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WILLIAM ARTHUR SIBLEY
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DISLOCATION NETWORKS AND VACANCIES IN IONIC CRYSTALS

APPROVED BY

Chalmers

Chen

Robert M. H. (Jr.)

Edward Prosser

Arthur Burnhart

DISSERTATION COMMITTEE

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DISLOCATION NETWORKS AND VACANCIES IN IONIC CRYSTALS

CHAPTER I

INTRODUCTION AND DEFINITIONS

Introduction

Alkali halide crystals represent a very remarkable medium for the study of crystalline imperfections. The crystals are obtained with comparative ease in a state of near perfection and known purity. Moreover, the physical properties of the alkali halides appear to be greatly influenced by the principal crystalline imperfections.

Another important aspect of the study of the alkali halides is that defects and dislocations have many features in common for both ionic crystals and metals. Plastic deformation or heat treatment can create point defects in both types of crystals which can then interact with dislocations. The density and distribution of point defects arising from impurities, thermal or mechanical treatment are often more readily measured in ionic crystals than in metals. For example, the electrical conductivity of alkali halide crystals provides a direct measure of the concentration and mobility of vacancies. It must be remembered, however, that

any comparison between point defects in ionic crystals and in metals may have certain limitations due to the difference in the type of bonding in the two crystals.

Point Defects

A point defect is a departure from crystalline order which extends over a few atomic lattice sites. The primary point defects recognized are:¹

- (a) Electrons and holes
- (b) Excitons
- (c) Vacant lattice sites and interstitial atoms
- (d) Foreign atoms in either substitutional or interstitial positions.

Since point defects may interact with each other, clusters of point defects may occur under suitable conditions. In this manner positive and negative-ion vacancy pairs, precipitates, and vacancy-divalent ion complexes may be formed.

Figure 1 illustrates the various point defects: (a) vacancies, (b) impurities, (c) vacancy-divalent impurity complexes, and (d) interstitial ions. A vacancy is defined as the empty lattice site formed when an ion is moved from the interior of the crystal to a position on the surface of the crystal. Impurities are foreign ions which frequently assume the regular lattice site positions of indigenous ions. The vacancy-divalent impurity ion

¹F. Seitz, Rev. Mod. Phys. 26, 7 (1954).

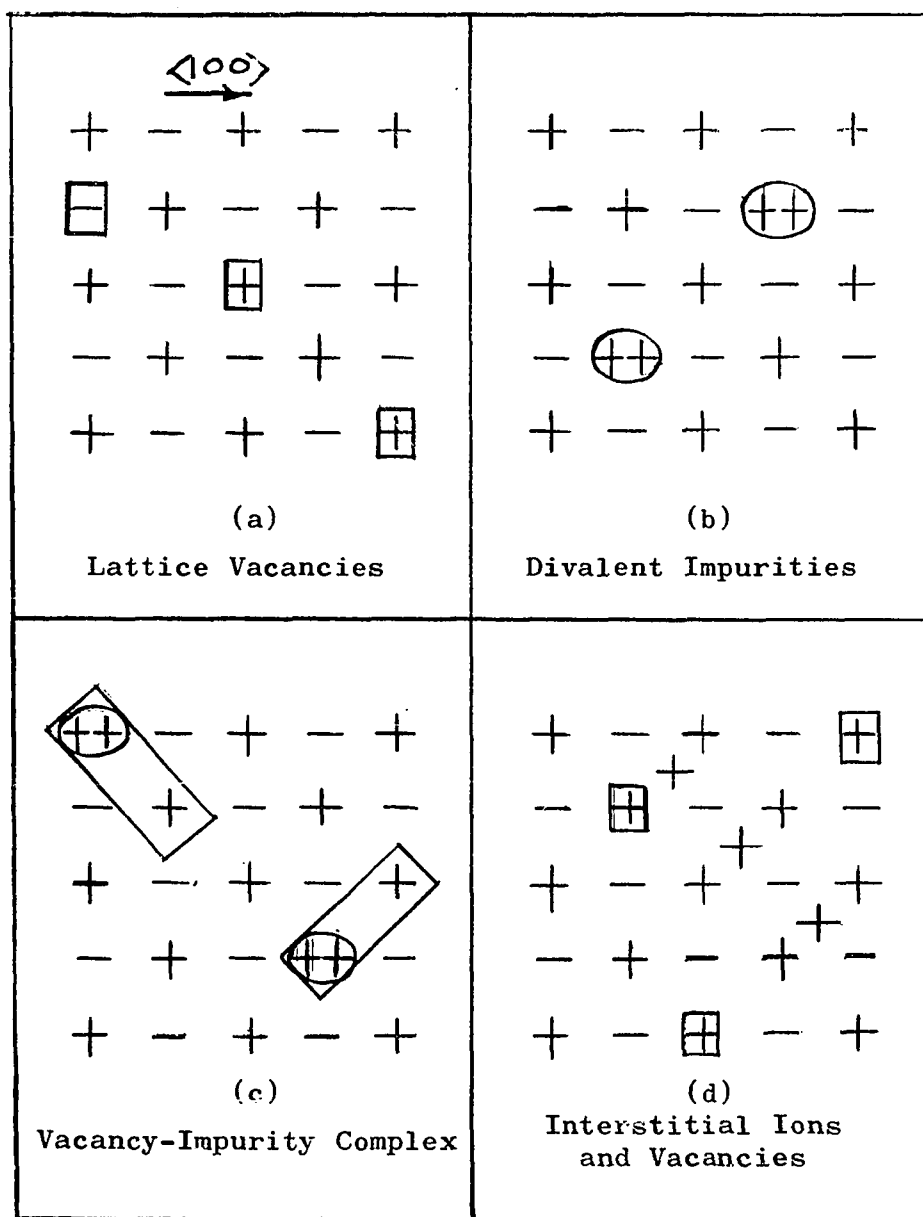


Fig. 1. Point Defects in Ionic Crystals

complex consists of a positive ion vacancy and a divalent impurity ion in close proximity. For our purposes we will consider the complex associated when the vacancy is the next neighbor of the impurity. Interstitials are characterized by an indigenous ion moving into a position between the normal lattice sites. However, interstitials have been observed in alkali halide crystals only after X-ray irradiation,² and it has been shown that the energy necessary to form an interstitial in KCl or KBr crystals is much greater than the energy needed to form a vacancy.³ Since this work involves only unirradiated KCl and KBr crystals we shall not be concerned with interstitials.

When equal numbers of positive and negative-ion vacancies are generated by thermal means alone we use the term Schottky defects. In this investigation vacancies and impurities in substitutional positions are the point defects of major interest, and we will be particularly interested in the vacancy-divalent impurity ion complexes which exist below 800°K.

Dislocations

In addition to point defects we shall be concerned with imperfections of greater size, such as vacancy clusters and dislocations. Since vacancy clusters are formed from individual vacancies, no further description of them is needed. However, a brief outline

²D. A. Wiegand and R. Smoluchowski, Phys. Rev. 110, 991 (1958).

³W. Schottky, Z. Phys. Chem. Abt. B29, 335 (1935).

of dislocation properties must be presented since they are of such import in this investigation. A much more detailed account of dislocations has been given by Cottrell,⁴ Friedel,⁵ and Read.⁶

Experiments reveal that the shear strength of real crystals varies from 10^{-3} to $10^{-5}G$, where G is the shear modulus. The material in the slip plane remains crystalline and slip occurs consecutively, rather than simultaneously, over the slip plane. The lowest theoretical estimate of the shear strength of an ideal crystal is about $G/30$. Thus, in order to explain the experimental observations, we are forced to conclude that sources of mechanical weakness are called dislocations and are such that slip can start from them at very low applied stresses.^{7,8}

General Properties of Dislocations

One of the characteristic features of any dislocation is the Burgers vector. This vector specifies the magnitude and direction of dislocation slip. If we consider a slip plane lying between two planes of atoms, then the Burgers vector, $\underline{b}$, gives the direction and distance by which atoms on the upper side of the slip

⁴A. H. Cottrell, Dislocations and Plastic Flow in Crystals (Oxford Press, London, 1956).

⁵J. Friedel, Les Dislocations (Gauthier-Villiar, Paris, 1956).

⁶W. T. Read, Dislocations in Crystals (McGraw-Hill Book Co. Inc., New York, 1953).

⁷G. I. Taylor, Proc. Roy. Soc. A145, 362 (1934).

⁸E. Orowan, Z. Phys. 89, 605 (1934).

plane have moved with respect to those on the lower side. This vector determines the "strength" of the dislocation and is the same for all parts of the dislocation line. The dislocation is illustrated in Figure 2.

Atoms within a crystal must slip from one equilibrium position to another because of the periodic force field associated with the crystal lattice. Therefore, the Burgers vector must always connect one equilibrium position with another and its magnitude, b , must be restricted to a class of discrete values determined by the crystal structure. It is often convenient to specify a Burgers vector by its components along the principal crystal axes. For example, if we consider a face-centered cubic crystal the vector associated with slip from a cube corner to a face centre has components $a/2, a/2, 0$, which may be written as $\left[a/2, a/2, 0 \right]$ or as $a/2 \left[110 \right]$, where a is the lattice constant and $\left[110 \right]$ is the slip direction.

The Burgers vector can also be related directly to the force exerted on a dislocation due to an applied shear stress and to the strain energy of a dislocation by means of the elastic theory of solids.⁹ The force per unit length on a dislocation line is given by $F = \sigma b$ where σ is the applied shear stress acting in the slip direction on a slip plane. The strain energy per unit length of a dislocation is proportional to the square of the Burgers vector. Since the strain energy is by far the greatest term in the change

⁹Cottrell, op. cit.

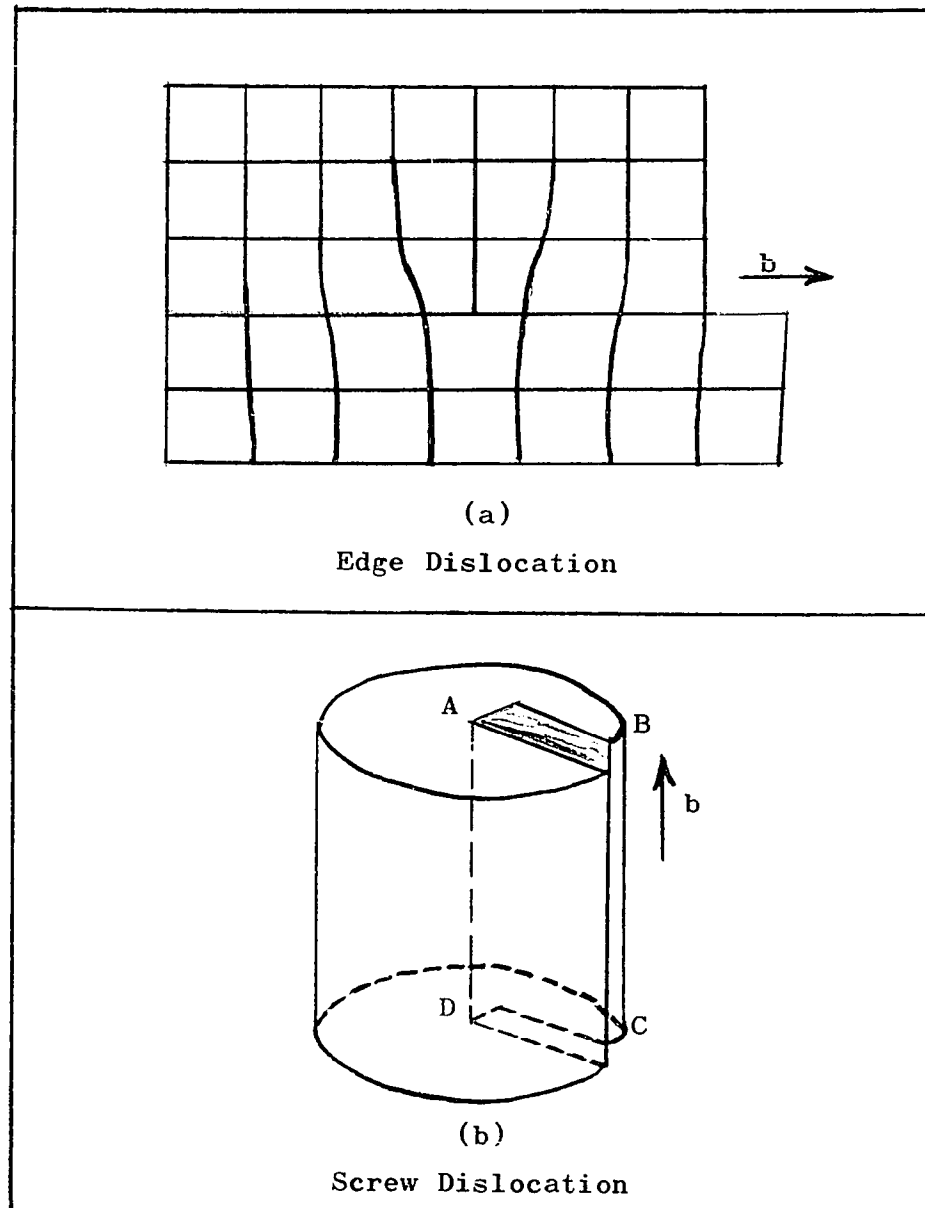


Fig. 2. Dislocations

of the free energy when a dislocation is formed in a crystal, we can estimate the probability of occurrence of different types of dislocations by comparing the square of their respective Burgers vectors. As an example we shall examine two cases. First, take a dislocation with Burgers vector $a/2 [10\bar{1}]$. It is possible for this dislocation to decompose into two dislocations with Burgers vectors $a/6 [211]$ and $a/6 [11\bar{2}]$ respectively. In this case there is an energy gain if decomposition occurs. In contrast, consider the reaction $a [100] \rightarrow a/2 [111] + a/2 [1\bar{1}\bar{1}]$. The product dislocations in this instance are unstable since energy must be added to the system for the reaction to proceed.

Edge Dislocations

A dislocation whose Burgers vector is perpendicular to the dislocation line is called an edge dislocation. In this case, as illustrated in Figure 2(a), $n+1$ atomic planes above the slip plane are joined onto n planes below; the dislocation line is the edge of this extra plane -- hence the name edge dislocation.

The exact arrangement of atoms along the dislocation line is not known, but the mathematical theory of elasticity has been used to predict the stress distribution in regions more than four lattice sites from the dislocation line itself. Because of the localized dilation of the lattice associated with the edge dislocation, vacancies and impurities can be attracted to the dislocation line and form an atmosphere or cloud of defects around the line.

