

EFFECTS OF Eu^{++} ON THE MECHANICAL
PROPERTIES OF KCl

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PREFACE

This study is concerned with the effect of divalent impurities on the mechanical properties alkali halides. The primary objective is to determine the strengthening of KCl single crystals as a function of the concentration of divalent impurity-vacancy pairs. The divalent impurity used is Eu^{++} and the concentration analysis of this ion in the crystal constituted a major problem in this study.

The author wishes to express his appreciation to his major adviser, Dr. J. J. Martin, for his guidance and assistance throughout this study. Appreciation is also extended to Dr. Zuhair Al-Shaieb for his assistance with the atomic absorption analysis.

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CHAPTER I

INTRODUCTION

Alkali halides are of interest as possible window materials for high power CO₂ lasers. KCl is of particular interest since it has a low optical absorption at 10.6 microns, the wavelength at which the CO₂ laser operates. KCl is also inexpensive and readily available. One of the disadvantages of pure KCl is its low mechanical strength.

This problem of low mechanical strength may have a possible solution in that significant hardening is observed when tetragonal lattice distortions are created in the crystal. One method of creating tetragonal lattice distortions is by irradiation with high energy electrons. Irradiation causes this type of defect by converting a negative ion into a neutral atom, moving the atom to an interstitial position, and leaving an electron in the vacancy that now exists in the original position. This forms a Farbzentren or F center. It has been shown by Sibley and Sonder (1) and Nadeau (2,3) that F center creation produces significant hardening of alkali halides. In 1932 Edner (4), Metag (5), and Schönfeld (6) showed that when small concentrations of divalent cations were grown into the crystal lattice of NaCl there was an increase in the flow stress. The divalent ions create tetragonal distortions, because for the sample to remain electrically neutral a positive ion vacancy is created nearby. The divalent ion pairs with the vacancy creating a tetragonal defect.

Divalent Eu has been shown to enter the KCl lattice substitutionally for a K^+ ion. In order to maintain charge neutrality a nearest neighbor K^+ vacancy is formed (7). This $Eu^{++} - K^+$ vacancy forms a tetragonal defect similar to the defect produced by divalent alkaline earth ions in alkali halides and, therefore, would be expected to significantly strengthen KCl. Since Eu^{++} can be detected optically, the KCl:Eu⁺⁺ crystal forms a particularly convenient system for mechanical property versus dopant concentration studies. The purpose of this work is to compare the increase in mechanical strength of Eu doped KCl with the increase in strength observed in earlier work done on alkaline earth doped alkali halides.

The degree of hardening obtained by the doping of KCl with Eu^{++} as compared to pure KCl was measured by uniaxial compression. There has been considerable work done with various alkali halides and many divalent ions. The increase in hardness observed in KCl when doped with Eu^{++} will be compared to theory, to work done on NaCl, NaBr, and KBr containing divalent additions of Ca^{++} , Sr^{++} and Ba^{++} . This work was done by Chin, et al. (8) and by Pratt et al. (9). The results will also be compared to results obtained by Sibley et al. (10) on KCl doped with Sr^{++} .

CHAPTER II

THEORY

Fleischer (11) has shown theoretically that the increased flow stress due to a tetragonal defect is proportional to the square root of the defect concentration. The crystal yields under stress by dislocations moving along slip planes. When impurity-vacancy pairs are present one must consider the dislocation-defect interaction. Fleischer assumes the interaction to be of a short range nature, and the defect concentration to be small. Only those defects which lie along the slip plane were considered. If each defect exerts a force F_{\max} on the dislocation, then the maximum force per unit length of dislocation is F_{\max}/ℓ , where ℓ is the average distance between defects. The stress necessary to move the dislocation must be increased by an amount

$$\Delta\tau = F_{\max}/b\ell ,$$

where b is the magnitude of the Burger's vector. The atomic defect concentration C on the slip plane is A/ℓ^2 where A is the area the defect occupies. Thus

$$\Delta\tau = F_{\max} C^{1/2}/bA^{1/2}$$

giving a $C^{1/2}$ relationship. Fleischer relates the force F_{\max} to the shear modulus G and geometrical factors. As a simplification the increase in the flow stress predicted by this theory can be written as

$$\Delta\tau = (G/n) C^{\frac{1}{2}} .$$

Fleischer has calculated n to be 10 for an interstitial defect and to be 100 for a divacancy defect. This theory is in good agreement with the results obtained by Chin, et al. (8) and by Sibley, et al. (10).

