Materials and Structures of High-Power Lasers, Raytheon Research Division, Quarterly Technical Reports Nos. 1 and 2, Contract DA-AH-01-72-C-0194, January and April (1972).

8. A. J. Barker, J. Phys. C. (London), 5, 2276 (1972).

9. T. C. McGill, R. W. Hellwarth, M. Mangir, and H. V. Winston, J. Phys. Chem. Soc., to be published; B. Bendow and S. C. Ying, Phys. Letters 42A, 359 (1973); B. Bendow, S. C. Ying and S. Yukon, Bull. Am. Phys. Soc. 18, 396 (1973); and D. L. Mills and A. A. Maradudin, Bull. Am. Phys. Soc. 18, 395 (1973).

10. M. Sparks and L. J. Sham, Phys. Rev. Lett., to be published.
11. A. A. Maradudin and D. L. Mills, Phys. Rev. Lett., to be published.
12. T. C. McGill, to be published.

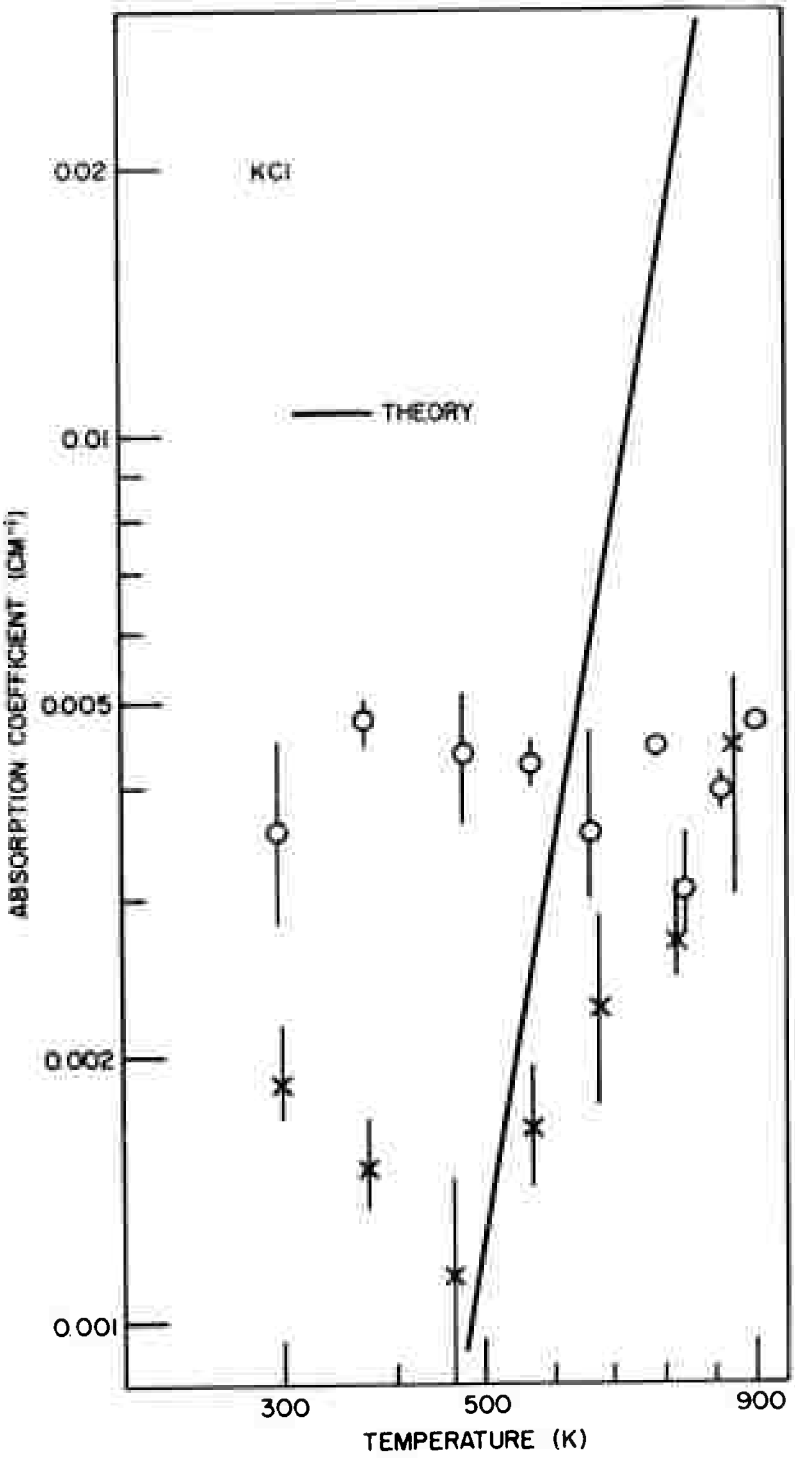

Fig. 1. Temperature dependence of absorption coefficient for KCl. The open circles are data from Harshaw KCl, the crosses data from a KCl sample obtained from Hughes Research Labs., Malibu. The temperature dependence calculated from Eq. 3 is shown as a solid line.

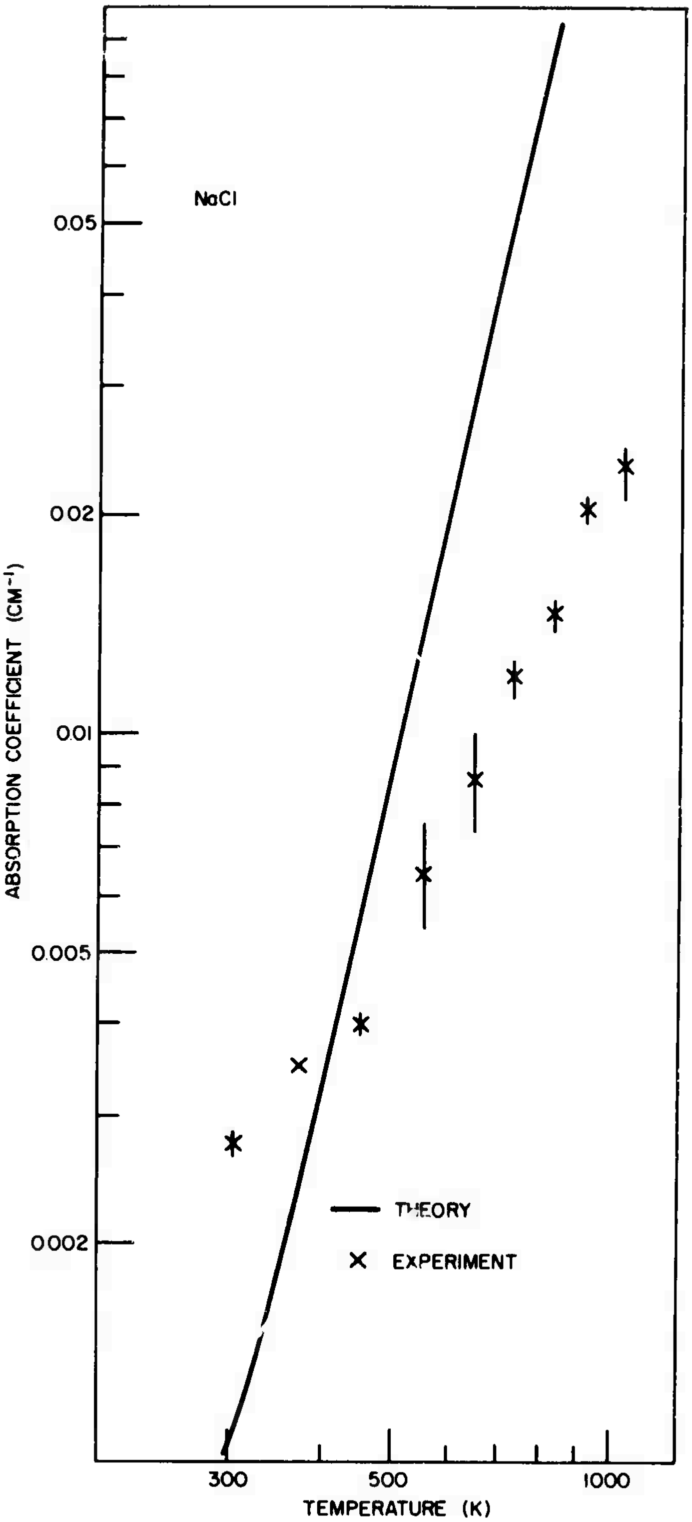

Fig. 2. Temperature dependence of absorption coefficient for NaCl. The solid line is the temperature dependence calculated from Eq. 3.