A special feature of the edge dislocation in ionic crystals, which may assist in the formation of a cloud of defects around the dislocation line, is that the edge of the extra half plane may have a net effective charge. Normally the dislocation line has no excess charge, but rather an equal number of alternating positive and negative electronic charges along the edge of the extra half plane. When vacancies condense on the dislocation line and take the place of ions jogs are formed in the line and a net charge may be produced on the dislocation line if unequal numbers of positive and negative ions are removed.

Screw Dislocations

A dislocation line which is parallel to the Burgers vector is defined as a screw dislocation. Figure 2(b) indicates how a screw dislocation is created by slip, the dislocation line AD is the boundary within the crystal of the slipped area ABCD. This diagram also shows that the crystal around the dislocation is not composed of parallel atomic planes one above the other; rather it is a single atomic plane in the form of a helicoid. A screw dislocation has no unique slip plane. The slip plane must contain both the dislocation and the Burgers vector: when these are parallel, the slip plane is not uniquely defined.

Since the screw dislocation must be jog free and has a stress field which is almost pure shear, there is little tendency to form clouds of vacancies around the dislocation line.

Irregular Dislocations

Although the Burgers vector is constant along a dislocation line it is clear that the structure of the dislocation changes with the inclination of the line to the slip direction. The Burgers vector of any arbitrary dislocation can be separated into two components such that the line can be thought of as consisting of edge and screw dislocations.

One type of irregular edge dislocation is the prismatic dislocation which is totally enclosed in the crystal and might be produced by the indentation of one face of the crystal by a punch. The prismatic dislocation might also be produced thermally by the production of a vacancy cluster which collapses to form extra half sheets completely enclosed in the crystal.

CHAPTER II

STATEMENT OF PROBLEM AND REVIEW OF PREVIOUS WORK

Statement of the Problem

It is well known that point defects and dislocations have a strong influence on the mechanical properties of materials and that physical properties controlled by diffusion-like processes are also strongly affected by these defects. There have been many investigations of dislocations in crystals, but in most cases the methods of investigation affect the dislocation density and arrangement within the crystals. In consequence, the information concerning the dislocations does not necessarily apply to dislocations in unstressed crystals grown by the usual techniques. While the yielding of a crystal is caused by dislocation motion, the yield stress is very sensitive to the vacancy-impurity clouds around the dislocations and to vacancies and impurities dispersed throughout the crystal. However, investigations of the dependence of the yield point on dislocation arrays and impurities are frequently hampered by the inability to observe the interior of a metal, while investigations of transparent crystals by the dislocation decoration technique of Amelinckx result in permanent damage to the crystal.

Earlier investigations in which the author has participated

have shown that light scattering in transparent crystals can be a powerful tool for the investigation of dislocations.¹ If the information obtained by light scattering experiments is correlated with the results obtained by chemical etching of crystal surfaces, yield strength, and hardness measurements, it is possible to extend our knowledge of dislocations and point defects in unstressed transparent crystals. Such is the aim of the present investigation.

Review of Previous Work

The principal types of experiments which have given information concerning vacancies, impurities and dislocations in ionic crystals are measurements of ionic conductivity in crystals containing known amounts of impurities, diffusion of ions in the crystal due to a concentration gradient, plastic deformation of single crystals, chemical etching of crystal surfaces and decoration of dislocations by colloidal particles. The results of these investigations are summarized below.

Electrical Conductivity

Electrical conductivity in ionic crystals is due to the motion of vacancies under the influence of an electric field. The mobility of the vacancies is dependent on the temperature in the form

¹C. A. Plint, O. Theimer, and W. A. Sibley, Ann. Phys. 5, 342 (1958).

$$M = A/T \exp (-E/kT) \quad (1)$$

where T is the absolute temperature, A is a constant, and E is the activation energy for displacement of a vacancy. Therefore, it is possible to measure the activation energy by conductivity experiments since the conductivity is proportional to the mobility. Conductivity measurements are usually divided into two ranges, the intrinsic range and the extrinsic range. The intrinsic range is characterized by carriers of the Schottky type while in the extrinsic range the carriers are the positive ion vacancies which are present because of the divalent impurities in the crystal. In the low temperature, extrinsic, range two distinct effects are noticed. As the temperature increases from about 25°C the conductivity changes because of the dissociation of vacancy-divalent impurity ion complexes and the increasing mobility of the free vacancies. With further increase in temperature all the complexes dissociate and then the conductivity depends only on the mobility. Thus, there are, in fact, three separate stages for the dependence of the conductivity on temperature: stages I and II in the extrinsic range and stage III in the intrinsic range.

In the intrinsic range, the vacancy concentration increases through the Schottky mechanism and the changing mobilities of positive and negative-ion vacancies. An expression for the fraction of Schottky defects in the lattice at a particular temperature can be written as

$$f = B \exp (-E_f/2kT) \quad (2)$$

B is a constant determined by experiment and E_f is the energy of formation of a separated pair of positive and negative-ion vacancies. For KCl, B is 42, E_f is between 2.1--2.4 e.v.^{2,3}, and the density of Schottky defects is about 10^6 cm^{-3} at room temperature and 10^{18} cm^{-3} at the melting point. The intrinsic range starts at the temperature where the number of Schottky defects is slightly greater than the number of positive ion-vacancies present because of the divalent impurity ions. Obviously the temperature at which the intrinsic stage begins is fixed by the impurity concentration of the crystal.

Stage I continues from somewhere below room temperature to the temperature at which all the positive-ion vacancy-divalent impurity ion complexes are dissociated. Stage II is the region where dissociation has occurred and the number of extrinsic vacancies is greater than the number of Schottky defects.

At present the most interesting region is stage I where the vacancy-divalent impurity ion complexes dissociate. The systems which have been studied by ionic conductivity methods are $\text{AgBr} + \text{CdBr}_2$,⁴ $\text{NaCl} + \text{CdCl}_2$,⁵ and $\text{NaCl} + \text{CaCl}_2$.⁶ In cases where the impurity concentration is high, Debye-Hückel shielding of the complex must be considered in order to obtain an accurate value for the true dissociation energy of the complexes. Etzel and Maurer

⁴J. Teltow, Ann. Phys., Lpz. 5, 63, 71 (1949).

⁵H. W. Etzel and R. J. Maurer, J. Chem. Phys. 18, 1003 (1950).

⁶C. Bean, Thesis, University of Illinois (1952).

have found for a cadmium-vacancy complex in NaCl a dissociation energy of about .25 e.v. Since the radii of cadmium and calcium ions are about the same, it would seem that the dissociation energies of the respective vacancy-impurity complexes should be about the same. However, Bean has found that apparently calcium-vacancy complexes in NaCl dissociate at temperatures above 250°C . Also, the magnitude of the conductivity for $\text{NaCl} + \text{CaCl}_2$ is only about half that of $\text{NaCl} + \text{CdCl}_2$. These two facts indicate that the association energy is stronger for a calcium-vacancy pair.

Dielectric loss experiments have been performed on ionic crystals to investigate the number of associated complexes at a given temperature. The dielectric loss results from a re-orientation of the impurity vacancy pairs under the action of an applied field. Haven⁷ has essentially found the same results for $\text{NaCl} + \text{CaCl}_2$ as Bean for the dissociation of the complexes.

The conductivity of NaCl was measured by Gyulai and Hartley⁸ immediately after a substantial plastic strain in the range of ten percent had been given the crystals. The conductivity was increased by two orders of magnitude and decayed to its original value after a twenty minute period at room temperature. This effect can be interpreted in terms of an electrolytic current associated with the generation of positive and negative-ion vacancies during plastic

⁷Y. Haven, Report of the Conference on Defects in Crystalline Solids, Physical Society, London (1954), p. 261.

⁸Z. Gyulai and D. Hartly, Z. Physik 51, 378 (1928).

flow. Since the proposed mechanism for ductility of the salts is the dislocation, it can be presumed that the vacancies are generated by the motions of dislocations. The mobility of the positive-ion vacancies is such that after a few minutes these vacancies could be "trapped" at the dislocation lines or migrate to negative-ion vacancies to form uncharged pairs. This, then, would remove the source of the extra carriers and so decrease the conductivity. This interpretation is further confirmed by the work of Vaughan, et al. and Davidge, et al. which will be discussed in a later section.

Diffusion

Diffusion measurements in potassium chloride crystals fix the charge carriers as positive-ion vacancies for temperatures below 600°C. However, in the intrinsic range the densities of positive- and negative-ion vacancies are essentially the same, and the mobility ratio of the two is approximately one.⁹ Also, measurements of diffusion of radioactive tracer elements along dislocation boundaries show that diffusion is much more rapid along the boundaries than in the rest of the crystal. This implies that there is a considerable vacancy concentration in the region around the dislocations.

The Nernst-Einstein relation shows the connection between the electrical mobility of a particle and its self-diffusion coefficient. This relation is written as

⁹F. Kerkhoff, Z. Physik 130, 449 (1951).

$$M = (e/kT) D_v, \quad (3)$$

where D_v is the diffusion coefficient, e is the electronic charge and k is Boltzmann's constant. This relationship is valid if the same particle is taking part in both processes. Since in the extrinsic range equation (3) is not satisfied, it is felt that diffusion in this region is the result of several different carriers, some of which could be neutral and not take part in conductivity.

The jump frequency ν of the positive ion vacancies can be found by using the relation

$$D_v = \nu R^2/6 \quad (4)$$

in which R is the spacing between neighboring positive-ion vacancies. Expressing ν in terms of a Boltzmann factor,¹⁰ we find

$$\nu = \nu_0 \exp (-E/kT), \quad (5)$$

where ν_0 is about 10^{14} sec^{-1} in KCl. From this equation it is possible to find the jump frequency of positive-ion vacancies at any temperature.

Plastic Deformation

Kear and Pratt¹¹ have investigated the hardening of sodium

¹⁰C. Wert, Phys. Rev. 79, 601 (1950).

¹¹B. H. Kear and P. L. Pratt, Phil. Mag. 4, 56 (1959).

chloride crystals as a result of quenching the crystals from various temperatures. This very extensive work brought out the following interesting points. Hardening in quenched crystals of NaCl is not only caused by thermal stresses which are connected with the quenching rate, but also depends on some other mechanism intrinsic to the crystals. The mechanism postulated by Kear and Pratt is that of vacancy pinning of dislocations and also of dispersion hardening due to vacancy clusters formed at high temperature. The experimental evidence certainly supports this concept, and the three stages associated with vacancies in the conductivity results also appear in this work.

The rate of formation of vacancies in KCl single crystals per percent plastic deformation has been measured by Vaughan, et al.¹² The change in density of Harshaw KCl crystals was measured for various degrees of deformation, and it was found that there was no change in density up to 11 percent plastic deformation. For larger strain values a density change occurred corresponding to the production of 3.02×10^{17} vacancies per cm^3 per percent deformation. Observations of the slip lines in the deformed crystals showed that these lines formed at 45° to the crystallographic axes and also parallel to these axes.

Davidge, et al.¹³ have duplicated Vaughan's work for NaCl.

¹²W. H. Vaughan, W. J. Leivo, and R. Smoluchowski, Phys. Rev. 110, 652 (1958).

¹³R. W. Davidge, C. E. Silverstone, and P. L. Pratt, Phil. Mag. 4, 985 (1959).

They were able to demonstrate that vacancies created by stress are probably due to dislocation motion in the crystal. This was shown by comparing straight loading and cyclic loading deformation. It was found that many more vacancies were created by fatigue in compression. They state that in ionic crystals the vacancies formed by compression appear to be stable in the form of small clusters.

Eshelby, et al.¹⁴ have found that the yield stress of sodium chloride exhibits maxima and minima when plotted as a function of temperature. This is explained by assuming that for a crystal in thermal equilibrium the dislocations in the crystal will be electrically charged and surrounded by Debye-Hückel clouds of vacancies. If the charge on the dislocation line is reversed because of the precipitation of impurities or the association of impurity atoms and vacancies, then the crystal will possess a yield point which will be a complicated function of the temperature. This viewpoint assumes that the vacancy cloud is essentially immobile and a finite force is required, therefore, to separate the dislocation from the cloud. This concept has been further advanced by Sproull¹⁵ and by Plint, et al.¹⁶

Decoration and Etching of Dislocations

¹⁴J. D. Eshelby, C. W. A. Newey, P. L. Pratt, and A. B. Lidiard, *Phil. Mag.* 3, 75 (1958).

¹⁵R. L. Sproull, *Bull. Amer. Phys. Soc.* II 5, 190 (1960).

¹⁶C. A. Plint, O. Theimer and W. A. Sibley, *Ann. Phys.* 5, 342 (1958).

It is possible by decorating the dislocation lines in alkali halide crystals to investigate dislocation networks.¹⁷ The decoration is accomplished by enclosing a stock of sodium metal in a cavity in the crystal and then heating the crystal to about 750°C. It was also found that the rate of cooling affected the decoration. For "pure" NaCl it was necessary to cool from 750°C to room temperature in 15 minutes. Dislocation networks have been observed in both the (111) planes and the (100) planes for NaCl and KCl. Amelinckx is unable to determine with certainty whether the dislocation nets he observes are caused by the heat treatment or whether they are a property of the "as grown" crystal.

Amelinckx¹⁸ has also obtained information on dislocations in NaCl by using etch techniques. The shape of the etch pit determines the direction of the dislocation line, and it is believed that all of the dislocations etch. It is found that dislocations tend to form arrays during long anneals.

Lithium fluoride has been extensively investigated by means of etching methods by Gilman and Johnston.^{19,20} They have also been able to show that precipitates are characterized by flat-bottomed etch pits and can easily be distinguished from the very

¹⁷S. Amelinckx, Report of a Conference on Dislocations and Mechanical Properties of Crystals, Wiley and Sons, Inc., New York (1957). p. 52.

¹⁸S. Amelinckx, Acta Met. 2, 848 (1954).

¹⁹W. G. Johnston and J. J. Gilman, J. App. Phys. 30, 129 (1959).

²⁰J. J. Gilman, J. App. Phys. 30, 1584 (1959).

distinctive dislocation etch pits. Precipitates in the form of particles (10^{-5} cm in diameter), needles (about 3×10^{-5} cm thick and 10^{-3} cm long), and ribbons (10^{-4} cm across and 10^{-3} cm in length) have been found. No estimate of the density of these precipitates has been given. Since in most of the experimental work to be presented in this paper light scattering techniques are used, it is very important to remember that scattering could be caused by precipitates as well as by dislocations.