Pratt, et al. (9) have proposed a treatment of the Snoek effect that considers the dislocation-defect interaction to be long ranged in nature. They suggest a long range ordering of the impurity-vacancy dipoles in the stress field of a moving dislocation. In an unstrained alkali halide lattice all of the twelve impurity-vacancy pair orientations are equivalent in energy, whereas in the stress field of a dislocation this is no longer true. The dipoles or impurity-vacancy pairs will assume the orientations of lowest energy provided they are free to reorient. Along a stationary dislocation the dipoles will be distributed in the stress field among the twelve possible orientations according to a Boltzmann distribution, lowering the energy of the dislocation. If it were now possible to freeze in this distribution and move the dislocation out of this ordered atmosphere into one of random distribution the difference in energy of the two states must be supplied by the applied stress. The depth of the energy well produced is proportional to the atomic concentration of dipoles. If the dislocation is moving, and the dipoles have enough time to reorient while it is passing them, the dislocation will appear to drag an ordered atmosphere along with it. In a steady state the dislocation will be part way up on the side of the potential valley, experiencing a continuous retarding force. Thus the flow stress would be predicted to be proportional to the concentration of dipoles. The work done by Pratt, et al. (9) on NaCl with Ca^{++} as the

divalent impurity is in good agreement with this theory. In summary, the two theories are, one that the interaction between the dislocation and impurity-vacancy pair is short ranged giving a $C^{1/2}$ dependency, and one suggesting a long ranged interaction giving a linear in C dependency.

CHAPTER III

EXPERIMENTAL PROCEDURE

Crystal Growth

The crystal growth phase of this project was to provide single crystals for mechanical measurements on pure KCl and KCl doped with varying concentrations of EuCl_3 . The crystals were pulled by the Kyropoulous-Czochralski method from starting material that was first treated by "Reactive Atmosphere Processing". To eliminate oxygen compounds in the starting material boules were grown in a Bridgman crystal growth system using a technique developed by Pastor and Pastor (12), in which CCl_4 vapor in an inert gas atmosphere is passed over the melt. At high temperatures the CCl_4 breaks down and Cl is released which displaces the oxygen compounds in the melt. The procedure is as follows. A vitreous carbon crucible is filled with Baker Analyzed KCl powder along with the appropriate amount of EuCl_3 for the desired dopant concentration. The crucible is placed in a mullite growth chamber, and the chamber purged of air with gettered Argon for a period of two to three hours. CCl_4 is then started bubbling into the chamber at a rate of 10 to 16 bubbles per minute. The gas and starting material are mixed by raising the temperature to 300°C and cycling the furnace at a rate of 15 mm/hr. This step is repeated at 600°C . After the 600°C cycle the furnace is raised to 900°C to melt the KCl, and a growth run is started at a furnace lift rate of 0.75 mm/hr. At the end of the growth run the furnace is pro-

grammed down to room temperature and the boule removed. Prior to being placed in the Kyropoulous furnace the top of the boule is removed so that any impurities which may have been picked up by the zone refining action of the Bridgman furnace are removed. The boule is then polished with HCl and rinsed in acetone. A number of crystals were grown with Eu concentrations from 0 to 500 atomic ppm.

Dopant Concentration Analysis

In order to determine flow stress as a function of concentration it was necessary to find a method whereby each sample could be non-destructively measured for dopant concentration.

Eu^{++} has two strong absorption bands between 200 and 400 nm (13) as shown in Figure 1. The absorption band peak at 243 nm can be used routinely to determine the Eu concentration in the mechanical samples if the peak has been calibrated against the Eu concentration as found by chemical means. This peak was selected because it shows less structure than the 330 nm peak. By performing this calibration it was found that the concentration could be found by the equation

$$C_{\text{Eu}} = 17.2 \alpha$$

where C_{Eu} is the Eu concentration in atomic parts per million and α is the 243 nm band peak absorption coefficient as measured with a Cary 14 spectrophotometer. This calibration equation was obtained in the following manner. The value α was measured on several samples of various concentrations, and then the actual concentration of Eu was measured by absorption spectroscopy.