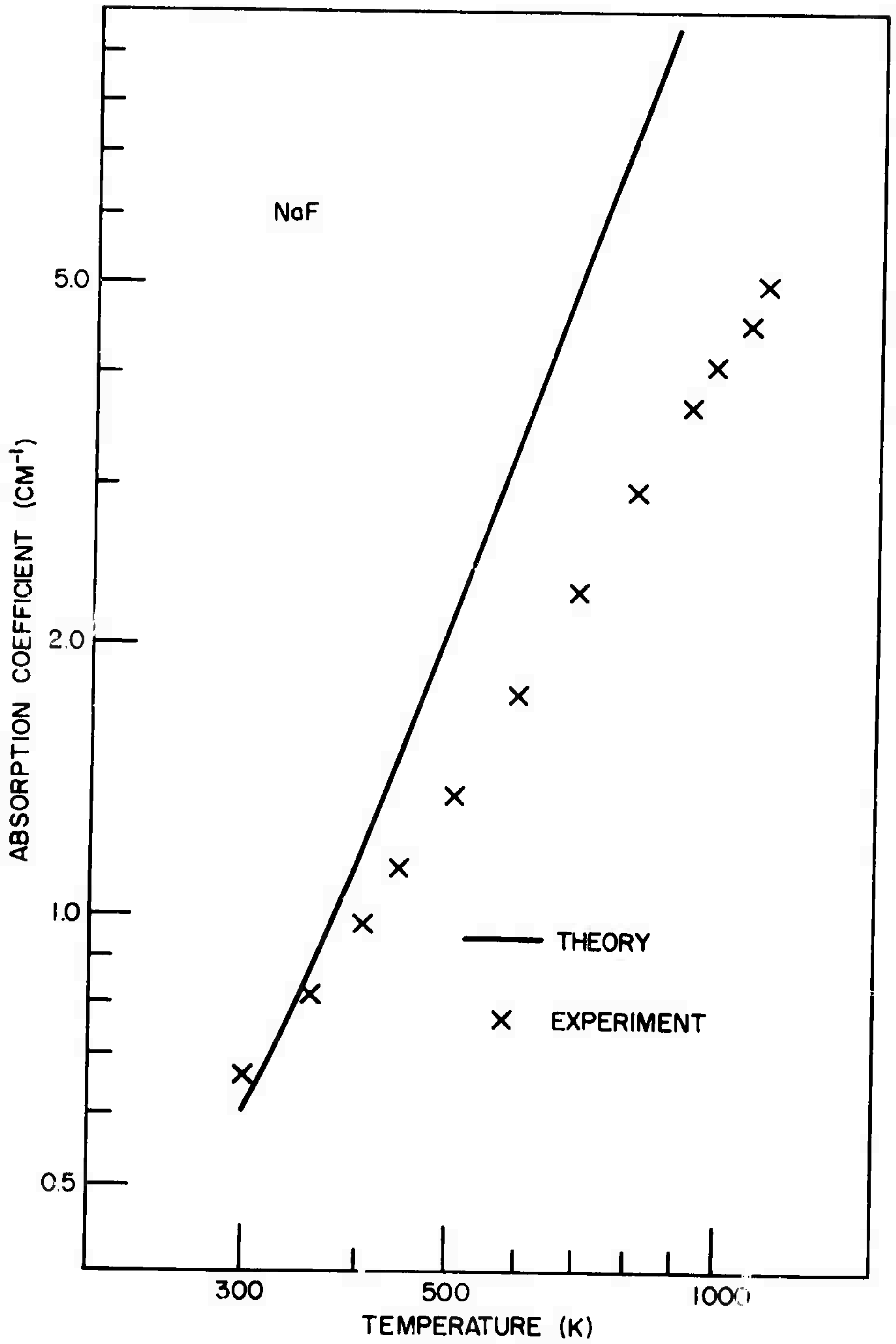

Fig. 3. Temperature dependence of absorption coefficient for NaF. The solid line is the temperature dependence calculated from Eq. 3.