It is important to note that in all the experimental work on the alkali halides reviewed here there is no experiment or group of experiments which give information about imperfections in an unperturbed crystal. Part of this investigation will be devoted to an attempt to obtain information about defects in "as grown" crystals.

CHAPTER III

THEORY OF POINT DEFECTS IN IONIC CRYSTALS

Diffusion of Vacancies by the Method of Random Walks¹

Let the displacement of a vacancy after n jumps be $\underline{R}$. If we superpose the initial positions of all the vacancies on to a common origin, we shall obtain an almost continuous distribution of end points of the vectors $\underline{R}$. The distribution will be a spherically symmetrical solution of the general diffusion equation

$$\frac{\partial n^*}{\partial t} = D \nabla^2 n^*, \quad (1)$$

where D is the diffusion coefficient and n^* is the concentration of vacancies. If we assume a large number of jumps of discrete length, we find as a solution of (1)

$$\overline{R^2(t)} = 6Dt, \quad (2)$$

where t is the time necessary for the performance of n jumps.

$\overline{R^2(t)}$ can be evaluated directly as follows:

¹W. Jost, Diffusion in Solids, Liquids, and Gases (Academic Press Inc., New York, 1952).

$$\overline{R^2(t)} = \left(\sum_{i=1}^n \underline{r}_i \right)^2 = \sum \overline{r_i^2} + 2 \sum_{i=1}^{n-1} \sum_{j=1}^{n-i} \overline{r_i \cdot r_{i+j}} , \quad (3)$$

where we denote successive jumps by $\underline{r}_1, \underline{r}_2, \dots, \underline{r}_i, \dots$

If the individual jump vectors are equal in magnitude, then

$$\overline{R^2(t)} = nr^2 + 2r^2 \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \overline{\cos \phi_{i,i+j}} , \quad (4)$$

where $\overline{\cos \phi_{i,i+j}}$ is the average value of the cosine of the angle between the i -th and the $(i+j)$ -th jump of a vacancy. If all the jumps are completely random and uncorrelated with previous jumps then $\overline{\cos \phi_{i,i+j}}$ is zero. In actuality, the probability for a jump is not the same for all possible jump directions but depends on the previous jump. Thus, the correlation between jumps must be considered. LeClaire and Lidiard² have shown that equation (4) may be rewritten as

$$\overline{R^2(t)} = nr^2 + 2r^2 \sum_{j=1}^{n-1} (n-j) \overline{\cos \phi_j} . \quad (5)$$

They were able to show $\overline{\cos \phi_j} = (\overline{\cos \phi_1})^j$ where $\cos \phi_1$ is the average of the cosine of the angle between consecutive jumps. Equation (5) may then be written

$$\overline{R^2(t)} = \frac{1}{6} \Gamma^2 r^2 \left(\frac{1 + \cos \phi}{1 - \cos \phi_1} \right) t , \quad (6)$$

where Γ is the average jump frequency for a vacancy and is given by $12c\nu$. The molar fraction of free, unassociated vacancies is c and ν is the jump probability per unit time of a vacancy.

²A. D. LeClaire and A. B. Lidiard, Phil. Mag. 1, 518 (1956).

It is interesting to calculate the net displacement of a vacancy in a given time. We consider potassium chloride. At 625°K, $\nu \sim 5 \times 10^6 \text{ sec}^{-1}$ and $r = \sqrt{2}a = 4.4 \times 10^{-8} \text{ cm}$. The correlation factor, $f = \left(\frac{1+\cos \phi}{1-\cos \phi} \right)$, is .72 for face-centered cubic crystals and we take c as 10^{-4} - 10^{-5} . For a time of two hours we have

$$\left[\overline{R^2(t)} \right]^{1/2} = 4 \times 10^{-5} \text{ cm} \quad \text{for } c = 10^{-5} \quad (7a)$$

$$\left[\overline{R^2(t)} \right]^{1/2} = 1.5 \times 10^{-4} \text{ cm} \quad \text{for } c = 10^{-4} \quad (7b)$$

At a temperature of 700°K

$$\left[\overline{R^2(t)} \right]^{1/2} = 8 \times 10^{-5} \text{ cm} \quad \text{for } c = 10^{-5} \quad (8a)$$

$$\left[\overline{R^2(t)} \right]^{1/2} = 2.5 \times 10^{-4} \text{ cm} \quad \text{for } c = 10^{-4} \quad (8b)$$

At first glance it would appear that for an equilibrium to obtain between the vacancies around the dislocations and the lattice vacancies would require an exceptionally long time at these temperatures. However, it must be remembered that very few vacancies are required to completely saturate the dislocation line. In fact, at 700°K, for a vacancy concentration of 10^{17} cm^{-3} and a heating time of two hours, more than twice as many vacancies are available to the dislocation than the number required for saturation.

In our experiments the total heating time is three hours. Thus it is possible for an equilibrium to exist between the lattice

³K. Compaan and Y. Haven, Trans. Faraday Soc. 52, 786 (1956).

vacancies and the vacancies in the dislocation cloud.

Vacancy-Divalent Impurity Complex⁴

Consider a crystal with $N_i = cN_o$ divalent impurity ions where N_o is the number of positive ion lattice sites and c is the mole fraction of impurity ions. There are then N_i positive ion vacancies in the crystal for temperatures up to 800°K , i.e. neglecting Schottky defects. If we let $\mathcal{S}_i$ be the Gibbs free energy of association, i.e. the work gained under conditions of constant pressure and constant temperature in bringing a vacancy from a distant position to a nearest neighboring position of the impurity ion, then the Gibbs free energy for the crystal due to the complexes may be written as

$$\Delta G = -n\mathcal{S}_i - kT \ln \left\{ z^n \prod_{s=0}^{n-1} \frac{(N_o + 2N_i - 2s)}{n!} \cdot \frac{[N_o + 2(N_i - n)]!}{N_o! (N_i - n)! (N_i - n)!} \right\} \quad (9)$$

the expression inside the braces being the product of the number of distinguishable ways of placing n complexes on the lattice and the number of ways of arranging the remaining $N_i - n$ impurity ions and $N_i - n$ vacancies. This equation is valid only if the impurity content is sufficiently low that the mutual interactions of the unassociated charges may be neglected. The equilibrium number of complexes can now be obtained by minimizing ΔG with respect to n . Using Stirling's theorem and the condition $N_i/N_o \ll 1$ we find

$$\frac{N_o n}{(N_i - n)^2} = z \exp(\mathcal{S}_i/kT) = K'_1 \quad (10)$$

⁴A. B. Lidiard, Handbuch der Physik 20, 246 (1957).

We define a degree of association such that cp is the molar fraction of complexes and obtain

$$cp = \frac{n}{N_o} ; \quad c = N_i/N_o.$$

Now equation (10) may be written as

$$\frac{cp}{[c(1-p)]^2} = z \exp(\bar{S}_i/kT) = K_1 \quad (11)$$

where for a face-centered cubic structure z is 12. The molar fraction of dissociated vacancies is then $d = (1-p)$. Equation (11) may be solved for p

$$p = 1 + \frac{1}{2cK_1} \left[1 + (1+4cK_1)^{1/2} \right], \quad (12)$$

from which we obtain

$$d = 1-p = \frac{1}{2cK_1} \left[-1 + (1+4cK_1)^{1/2} \right]. \quad (13)$$

Equation (13) can be rewritten in a form more suitable for our purposes as

$$n_d = \frac{N_o}{2z} \exp(-\bar{S}_i/kT) \left[-1 + (1+4cze^{\bar{S}_i/kT})^{1/2} \right] \quad (14)$$

where n_d is the number of dissociated free vacancies.

$\bar{S}_i$ may be written as the sum of two terms: a temperature dependent component and a temperature independent expression containing the thermal entropy, S . Thus, we can express K_1 as

$$K_1 = ze^{\bar{S}_i/kT} = ze^{-S/kT} e^{\epsilon_D/kT} = zK^{-1} e^{\epsilon_D/kT} \quad (15)$$

where ϵ_D is the effective dissociation energy of the complex.

Trivalent Impurities in Ionic Crystals

The Harshaw potassium bromide crystals used in this work contain aluminum as the primary impurity. If it is possible to show that aluminum is present in the crystal as a divalent impurity rather than as a trivalent ion, then the analysis of the previous section may be used to find the dissociation energy of a vacancy-divalent aluminum ion complex.

It is possible for a normally trivalent atom to be present in a crystal as a divalent atom if the gain in ionization energy were sufficiently great to offset the loss of electrostatic energy in the Madelung potential field. Lidiard⁵ has considered in detail the case of cadmium in NaCl and KCl. We will use his analysis for aluminum in KBr.

We start with a perfect crystal containing equal numbers of K^+ and Br^- sites and add two molecules of $AlBr_3$. If the aluminum enters as Al^{+++} ions there will be six new anion and six new cation sites. On the other hand, if the aluminum ions enter as Al^{++} ions there will be four new anion and four new cation sites. The latter state can be obtained from the first by carrying out the following operations, which require energy as indicated:

(1) Remove two Br^- ions from the crystal to a rest position at infinity. The corresponding work required will be denoted by $2 W_0^-$.

(2) Remove one electron from each Br^- ion, thus forming two neutral Br atoms. This requires twice the electron affinity

⁵Ibid.

of bromine $\equiv 2A$.

(3) Combine the two neutral Br atoms together into a bromine molecule, thus gaining the heat of formation $\equiv F$.

(4) Place the two electrons, (2), on each of the two Al^{+++} ions to make Al^{++} . This gains twice the ionization energy of $Al^{++} \equiv 2I$. This also gains twice the potential energy of an Al^{++} ion in the lattice relative to that of an Al^{+++} ion in the lattice. We designate this quantity by $2M$.

(5) Next, we remove the two pairs of vacant sites of opposite type from the crystal. In doing this we gain an energy $2(W_o^+ + W_o^- - W_L)$ where W_o^+ is the energy to remove one cation to infinity and W_L is the average lattice energy per ion pair. Adding the factors in steps (1) to (5) we require an amount of work

$$\Delta W = 2W_L + 2A - F - 2I + 2M - 2W_o^+, \quad (16)$$

If this quantity is positive, then the ions will enter as Al^{+++} ; and if it is negative they will enter as Al^{++} . The first four terms in the equation are known empirically and the other two must be calculated from lattice theory. Bassani and Fumi⁶ have calculated M for certain types of impurities and we have used their work to estimate M for aluminum.

Now ΔW can be calculated for the specific case of aluminum in KBr. W_L is 6.91 e.v., W_o^+ is 4.23 e.v., the ionization energy of aluminum is 28.5 e.v., the electron affinity for bromine

⁶F. Bassani and F. G. Fumi, Nuovo Cim. 11, 274 (1954).

is 3.8 e.v., and F is 2.01 e.v. The value of M is about 17.1 e.v. for aluminum. Therefore, ΔW is about -12 e.v. which implies that aluminum will most probably be present in KBr as a divalent ion.

Debye-Hückel Shielding

The situation under consideration is similar to an electrolyte solution containing "ions" of charge $+q$ (unassociated impurity ions and negative-ion vacancies) and "ions" of charge $-q$ (unassociated positive ion vacancies) dispersed in a medium of dielectric constant ϵ_s but unable to approach closer than a distance R . The distance R is the separation below which we regard an impurity ion and a positive-ion vacancy as associated. In an electrolytic solution positive ions tend to have a surrounding negative cloud which then reduces the field due to the positive ion. The Debye-Hückel theory considers the screening by ions of the opposite sign and takes account of Coulomb interactions among unassociated ions.

Consider positive-ion vacancies with a concentration N_1 and impurities, or negative-ion vacancies, with a concentration N_2 . Take N_1 and N_2 as approximately equal and consider the two defects a distance r apart. The potential energy of the first type defect at a distance r from the second type is $+q V(r)$ and that of type 2 a distance r from another type 2 defect is $-q V(r)$. Therefore, in equilibrium

$$N_1 = N e^{qV(r)/kT} \quad (17a)$$

$$N_2 = N e^{-qV(r)/kT} \quad (17b)$$

and the charge density is

$$\rho(r) = \left[N_1(r) - N_2(r) \right] q. \quad (18)$$

We can now write

$$\rho(r) = -2Nq \sinh \left[qV(r)/kT \right]. \quad (19)$$

Poisson's equation may be written

$$\nabla^2 V(r) = \frac{4\pi}{\epsilon_s} \rho(r) \approx \frac{8\pi Nq^2 V(r)}{\epsilon_s kT}, \quad (20)$$

which leads to a Debye screening radius of

$$\chi^2 = \frac{8\pi Nq^2}{\epsilon_s kT}, \quad (21)$$

and an interaction energy between particles of

$$W_D = \frac{\chi q^2}{\epsilon_s (1 + \chi R)}. \quad (22)$$

The relations (21) and (22) are reasonably valid for low concentrations and high dielectric constants, but for KCl and KBr the results can be at most qualitative since the dielectric constants are so small.

Several major difficulties arise in attempting to find χ . The first is that N is the concentration of dissociated positive-ion vacancies at a particular temperature T , which is not well-known for KCl with calcium impurities. Second, it is not certain

that it is proper to use the macroscopic dielectric constant or some "weighted" value of ϵ_s . In order to estimate the magnitude of W_D we assume that one-half of the vacancies and impurity ions are dissociated at 700°K, ϵ_s is 6.5 and R is 6.3×10^{-8} cm. We have an impurity concentration of 10^{18} cm^{-3} at most. Therefore,

$$\chi = 2.2 \times 10^6 \text{ cm}^{-1}$$

and

$$W_D = .057 \text{ e.v.}$$

The values used in the calculation were the maximum for the crystals of this investigation. Therefore, we may state that for our work the W_D above is the maximum possible.

CHAPTER IV

EXPERIMENTAL METHODS

General

Single crystals of potassium chloride and potassium bromide grown by both the Harshaw Chemical Company and the Naval Research Laboratory were used in this investigation. For convenience the Harshaw crystals will be designated by HAR and those grown by the Naval Research Laboratory will be referred to as NRL crystals. Table I gives all of the available information concerning size and impurity content for each crystal used in the experiment.