In order to calibrate the Perkin Elmer model 403 atomic absorption

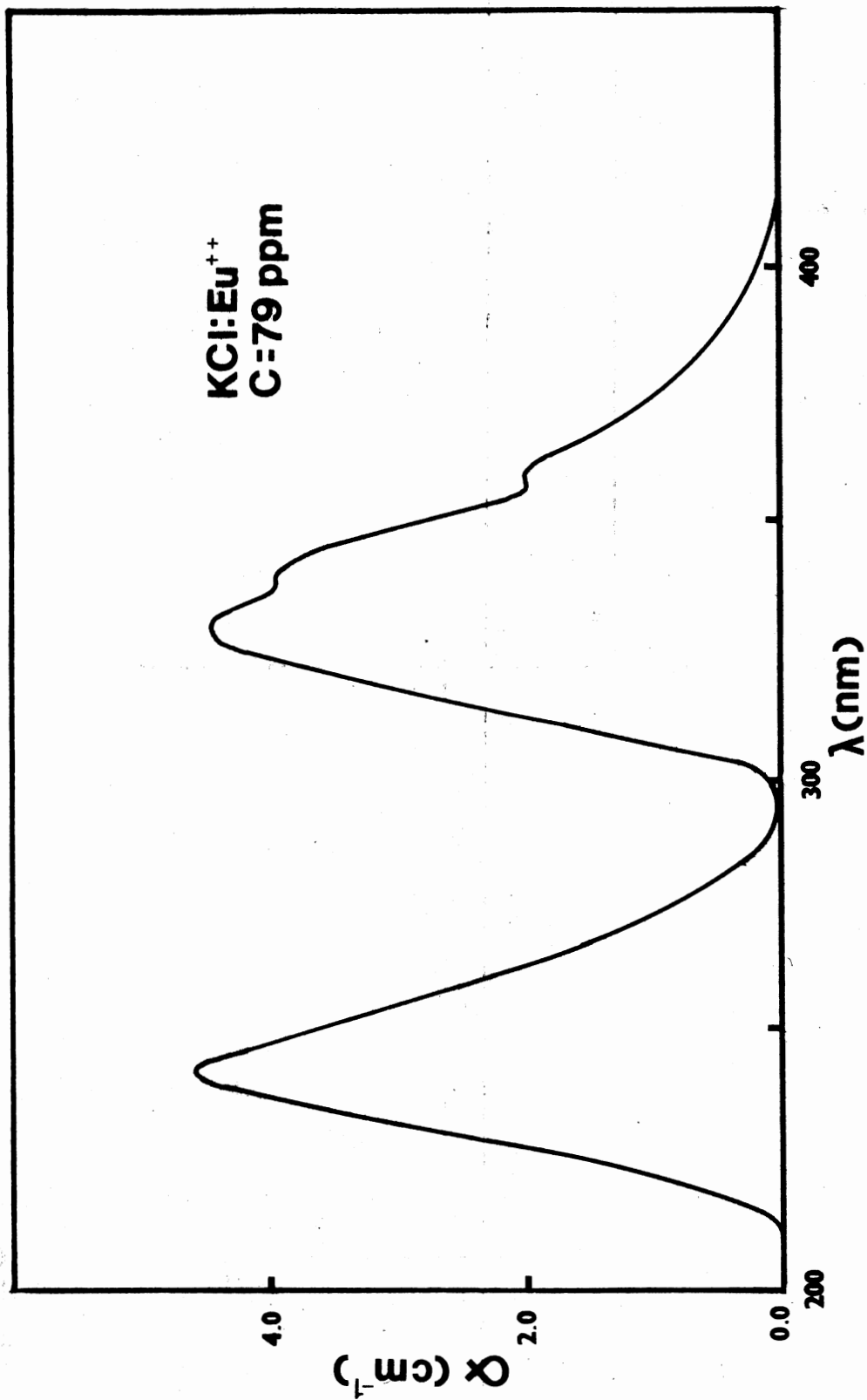


Figure 1. Optical Absorption Curve for Eu⁺⁺

spectrometer standard samples were prepared by dissolving known quantities of EuCl_3 in distilled water. The atomic absorption spectrometer was calibrated to read in parts per million per milliliter by ionizing the standards in a nitrous oxide and acetylene flame and measuring the absorption of the $\text{Eu } 4594\overset{\circ}{\text{A}}$ line. The calibration measurements were in agreement to within 1.5% both before and after the test run.

Optical test samples were prepared in the following way. Thin samples were cleaved from several doped crystals of different concentrations. The samples were cleaved perpendicular to the growth axis in order to have samples of uniform dopant concentration. These samples were measured on a Cary 14 spectrophotometer to obtain their optical absorption in order that the value for α could be determined for the 243 nm band.

These optical samples were subsequently run on the atomic absorption spectrometer to evaluate the Eu concentration. The masses of the samples were determined by measuring on an analytical beam balance. The samples were dissolved in known quantities of distilled water, and the atomic absorption measured. Each sample was measured several times, and all values were within 1.4% of each other. All atomic absorption samples had Eu concentrations between 0.0 and 19.0 ppm per milliliter of H_2O . This result gave the optical samples concentrations ranging from 0 to approximately 430 ppm atomic with corresponding α values between 0 and 25 cm^{-1} . Figure 2 shows that Eu concentration varies linearly as a function of the 243 nm band peak absorption coefficient and that the C_{Eu} versus α line has a slope of 17.2. From this the equation

$$C_{\text{Eu}} = 17.2 \alpha$$

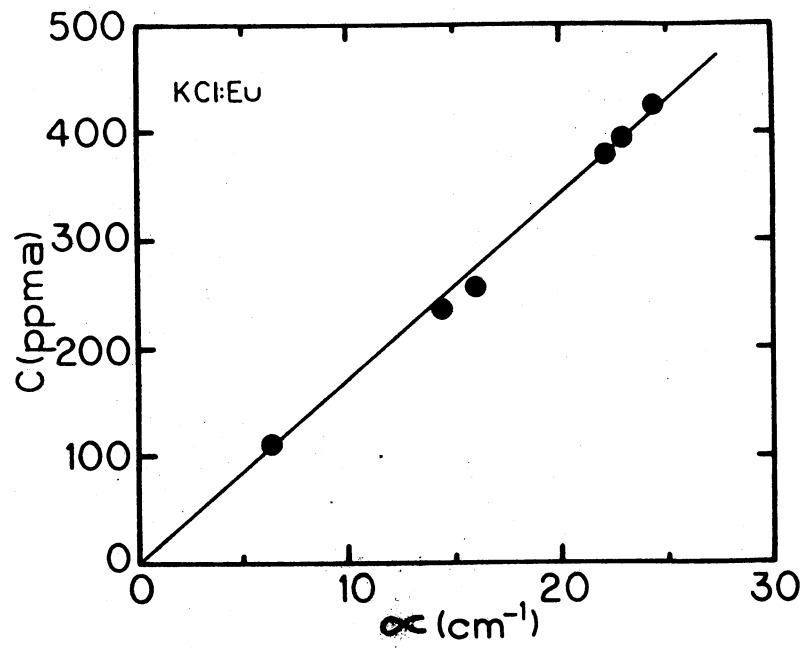


Figure 2. A Plot of Eu Concentration Versus the 243 nm Band Peak Absorption Coefficient

is obtained.

Flow Stress Measurements

The mechanical strength of KCl:Eu as a function of Eu concentration was measured under uniaxial compression for a series of samples from different crystal boules. From this the flow stress or yield point was compared to the dopant concentration. In order to insure homogeneity thin slabs were cleaved from single crystal ingots perpendicular to the growth axis. Each slab measured approximately 1.5 mm in thickness. The u.v. optical absorption of each slab was then measured on a Cary 14 spectrophotometer. The absorption coefficient α was calculated and used to determine the Eu concentration.

In order to insure uniformity in thermal strain and aggregation of the Eu^{++} and associated K^+ vacancy in the different slabs, the slabs were held at 675°C and quenched on a metal block. No observable strain was detected under crossed polarizers.