Light Scattering

Wavelength Dependence

The crystals were immersed in freshly distilled reagent quality benzene contained in a glass vessel fitted with light traps, plane windows and blackened exterior. The incident light was provided by a 500 watt projection lamp and a system of lenses mounted on an arm which could be rotated about a vertical axis passing through the center of the crystal. Thus, angular measurements could also be made with this system. Figure 3 shows the wavelength dependence apparatus.

TABLE 1
SPECIFICATIONS OF CRYSTALS IN THIS INVESTIGATION

Crystal Number	Type	Source	Primary Impurity	Percent Impurity	Size
1	KCl	HAR	Calcium	.001%	Cylinder 1.5" dia.
2	KCl	HAR	Calcium	.001%	Block 1"x1"x1"
3	KCl	HAR*	Calcium	.001%	Cylinder 1" dia.
4	KCl	HAR	Calcium	.001%	Cylinder 1" dia.
5	KCl	HAR	Calcium	.001%	Cylinder 1" dia.
6	KCl	HAR	Calcium	.001%	Cylinder 1" dia.
7	KCl	HAR	Calcium	.001%	Cylinder 1" dia.
8	KCl	HAR	Calcium	.001%	Cylinder 1" dia.
9	KCl	HAR	Calcium	.001%	Cylinder 1" dia.
10	KCl	HAR	Calcium	.001%	Cylinder 1" dia.
11	KCl	HAR	Calcium	.001%	Cylinder 1" dia.
12	KCl	HAR	Calcium	.001%	Cylinder 1" dia.
13	KCl	NRL	Cadmium	.0003%	Cylinder 1" dia.
14	KCl	NRL	Cadmium	.1%	Cylinder 2.5" dia.
15	KBr	HAR	Aluminum	.01%	Block 1"x2"x $\frac{3}{4}$ "
16	KBr	HAR	Aluminum	.01%	Block 1"x2"x $\frac{3}{4}$ "

* Crystals 3-13 were all cleaved from the same mother crystal.

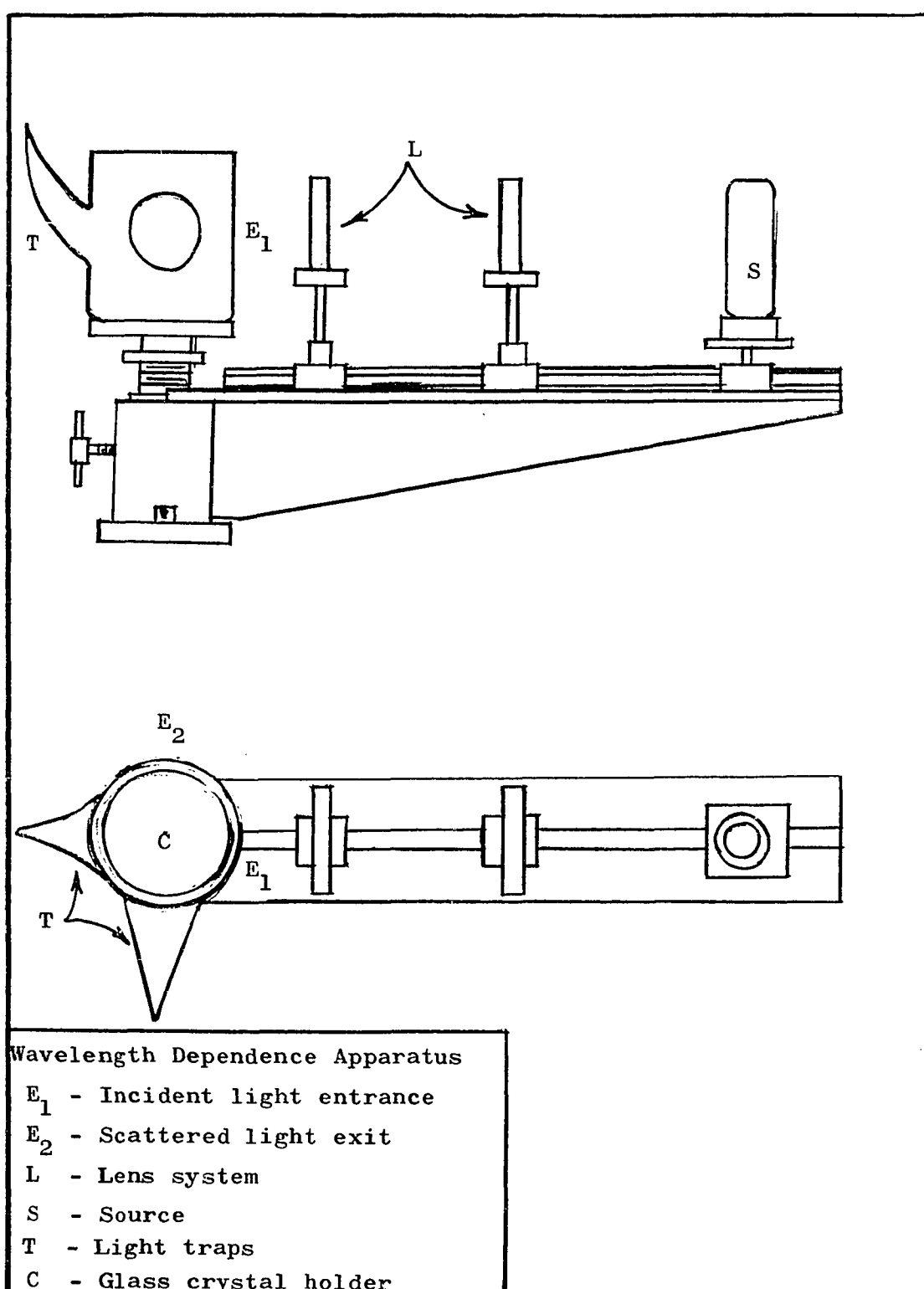


Fig. 3. Apparatus for Measuring Wavelength Dependence of the Light Scattering.

The incident light beam passing through the crystal was nearly parallel and had a cross-sectional area of about 1 cm^2 . The scattered light entered a Hilger E-1 quartz spectrograph whose cone of observation did not touch the directly illuminated walls of the crystal, while those portions of the front and rear walls which are in the cone were illuminated by the scattered light only. This arrangement, together with the very close matching of the refractive indices of the crystal and the benzene, ensured that the intensity of parasitic light was negligible. The effectiveness of the arrangement was tested by observation of the scattering from a bottle of highly distilled benzene substituted for the crystal. The benzene scattering followed Rayleigh's $1/\lambda^4$ -law throughout the spectral range investigated.

In order to make relative intensity measurements a seven step JACO rhodium-quartz filter was placed before the slit of the spectrograph. Spectra of the light scattered by the crystal and by the very pure benzene were recorded with equal exposure times on the same 103-ab or 103-ao Kodak photographic plate. The exposure varied from 6 to 12 hours depending on the composition of the sample and the orientation of the crystallographic axes with respect to the direction of the incident beam. Since the optical density of each filter step was known for the spectral range covered in the experiment and the benzene was known to follow Rayleigh's law, the intersections of the microphotometer traces for the various filter steps of the two spectra gave a direct measure of the absolute scattering power of the crystal as a function of

wavelength.

Angular Dependence and Polarization

The device shown in Figure 4 proved to be more convenient for large angular variation at constant wavelength than that described above. A cylindrical glass vessel, V, fitted with a pair of diametrically opposite side arms, P and Q, was surrounded by a close fitting aluminum cylinder, A. The crystal, C, rested on a glass table, T, and was immersed in benzene, B. Monochromatic mercury light ($\lambda = 4358\text{\AA}$) entered the system at P through a plane window. The scattered light passed through the slots, S, which were spaced at 5° intervals around A. The scattered light was recorded on a strip of photographic film, F, held around the outside of the apparatus by a clamp, H.

Kodak Royal Panchromatic film was used and was calibrated by using the JACO seven step filter. An H-D curve was found for every box of film used in the experiment. The exposure time for all angular dependence pictures was 30 minutes, and in order that scattering intensities could be compared accurately a consistent development procedure was followed. Eight pictures were developed simultaneously in developer Dk 60-a at 20°C for 4 minutes.

Exposures were taken with film on both sides of the apparatus in order to detect any assymetry in the scattering. Experiments with the benzene bottle in place of the crystal showed that the apparatus gave reliable results for scattering angles in the range 40° - 140° , if the observed scattering was corrected with the

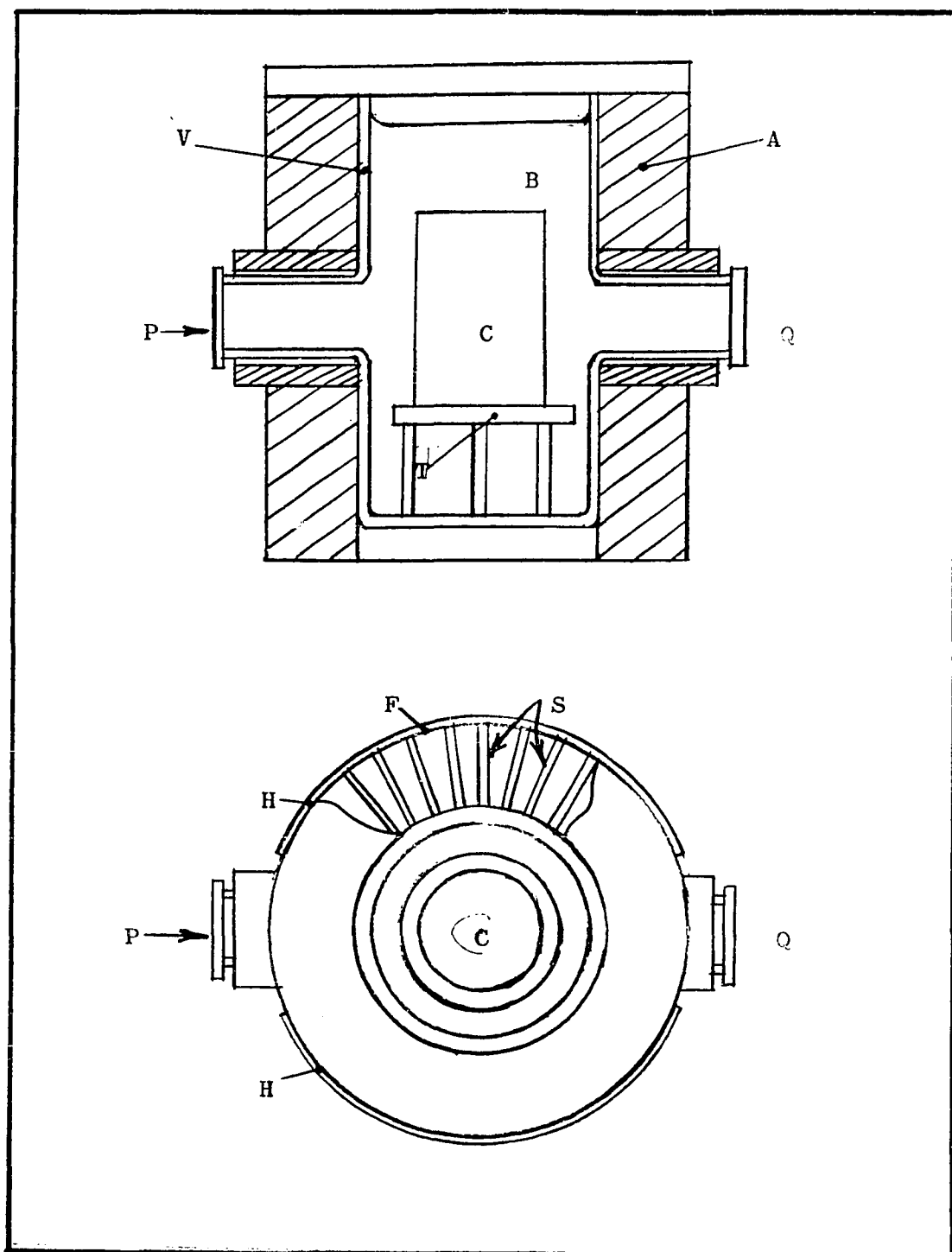


Fig. 4. Apparatus for Measuring Angular Dependence of the Light Scattering

factor $\sin 2\theta$ which takes into account that the scattering volume "seen" by the film through a slit depends on the scattering angle as $1/\sin 2\theta$.

Measurements of the polarization of the scattered light were made by the insertion of polaroid sheets between the film strips and the aluminum cylinder. A recording microphotometer was used to measure the photographic densities.

Heat Treatments

Quench

Crystals of Harshaw KCl and KBr were heated at $5^{\circ}\text{C}/\text{min.}$ to a temperature, T_Q , held at that temperature for two hours and then quenched at $15\text{-}25^{\circ}\text{C}/\text{min.}$ to room temperature in still air. This method produces a minimum amount of thermal stress in the crystal. A Hevi-Duty oven, equipped with a chromel-alumel thermocouple and capable of maintaining temperatures up to 1100°C , was used. A 600°C mercury-in-glass thermometer was also used to measure the temperature of the samples for temperatures up to 550°C . The crystals were placed on a Vycor boat throughout the heat treatment in order to minimize the possibility of diffusion of impurities into the crystal.

Anneal

In the annealing process the crystals were taken to 680°C rather slowly (less than $5^{\circ}\text{C}/\text{min}$) and held at that temperature for four hours. The crystals were then allowed to cool very slowly

at the rate of approximately 3°C/hr. This process took nine days.

Plastic Deformation

Cylindrically shaped single crystals of Harshaw KCl were placed in an Instron Tensile Testing Instrument, type TT-C-L, in such a way that they would be compressed in the axial direction. To prevent barreling, very smooth $\frac{1}{8}$ -inch thick plate glass plates, lubricated with water, were used in contact with the specimen. Care was taken to apply axial compression. Calibration curves of the holder were made before and after the samples were deformed. Essentially no change in the calibration was noted.

The deformation and recovery of the samples were measured and recorded automatically by the machine. By subtracting the zero point of deformation from the final recovery point, a measure of the plastic deformation was obtained. This value was checked by means of a micrometer measurement and the agreement of the two values was very good. It was also possible to obtain the stress-strain curves for the crystals.

Hardness Tests

Rockwell Tester #119 was used to do a superficial hardness test on crystals of Harshaw KCl. The test was made using a $\frac{3}{4}$ inch ball with no preload and a 15 Kg. weight. All the samples tested were cleaved from one large crystal and had the same type of surfaces.