The flow stress was measured under uniaxial compression along the $\langle 100 \rangle$ on an Instron testing machine which records the applied force on a sample as it is being compressed at a constant strain rate. From the previously prepared KCl:Eu slabs flow stress samples were cleaved. A typical sample would measure 1.5 x 2.5 x 6 mm. Since the sample length was over three times the width, end effects were small and could be neglected. Samples were compressed with a crosshead speed of 0.05 cm/min. This corresponds to a strain rate of 10^{-3} sec^{-1} . Some typical stress-strain curves for KCl:Eu are given in Figure 3. The engineering flow stress τ_e , is taken to be the value at the intersection of the tangents to the elastic and the first plastic portions of the curve as

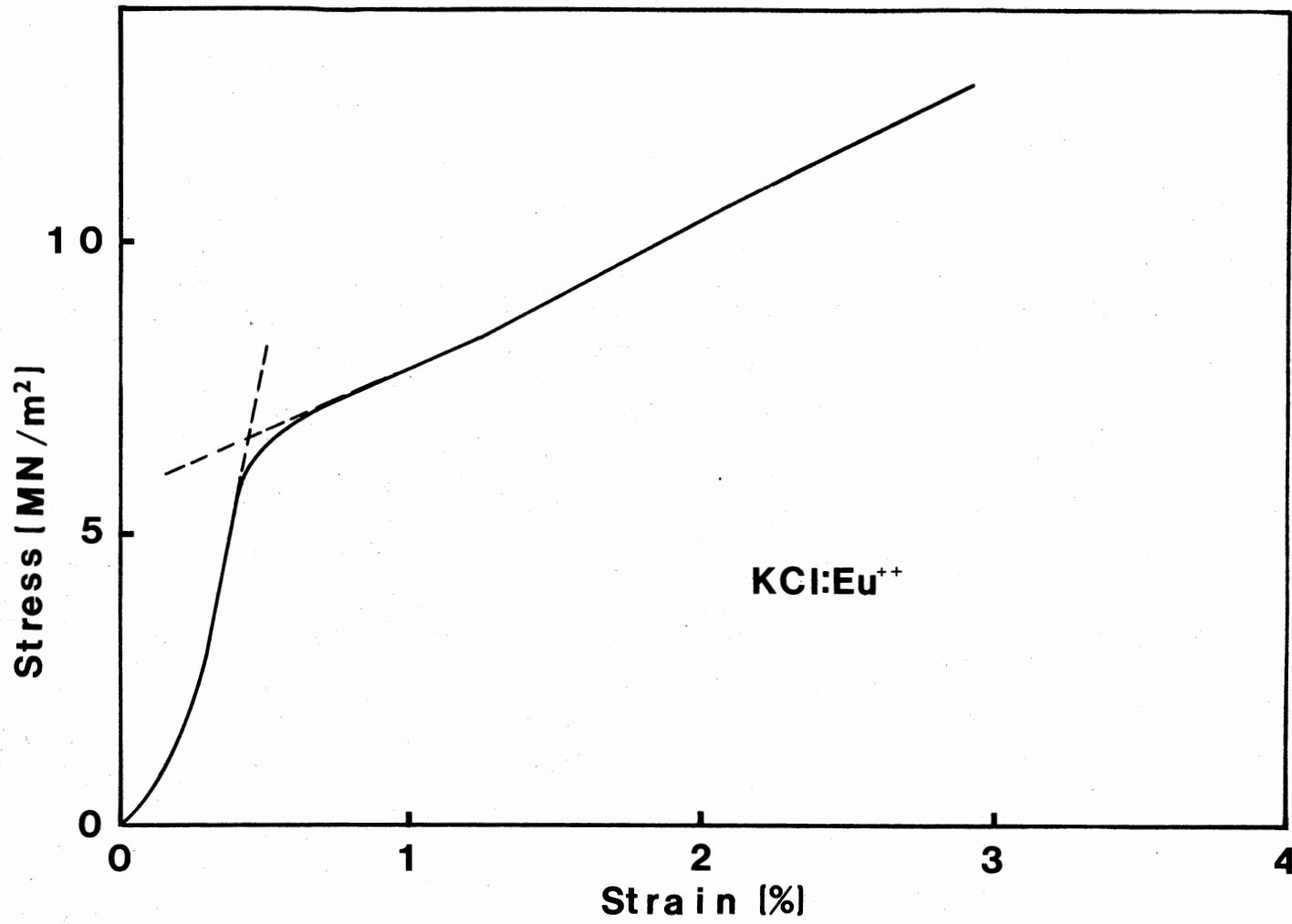


Figure 3. Stress-Strain Curve for a Typical Eu⁺⁺ Dope KCl Crystal. The Flow Point is Taken to be Point of Intersection of Tangent Lines

shown in Figure 3. The individual flow stresses of from five to seven samples were averaged to obtain the values recorded for each dopant concentration. In order to compare the results with theory, the resolved flow stress τ_r , the component of the flow stress parallel to the primary slip directions was calculated. In KCl the primary slip direction is in the $\langle 110 \rangle$; therefore, the resolved flow stress will equal one half the engineering flow stress.

CHAPTER IV

RESULTS AND DISCUSSION

Eu^{++} was found to be an effective strengthening dopant for KCl single crystals. The increase in flow stress was shown to be a function of the concentration and the amount of aggregation of the impurity-vacancy pairs. Figure 4 shows the flow stress versus Eu concentration for samples cleaved from freshly grown crystals, annealed at 675°C and quickly cooled to room temperature. The flow stress is seen to increase linearly with concentration. This result is in contrast to the results for KCl:Sr obtained in this laboratory (10) which show a \sqrt{C} dependence. The KCl:Sr curve is also shown in Figure 4. The data for the quickly cooled samples show that Eu^{++} is an effective hardening agent but that it is less effective than the alkaline earths. Crystals that were allowed to age at room temperature for 6 months or more often showed an increase in flow stress as shown by the solid points in Figure 5 which appear to approach the KCl:Sr line.

The linear in C relationship does not agree with the theory suggested by Fleischer (11). Since Fleischer's theory assumes that the interactions are short ranged in nature, one can construe that the interactions are of a long range nature. This is in agreement with the treatment of the Snoek effect by Pratt, et al. (9) that there is a long ranged ordering of the impurity-vacancy pairs when in the stress field of a moving dislocation. This also suggests that the majority of the

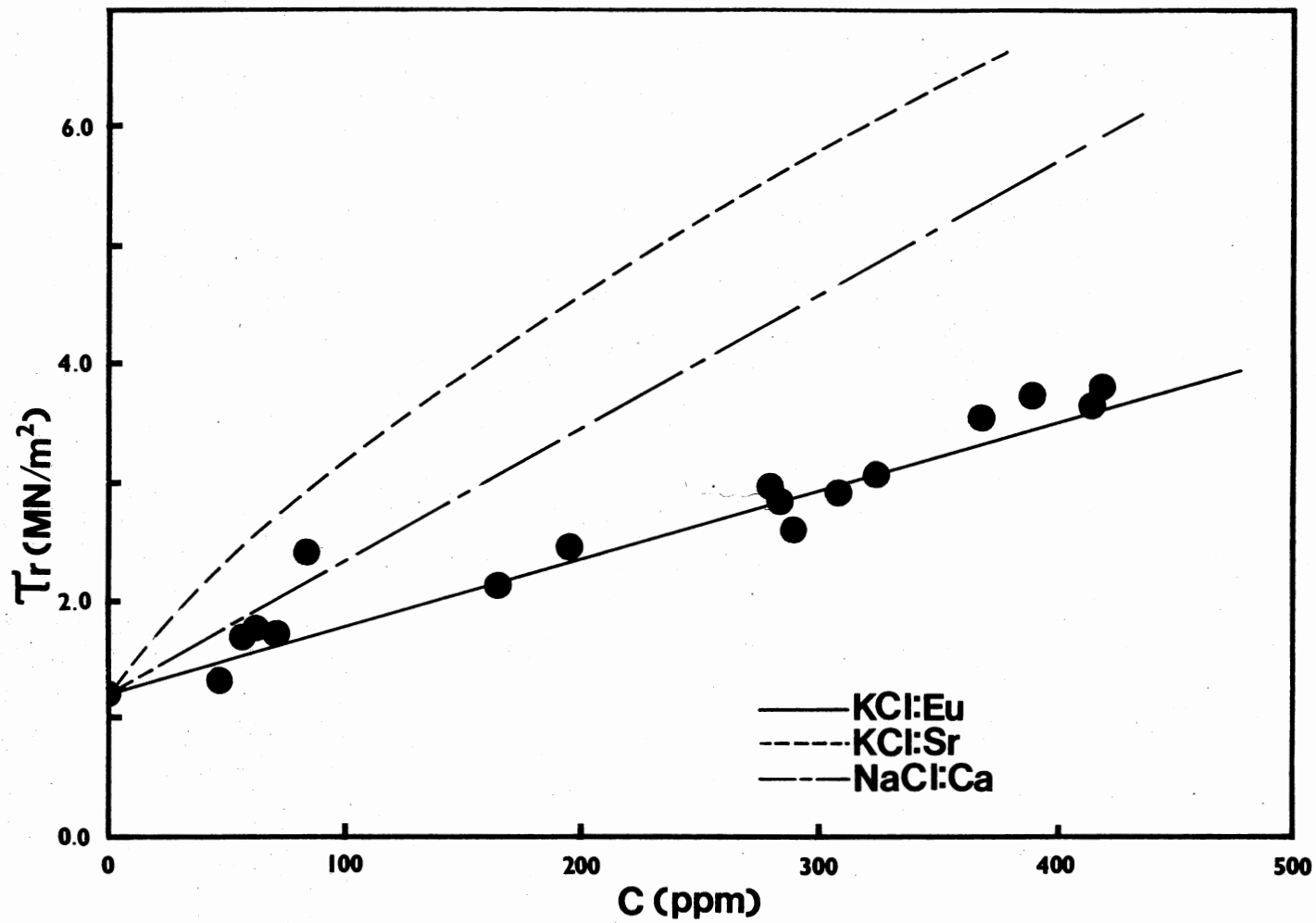


Figure 4. The Closed Circles Show the Results for Eu Doped KCl Found in This Study. The Results for KCl:Sr Found by Sibley et al. (10) and for NaCl:Ca Found by Pratt et al. (9) are Shown for Comparison