This test gave only qualitative results due to the size of

the ball which had to be used. The ideal test would be to use a diamond indenter on a freshly cleaved surface.

Dislocation Etching

Large imperfections in the crystalline lattice which have an intrinsically higher vacancy concentration around them, such as dislocations and precipitates, will be preferentially attacked when the crystal surface is chemically etched. Dislocations are characterized by pyramidal pits and precipitates etch as large flat-bottomed pits.

There are several etchants suitable for KCl crystals. Sakamoto and Kobayashi³ have used dehydrated glacial acetic acid followed by an acetone rinse. They have also used acetic acid to which zinc ions have been added as an inhibitor. Moran⁴ used an etchant in which 95% by volume of the mixture consists of ethyl alcohol 25% saturated with barium bromide. The remaining 5% consists of methanol containing 100 grams per liter of BaBr₂.

In this investigation the etchant of Sakamoto and Kobayashi was found suitable for both KCl and NaCl. The etch time, however, was only about 5 seconds with zinc ions present in the solution compared to the 20 seconds found in their work. The etchant gave very good results on freshly cleaved surfaces if the etched surface was blotted on absorbent paper immediately after the acetone rinse.

³M. Sakamoto and S. Kobayashi, J. Phys. Soc. Japan 13, 800 (1958).

⁴P. R. Moran, J. App. Phys. 29, 1768 (1958).

CHAPTER V

LIGHT SCATTERING BY "AS GROWN" IONIC CRYSTALS

Wavelength Dependence

It is well known that the light scattering of benzene follows the Rayleigh - $1/\lambda^4$ law. Therefore, when the logarithm of the scattering power of benzene, B , at a particular scattering angle, 2θ , is plotted versus the logarithm of the wavelength of the incident light a straight line of slope -4 results. Thus, it is possible to use benzene scattering as an equipment check, and in Figure 5 it is evident that for the range of wavelengths employed the apparatus is reliable. Notice that the scattering by potassium chloride crystals for one scattering angle, $2\theta = 90^\circ$, differs for different orientations, ϕ , of the crystallographic axes with respect to the incident beam. It should also be noted that deviations from Rayleigh scattering occur at two distinct places in the figure. From this we could conclude, using the Mie theory as an approximation, that scattering centers of two different sizes are present. It is virtually impossible, however, to arrive at an estimate for the size of the scattering centers using this theory since solutions to the equation have been tabulated only for spherical scatterers. Because the observed scattering

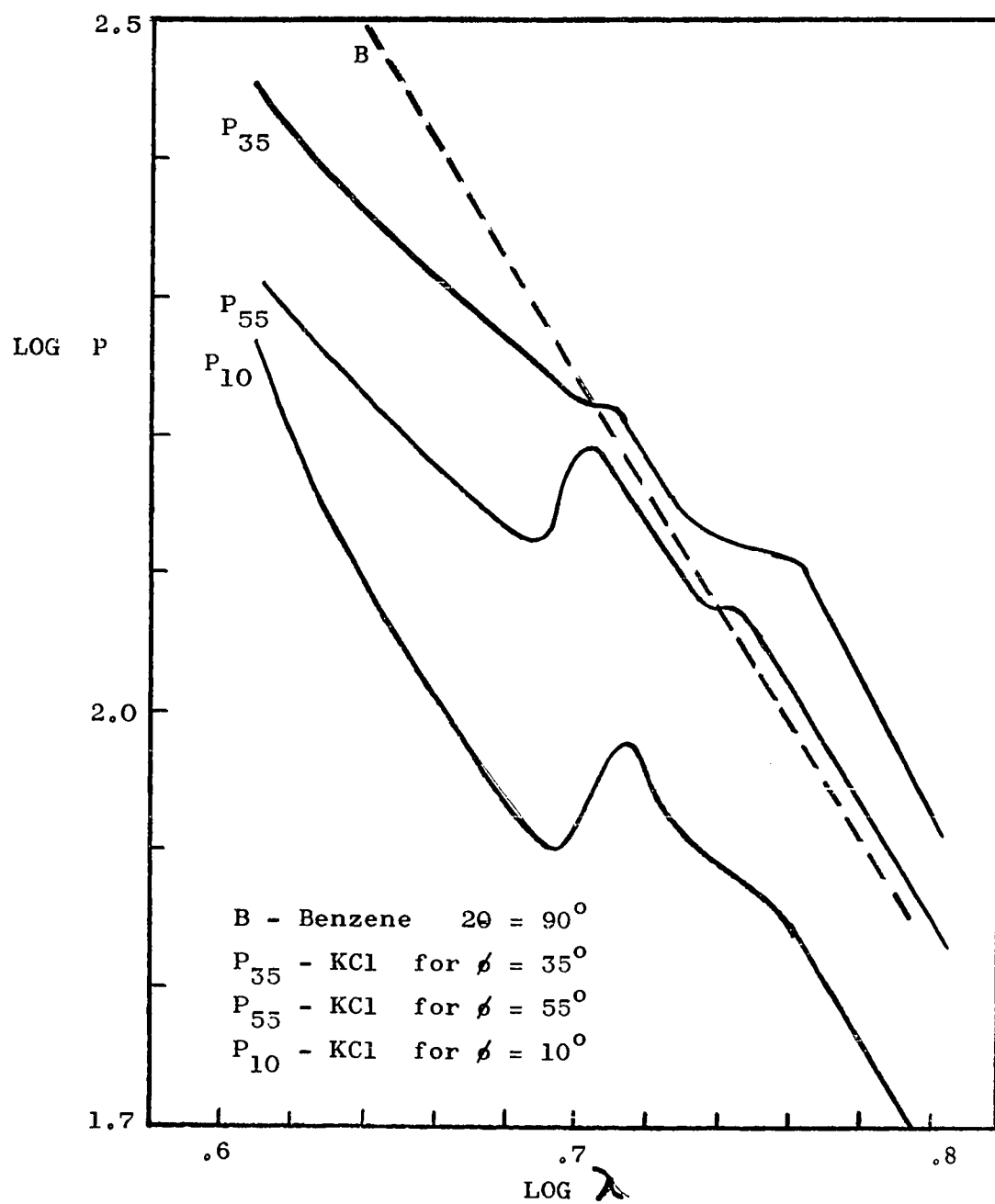


Fig. 5. Wavelength Dependence of Light Scattering by Benzene and KCl.

depends strongly on the orientation of the crystal we can almost certainly state that the scattering centers are not spherical.

Angular Dependence

Figure 6 illustrates that the apparatus used in investigating the angular dependence of light scattering is reliable for scattering angles from 40° to 140° . The upper curve, P_π , is the normal component benzene scattering. P_σ is the horizontal component and the dashed line is the horizontal component after the Thompson factor, $\cos^2 2\theta$, has been subtracted. The depolarization ratio for benzene from Figure 6 is .44; this can be compared with the experimental value of .42 given by Bhagavantam.¹

As illustrated by the figures the scattering power, P , depends strongly on the orientation of the crystal with respect to the incident light beam, measured by the angle ϕ . For each constant angle ϕ , $P(\theta)$ has pronounced principal maxima at $\theta = \theta_{\max}$ and $\theta = \theta_{\max-180^\circ}$, and if ϕ varies by an amount $\Delta\phi$, $2\theta_{\max}$ is shifted by an amount $2\Delta\phi$ (compare Figure 7). Thus, the principal scattering maxima show an angular variation characteristic for reflection by two planes or rods making an angle of 90° with each other and having a fourfold axis of symmetry.

Scattering by the NRL crystals is shown in Figure 10. There is no orientational dependence of these crystals and no peaks of the scattering power exist. Note the difference in scattering

¹S. Bhagavantam, Scattering of Light and the Raman Effect-(Andhra University, Waltair, 1940).

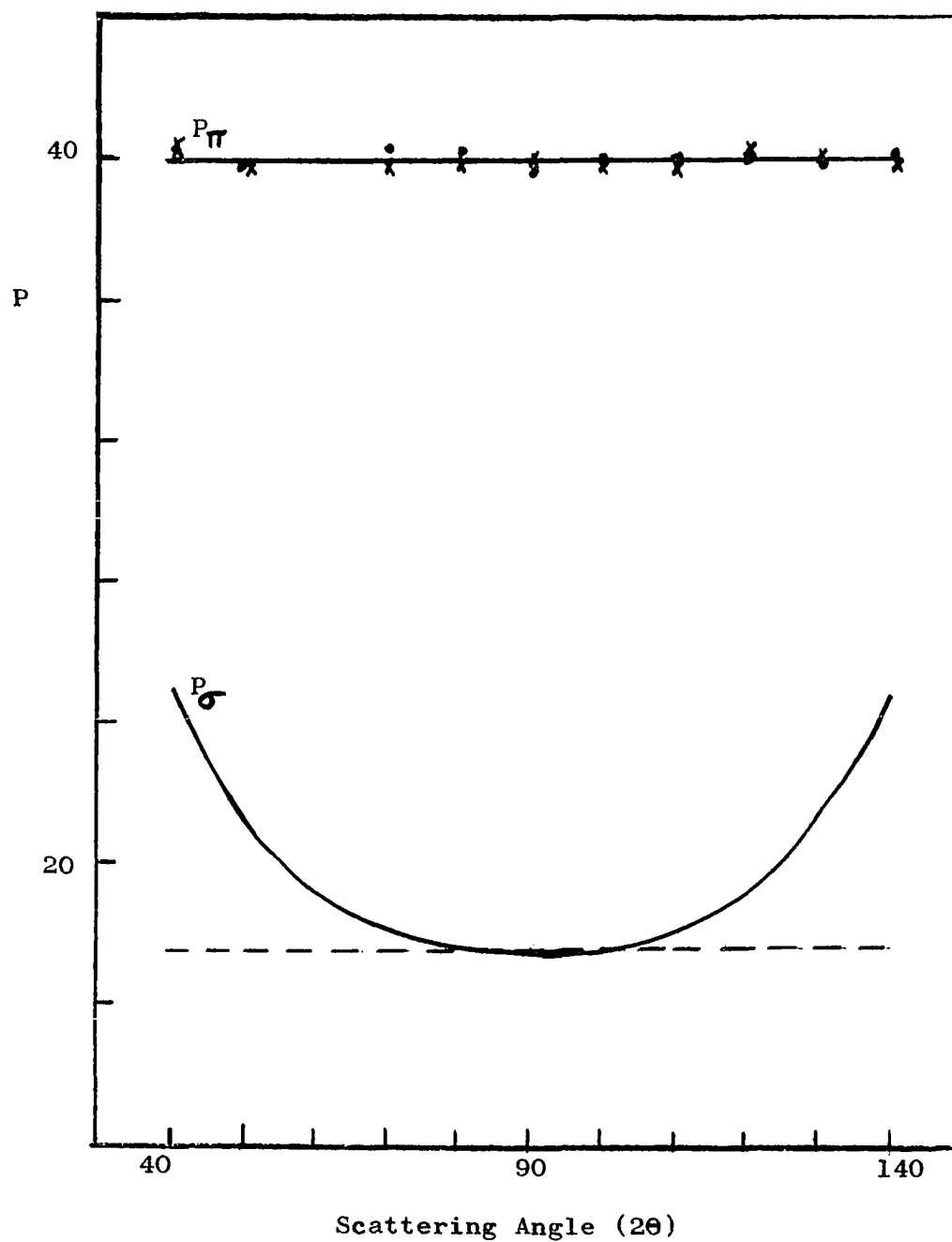


Fig. 6. Light Scattering by Benzene

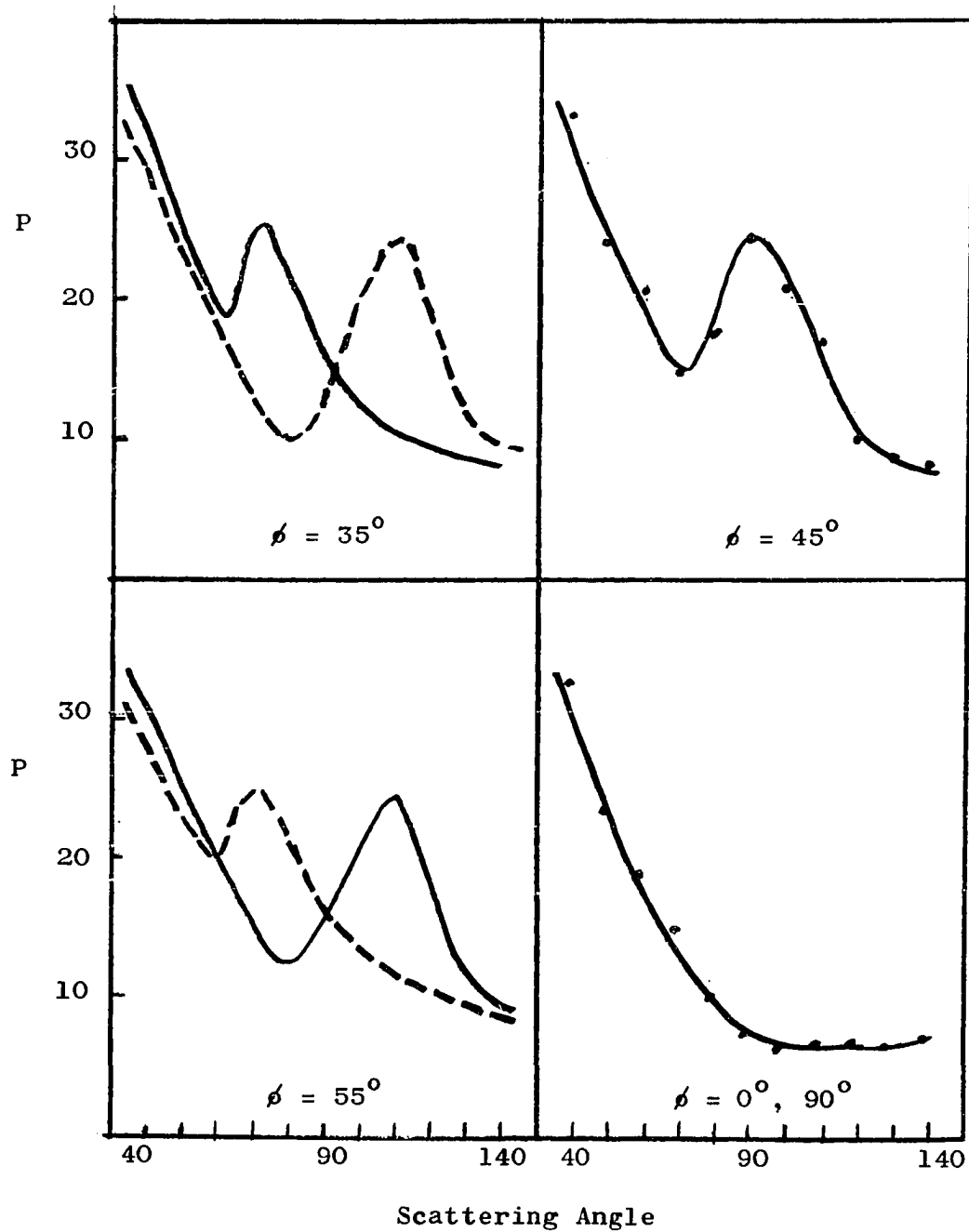


Fig. 7. Orientational Dependence of Light Scattering by Crystal HAR 1.