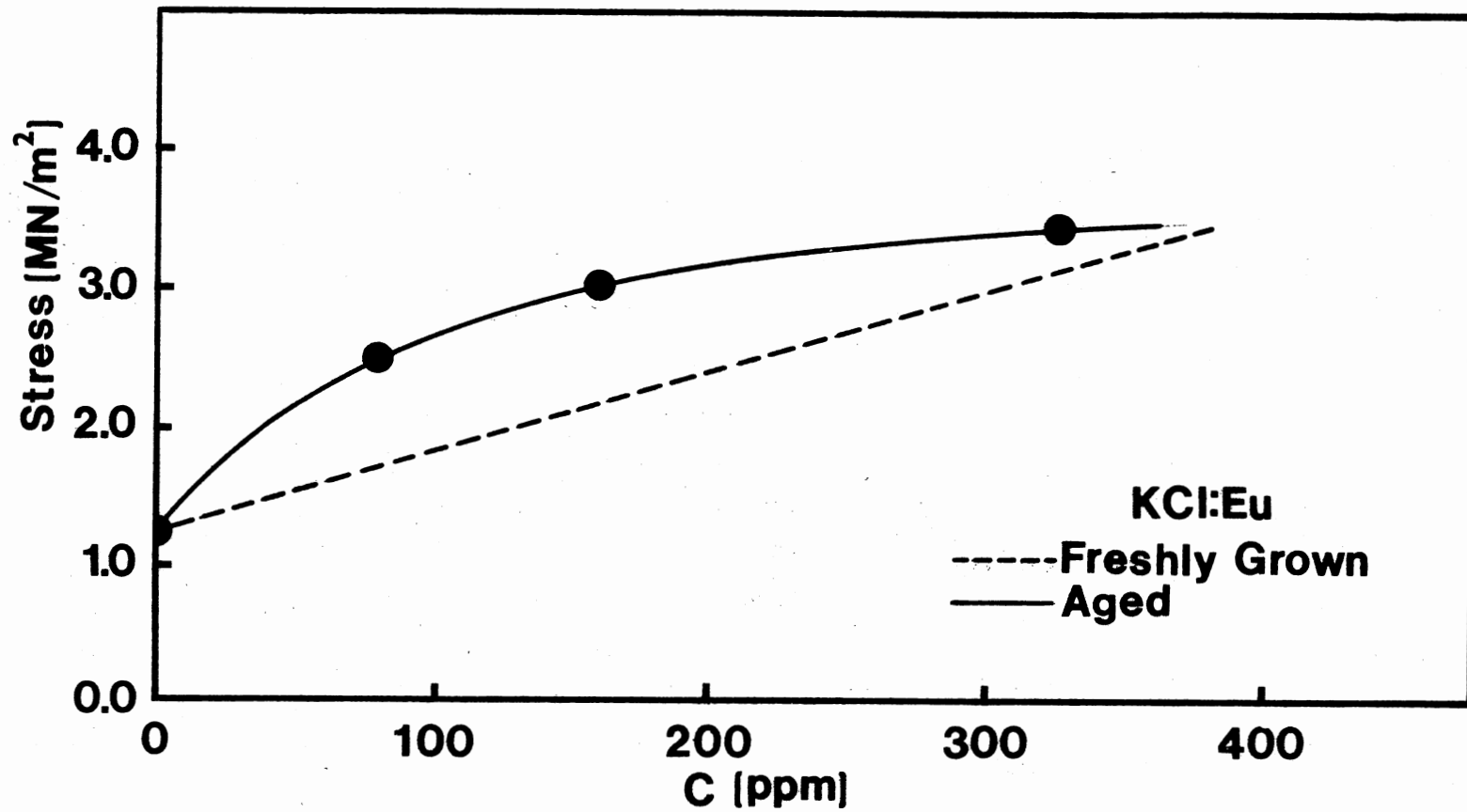


Figure 5. A Result for the Resolved Flow Stress Versus Eu Concentration for Aged Crystals are Compared to the Results for Freshly Grown Crystals

impurity-vacancies are arranged as simple dipoles rather than in larger aggregates. If the dipoles had combined to form larger complexes, then the vacancies would no longer be free to reorient themselves and should then approach some C^u dependency as described by Fliescher, where u is some order less than one. This order will be dependent on the amount of aggregation of the dipoles. A dependence of this nature has been observed in the aged crystals. The crystals used in Figure 5 have been aged for approximately one year then quick cooled from 675°C . This suggests that there is an aggregation of the Eu^{++} -vacancy dipoles with time.

When comparing the results obtained from the Eu^{++} doped KCl crystals to the results of Pratt, et al. (9) for NaCl doped with Ca^{++} one sees agreement in the linear in C dependence obtained for the freshly grown crystals.

In the aged Eu^{++} doped crystals there is a great similarity between the results obtained and the results obtained for KCl: Sr by Sibley, et al. (10). The aged crystals also agree with the results by Chin et al. (8).

CHAPTER V

FUTURE WORK