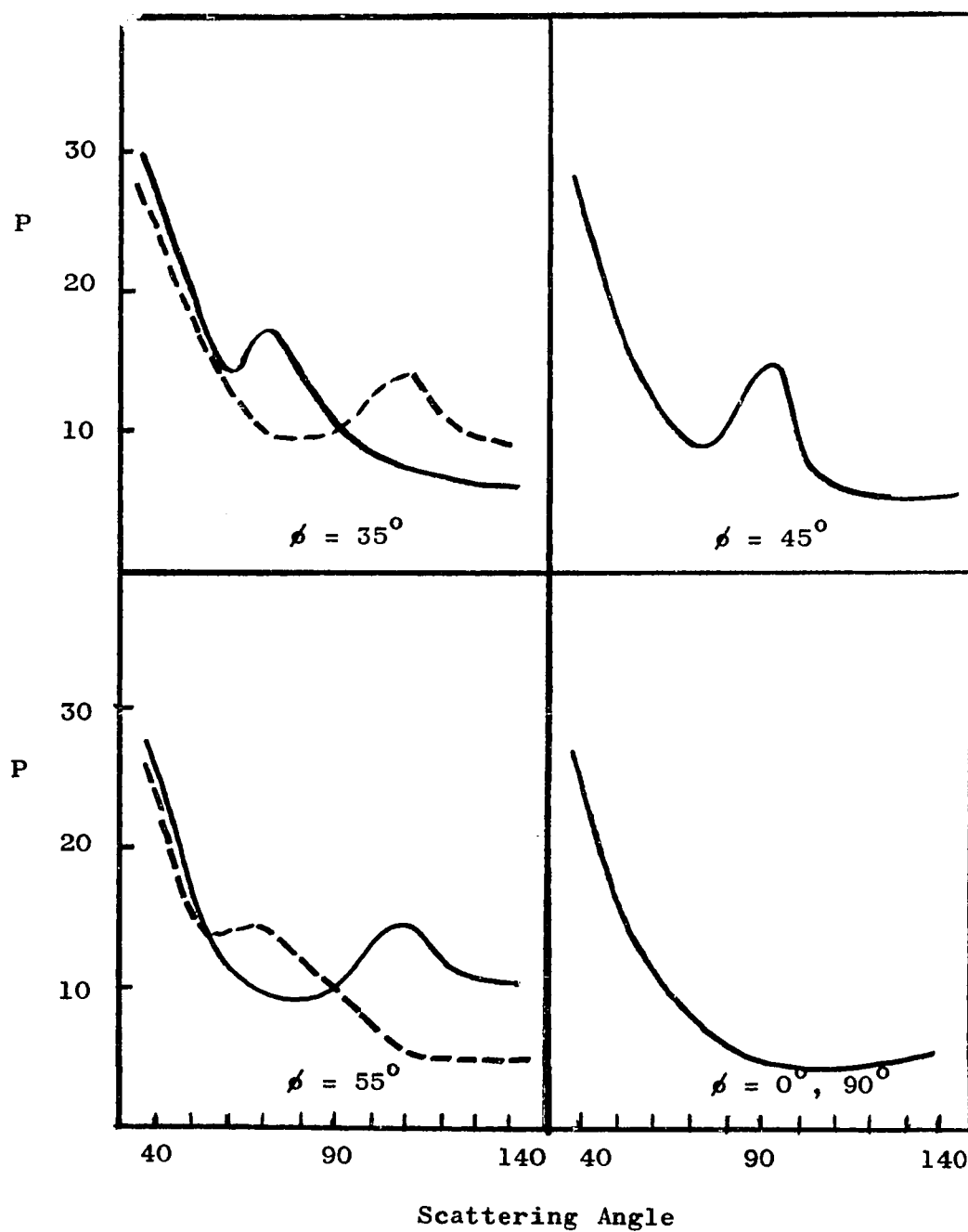


Fig. 8. Orientational Dependence of Light Scattering by Crystal HAR 2.

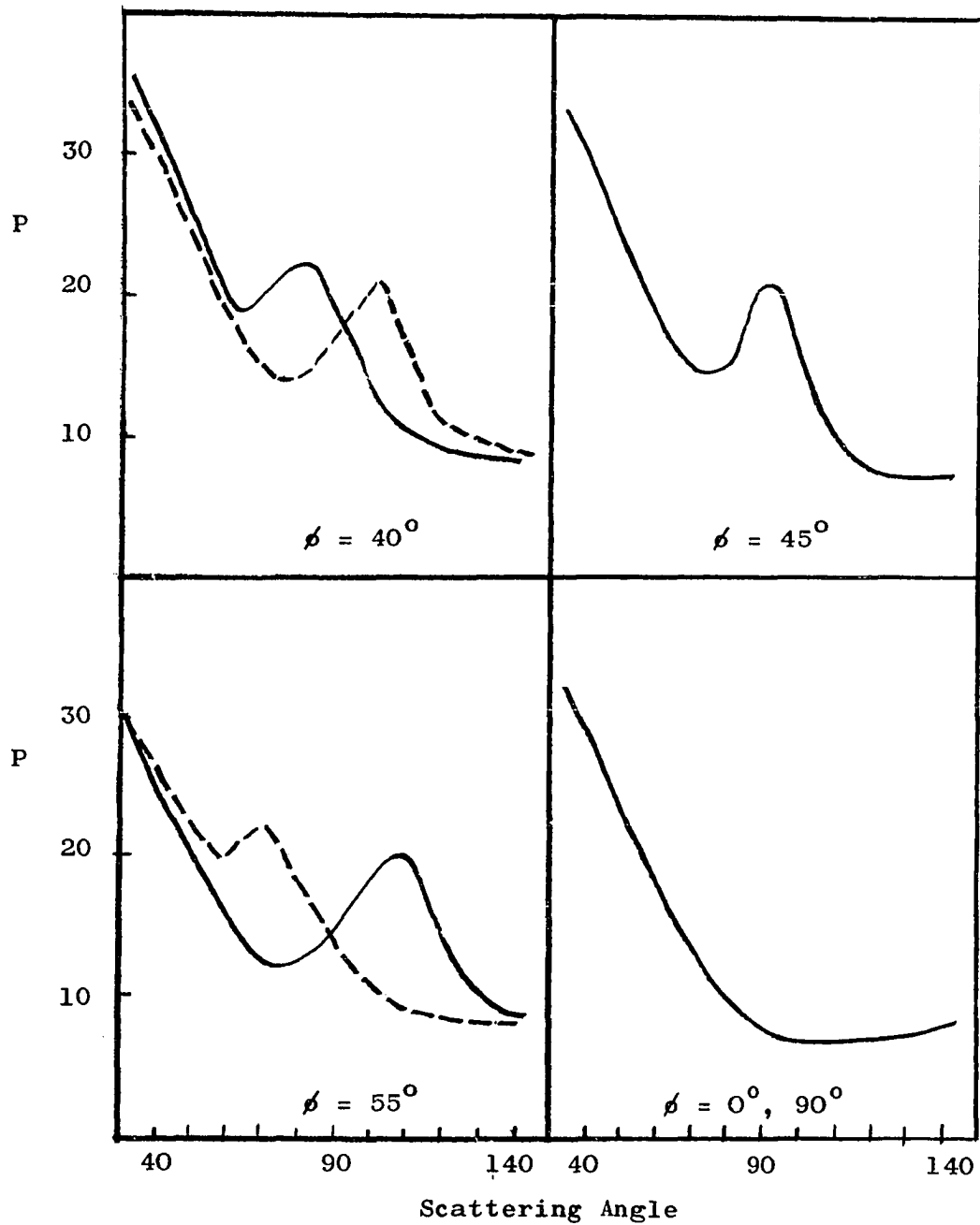


Fig. 9. Orientational Dependence of Light Scattering by Crystals HAR 3-12.

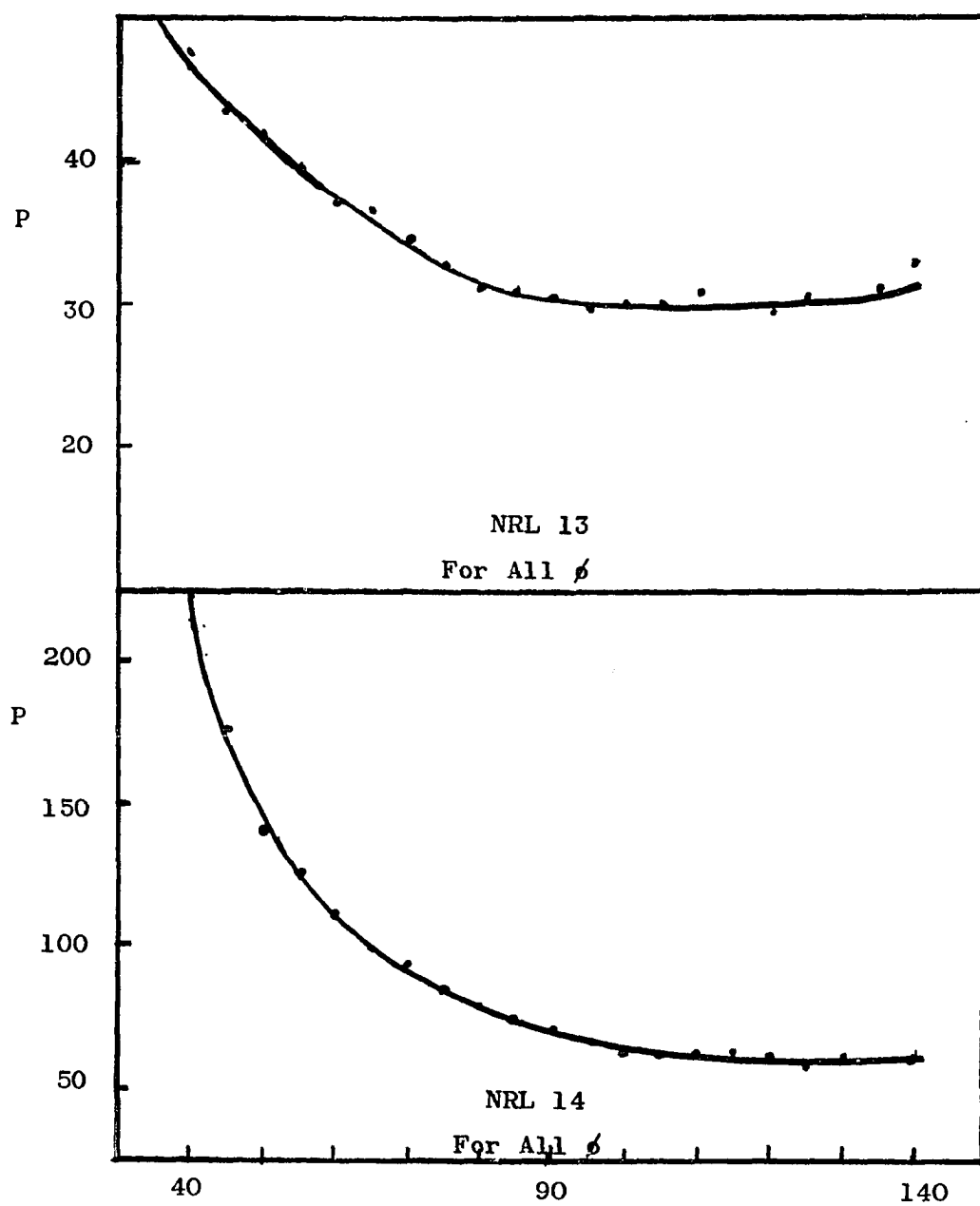


Fig. 10. Light Scattering by NRL 13 and NRL 14.

power of the two crystals and that despite this difference the two scattering patterns are very similar in shape. The principal difference between the crystals is that NRL 14 is much more heavily "doped" with impurity than is NRL 13.

Measurements at only one orientation, $\phi = 0$, were made with Harshaw potassium bromide. The "as is" angular dependence of the scattering is shown in Figure 11. No relative maxima appear in the scattering for this orientation, and the shape of the crystals in combination with a poor refractive index match with the immersion fluid precluded any study of other orientations.

Discussion of Results

In order that an adequate discussion can be made we present a very brief theoretical treatment of light scattering by dislocations.