The difference in results from the freshly grown crystals and aged crystals should have further study. The flow stress as compared to aggregation could be studied by measurement of the dielectric constant. A possible method of producing reproducible aggregation levels would be heat treatment to enhance aggregation or break up aggregates depending on the temperature used.

A study of this nature may aid in explaining the difference in results obtained when KCl is doped with Eu^{++} and Sr^{++} .

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APPENDIX

TABULATION OF FLOW STRESS OF KCl:Eu^{++} CRYSTALS

| Crystal Number | Concentration (Atomic ppm) | Flow Stress (MN/m ²) | Condition |
|----------------|-------------------------------|-------------------------------------|-----------|
| 020874 | 0 | 1.68 | Fresh |
| 051975 | 0 | 1.24 | Fresh |
| 030475 | 47 | 1.32 | Fresh |
| 030475 | 60 | 1.72 | Fresh |
| 030475 | 61 | 1.78 | Fresh |
| 031775 | 72 | 1.74 | Fresh |
| 031775 | 84 | 2.42 | Fresh |
| 060475 | 164 | 2.14 | Fresh |
| 032775 | 194 | 2.70 | Fresh |
| 042975 | 279 | 2.96 | Fresh |
| 040275 | 283 | 2.86 | Fresh |
| 040275 | 290 | 2.60 | Fresh |
| 061675 | 308 | 2.92 | Fresh |
| 061675 | 325 | 3.07 | Fresh |
| 042975 | 368 | 3.57 | Fresh |
| 060475 | 389 | 3.77 | Fresh |
| 061675 | 414 | 3.67 | Fresh |
| 040275 | 418 | 3.83 | Fresh |
| 061675 | 320 | 3.04 | Aged |
| 061675 | 308 | 2.88 | Aged |
| 061675 | 470 | 3.99 | Aged |

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