Consider a crystal of volume V_1 containing $n(x,y,z)$ isotropic point imperfections per unit volume in position $\underline{r}_k$ with effective polarizability sufficiently small to justify neglect of multiple scattering. The scattering power P for natural incident light at distance R from the crystal is given by the formula

$$P(\theta, \lambda) = \sigma(\theta, \lambda) \left| \sum_k \alpha_k^* e^{-i\mathbf{k} \cdot \mathbf{r}_k} \right|^2 \quad (1)$$

where

$$P(\theta, \lambda) = I(\theta, \lambda) / I_0.$$

I_0 , $I(\theta, \lambda)$ = intensity of the incident and scattered light respectively

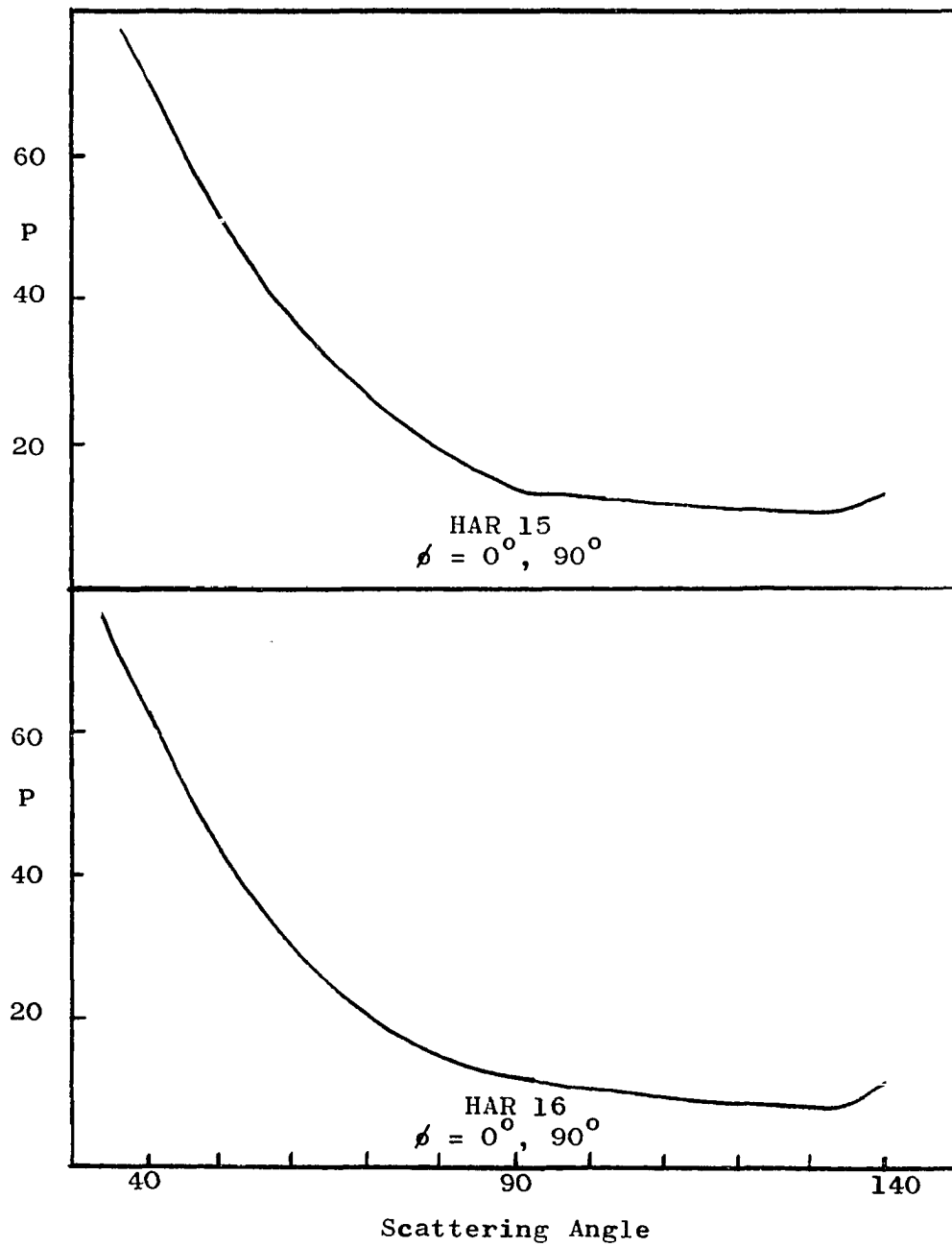


Fig. 11. Light Scattering by HAR 15 and HAR 16

2θ = angle of deflection

$\lambda = \lambda_0/n$ = wavelength in medium

$$\sigma = 8\pi^4 (1 + \cos^2 2\theta) / \lambda_0^4 R^2$$

$$\underline{\mu} = (2\pi/\lambda)(\underline{S} - \underline{S}_0), \quad |\underline{\mu}| = (4\pi/\lambda) \sin \theta$$

$\underline{S}_0, \underline{S}$ = unit vectors in direction of the incident and scattered light respectively; they define the plane of observation.

The vector $\underline{\mu}$, situated in the plane of observation, bisects the scattering angle 2θ and may be formally interpreted as the normal to a reflecting plane which produces the angular deflection. Since $\underline{\mu}$ has the dimension of a reciprocal length, $P(\theta, \lambda)$ interpreted as a function $P(\underline{\mu})$ is often referred to as the distribution of scattering power in reciprocal space. If the scattered light is observed through an analyzer which transmits light polarized normal to the plane of observation, the coefficient σ reduces to $8\pi^4/\lambda_0^4 R$ and the angle dependence of the scattering intensity is solely determined by the vector $\underline{\mu}$ in the phase exponential. We will consider only this simple case.

The summation over point imperfections may be replaced by an integration if the continuous density distribution $\rho(x, y, z)$, or pair distribution $P(x, y, z)$, is introduced into the theory. Equation (1) is then transformed into equivalent relations

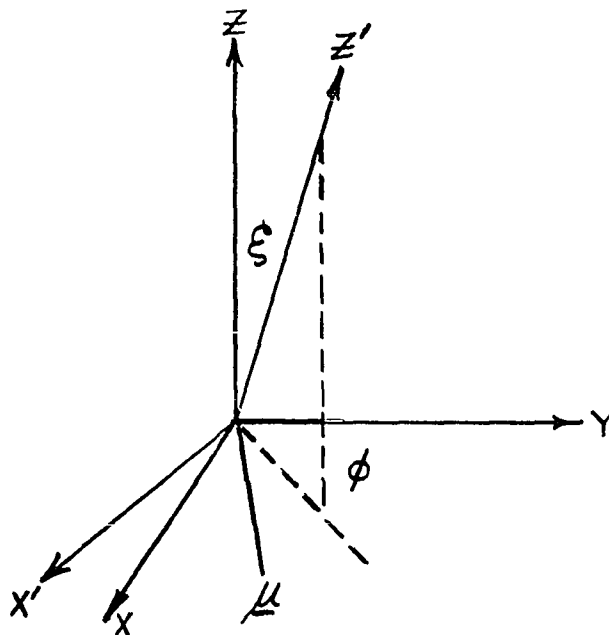
$$P(\theta, \lambda) = \sigma(\overline{\alpha^*})^2 \left| \iiint \rho(r) e^{i\underline{\mu} \cdot \underline{r}} d\underline{r} \right|^2 = \sigma(\overline{\alpha^*})^2 \iiint P(r) e^{-i\underline{\mu} \cdot \underline{r}} d\underline{r} \quad (2)$$

where

$$\overline{\alpha^*} = \sum_{\underline{r}} \bar{n}_{\underline{r}} \alpha_{\underline{r}}^* + \Delta \alpha_0 \quad (3)$$

is the average effective polarizability per unit volume of the system. It is represented as the sum of two terms: the direct contribution $\sum_l \bar{n}_l \alpha_l^*$ of the point imperfections of type l with average concentration $\bar{n}_l$, and the change, $\Delta\alpha_o$, in the polarizability in the ideal crystal matrix produced by the electric and elastic fields surrounding the point imperfections. We shall assume that $\bar{\alpha}^*$ is isotropic to a first approximation.

We shall now briefly outline the treatment of scattering by dislocations as presented by Lester.² The reader is referred to the original work for a more complete presentation. In order to apply equation (2) to the scattering from a bad region of cylindrical form, we define the following vectors and coordinate systems:



²D. M. Lester, Thesis, University of Oklahoma (1960).

The primed system is fixed in the bad region with Z' along the axis. The incident light is in the y direction, $\underline{r}$ is the position vector of a volume element, ξ is the inclination of the bad region axis to the vertical and ϕ is the orientation angle of the projection of the bad region axis into the xy -plane.

The integral in equation (2) must be in terms of cylindrical coordinates in primed space while $\underline{\mu}$ is expressed in the unprimed system. It is readily shown that

$$\underline{r}' \cdot \underline{\mu}' = A r \cos \chi - B r \sin \chi + C z \quad (4)$$

where

$$A = \mu \cos (\theta - \phi)$$

$$B = -\mu \sin (\theta - \phi) \cos \xi$$

$$C = -\mu \sin (\theta - \phi) \sin \xi$$

$$\chi = \text{angle between } \underline{x}' \text{ and } \underline{r}.$$

The scattering power then becomes

$$P(\theta, \lambda) = \sigma \overline{\alpha}^*{}^2 \left\{ \iiint r \rho(r) \exp \left[-i(A r \cos \chi - B r \sin \chi + C z) \right] dr d\chi dz \right\}^2 \quad (5)$$

The integration over z can be carried out without specifying ρ since ρ is only a function of r and χ at most. Thus

$$P(\theta, \lambda) = 4\sigma \overline{\alpha}^*{}^2 \frac{\sin^2 C z^*/2}{C^2 z^{*2}} \left[\iint r \rho(r) e^{-i(A r \cos \chi - B r \sin \chi)} dr d\chi \right] \quad (6)$$

We specify a radial distribution function $\rho(r)$ which has the form

$$\rho(r) = \frac{V^*}{2\pi r^* z^*} r^{-1} e^{-r/r^*} \quad (7)$$

where the term in the parenthesis is determined by the normalization condition

$$\int_0^{2\pi} \int_0^{\infty} \int_{-z^*/2}^{z^*/2} \rho(r) r dr d\chi dz = V^* \quad (8)$$

In (7) r^* is a characteristic radius of the cylindrical bad region and V^* is its "weighted" volume. Using $\rho(r)$ as given by equation (7) we have by integration over r ,

$$P(\theta, \lambda) = \sigma \alpha^{*2} \left(\frac{\sin(z^*/2)}{C z^*} \right)^2 \left(\frac{V^*}{\pi} \right)^2 \left[\int_0^{2\pi} \frac{d\chi}{1 + i r^* (A \cos \chi + B \sin \chi)} \right]^2 \quad (9)$$

Integration over χ gives

$$P(\theta, \lambda) = 4 \sigma \alpha^{*2} \left(\frac{\sin(z^*/2)}{C z^*} \right)^2 V^{*2} \left[\frac{1}{1 + r^{*2} (A^2 + B^2)} \right] \quad (10)$$

When this equation is evaluated for dislocations about 50,000 Å in length, 200 Å in diameter and oriented along the crystallographic axes, the results compare very well with the experimental observations. Only in the forward scattering is there any difference between theory and experiment.

Now we would like to calculate the size of the scattering centers and show that they are most probably dislocation lines. To do this we must first consider the capabilities and limitations of the light scattering method. Therefore, we present a brief treatment of what information can be obtained from light scattering. For a more detailed treatment the reader is referred to the paper by Theimer, et al.³

³O. Theimer, C. A. Plint, and W. A. Sibley, Ann. Phys. 9, 475 (1960).

If the scattering system is inhomogeneous, e.g. containing numerous bad regions of similar shape, a large fraction of the distribution functions $\rho(\underline{r}'+\underline{r})$ are similar and their superposition leads to a structure having the average shape of all the different bad regions. Consider, for instance, a cubical network of dislocation lines along the x,y,z axes approximately with strongly varying meshwidth. The pair distribution function, defined by

$$P(r) = \iiint_{-\infty}^{\infty} \rho(r') \rho(r'+r) d\underline{r} \quad (11)$$

will have the form of a three-dimensional cross with diffuse boundaries and with arms having a half length inversely proportional to the angular spread of the dislocation lines along the x,y,z axes.

No trace of a network will survive the averaging process if the meshwidth is sufficiently irregular and the system scatters like an equivalent system of independent, "identical," "virtual" scattering units, crosses in our case, which are randomly distributed in space and do not have systematic phase relations among each other. The form and orientation of the virtual scattering units is determined by $p(\underline{r})$. But from the virtual units, only the average properties of the scattering regions can be obtained and only if these regions are similar in shape and orientation can the virtual units be identified with the true scattering regions.

The method of a Fourier analysis of light scattering data⁴

⁴Ibid.

has been described in detail elsewhere. The distribution of scattering power in reciprocal, μ , space can be approximately represented by the expression

$$P(\mu) = P_0 e^{-b(|\mu_x| + |\mu_y|)} \left[1 - a|\mu_x||\mu_y| \right] + P_n(\mu) \quad (12)$$

where $b \sim .11 \times 10^{-5} \text{ cm}$, $a \sim .38 \times 10^{-10} \text{ cm}^2$, $P_n(\mu)$ is thermal scattering plus scattering by uniformly distributed point imperfections, and $P_0 \sim 29$ in arbitrary intensity units in which scattering by benzene is 39. Both intensities refer to scattering experiments in which only scattered light polarized normal to the plane of observation is measured.

By means of the Fourier analysis, equation (12) may be used to find an expression for the projection of the pair distribution function into the plane of observation. This may be written approximately as

$$P'(x,y) = \frac{P_0}{2\pi^3 \sigma \alpha^{*2} (b^2 + x^2)(b^2 + y^2)} \left[b^2 - \frac{a(b^2 - x^2)(b^2 - y^2)}{(b^2 + x^2)(b^2 + y^2)} \right] \quad (13)$$

Figure 12 depicts $P'(x)$ as a function of x for several constant y values. From this graph we can obtain a characteristic radius, r^* , for the cross-section of the scattering center. In this case $r^* = 1 \times 10^{-6} \text{ cm}$. Since the pair distribution function determines only the shape of the virtual scattering units we cannot extend this evaluation much further.

It is rather well known that edge dislocations in the alkali halides lie in $\{110\}$ slip planes in $\langle 100 \rangle$ directions.

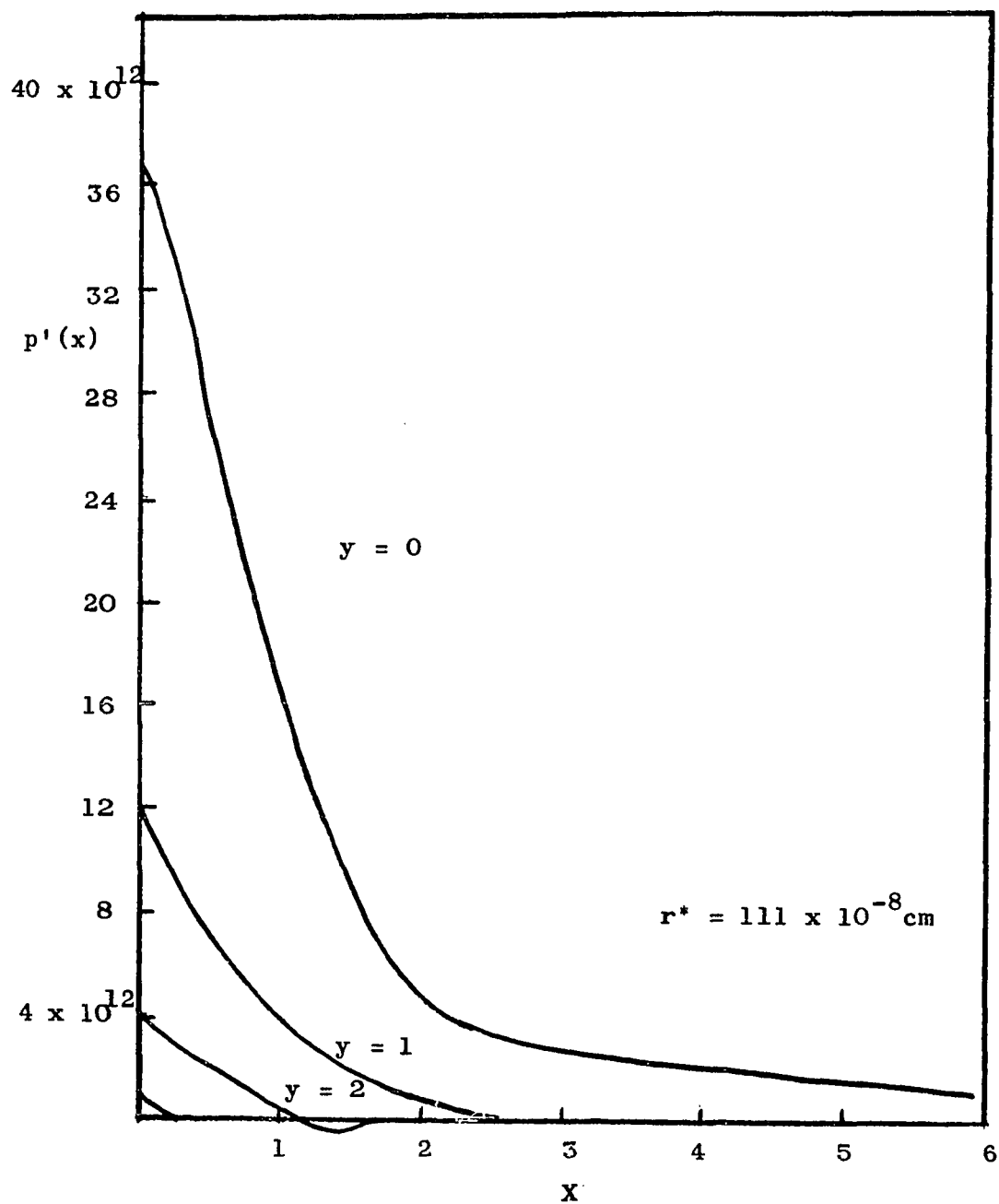


Fig. 12. Pair Distribution Function for HAR 3-12.

This means that these dislocations would form a network which would be characterized by the same pair distribution function and symmetry as we observe experimentally. As mentioned previously, the edge dislocations possess both an elastic strain field and an electrostatic field so that they should be, if one includes the cloud of point defects, somewhat larger than the screw dislocations. Screw dislocations lie in $\langle 110 \rangle$ directions on $\{100\}$ slip planes.

In summary, we may say that the scattering centers are most probably edge dislocations having a characteristic diameter of between 100 and 200×10^{-8} cm and a length of about $50,000 \times 10^{-8}$ cm.

The NRL crystals apparently have scattering centers with a characteristic size of 1300 to 1600×10^{-8} cm. Again the disadvantage of having to use a pair distribution function arises. For instance, the scatterers could be spheres with diameter 1500×10^{-8} cm, or they could be rods of length 1500×10^{-8} cm which are randomly oriented in the crystal. The pair distribution function cannot distinguish between individual scattering units in cases where the sample has the same scattering pattern for all ϕ .

Since only one orientation of the Harshaw potassium bromide crystals could be investigated because of the shape of the crystals, no analysis of the pair distribution function for these crystals could be attempted.

Another interesting aspect of the scattering data is the magnitude of the scattering power, P . A comparison of the scatter-

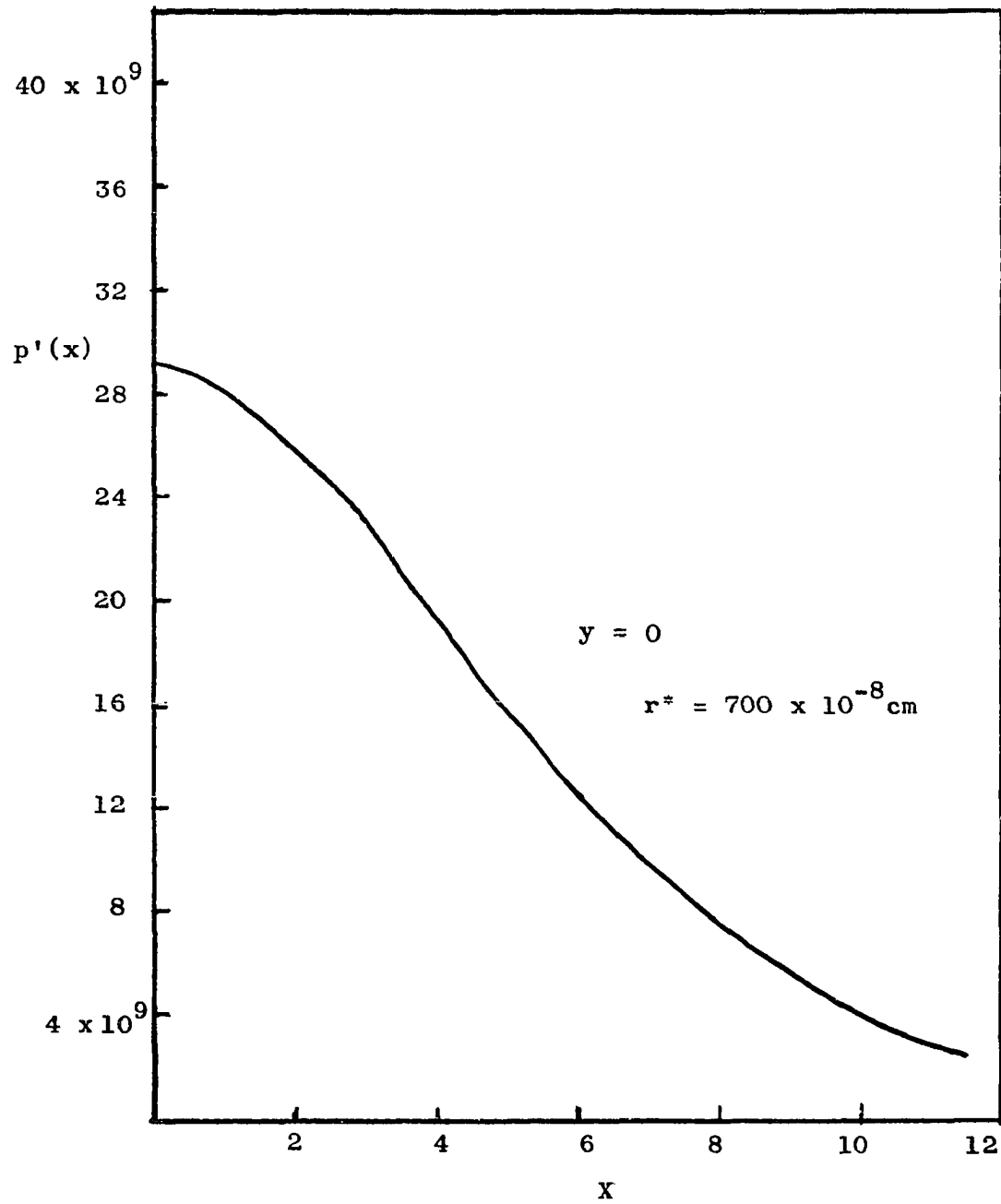


Fig. 13. Pair Distribution Function for NRL 14.

ing power of KCl to that of Benzene shows that at room temperature the magnitude of the scattering power is about thirty times larger than thermal scattering. From the scattering formula of equation 10 a relationship can be determined between the scattering power, the number of dislocations, N^* , the volume of the dislocation line, V^* , and the number of point scatterers around the line, n^* . This is written as

$$P'(\theta, \lambda) \simeq 10^{-44} N^* n^{*2} V^{*2}. \quad (14)$$

The value for P' is fixed at about 10^{-24}cm^3 by benzene scattering, and this gives a relation between N^* , n^* , and V^* . As will be shown later when N^* and V^* are given values consistent with experimental and theoretical considerations, we find $n^* \simeq 10^{20} \text{cm}^{-3}$.

CHAPTER VI

EFFECT OF HEAT TREATMENTS ON DISLOCATIONS IN IONIC CRYSTALS

Quench Effects

Experimental Results

The purpose of performing the quenching experiments was to determine the activation energies of any reactions involving point defects and dislocations. In the discussion of previous work, Chapter II, two possible interactions between vacancies and dislocations were found. As the edge dislocation line has an affinity for vacancies because of the elastic and electrostatic fields associated with it, we might expect free vacancies to be trapped at the dislocation line. Vacancy-impurity ion complexes, however, should be relatively weakly attracted to the region of the dislocation line. Thus, as the vacancy-impurity ion complexes are dissociated it is possible that a number of the freed vacancies will migrate to dislocations. Similarly, it is possible that as Schottky defects are formed they will move to dislocations.

To facilitate the determination of activation energies we have plotted $\log_e P$ against $1/T_Q^{\circ} \text{K}^{-1}$ in Figures 14 and 15. T_Q is the highest temperature reached before quenching the crystal. In

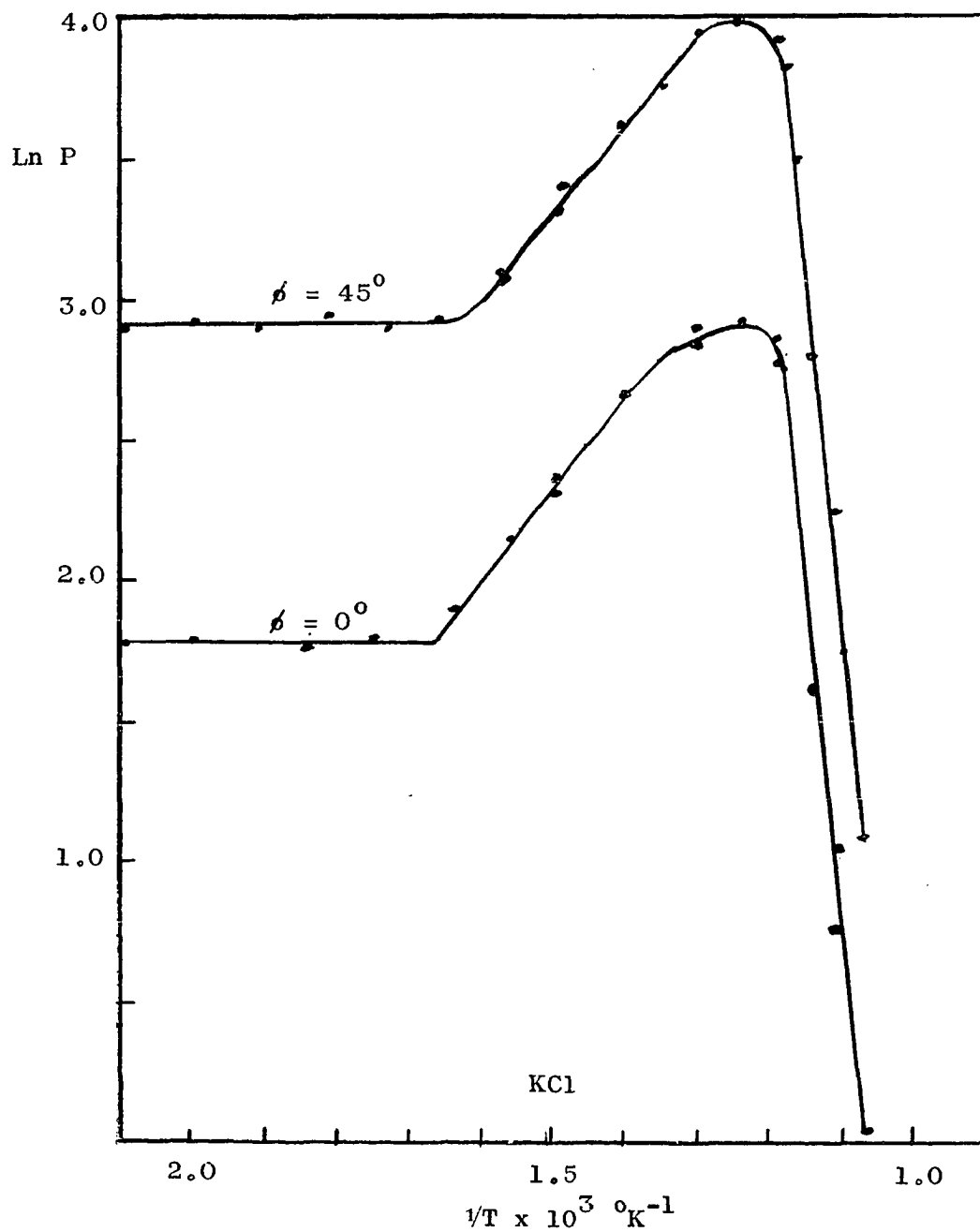


Fig. 14. Light Scattering by HAR 3-9 after Quench from Various Temperatures

the figures the slopes of the experimental curves depend on the activation energies of the reactions. It must be admitted that the defect configuration which is quenched into the crystal may not correspond identically to the equilibrium configuration at T_Q since some annealing will occur. It should also be pointed out, however, that defects in the vicinity of edge dislocations are much less mobile than defects in the good part of the crystal due to the binding effect of the dislocations on point defects. For this reason the defect configuration around the dislocation line should be very nearly that corresponding to the temperature T_Q .

Figure 14 shows the change in scattering power for different quench temperatures, T_Q , in potassium chloride. Seven different crystals, all from the same growth melt, were used, and it was found that the scattering was independent of past history as far as heat treatments are concerned. For example, the seven crystals were individually quenched from different T_Q in the range 150°C to 625°C . Then the crystal which had been quenched from 150°C was successively quenched from 250°C , 300°C , 400°C , 475°C , and 625°C , and the data from this crystal matched the data from those which had no prior heat treatment but were taken directly to a particular temperature and then quenched. After demonstrating this, it was possible to use one crystal to duplicate the complete "quenching" curve. We were also able to show that no essential differences occurred if the crystals were furnace cooled rather than "still

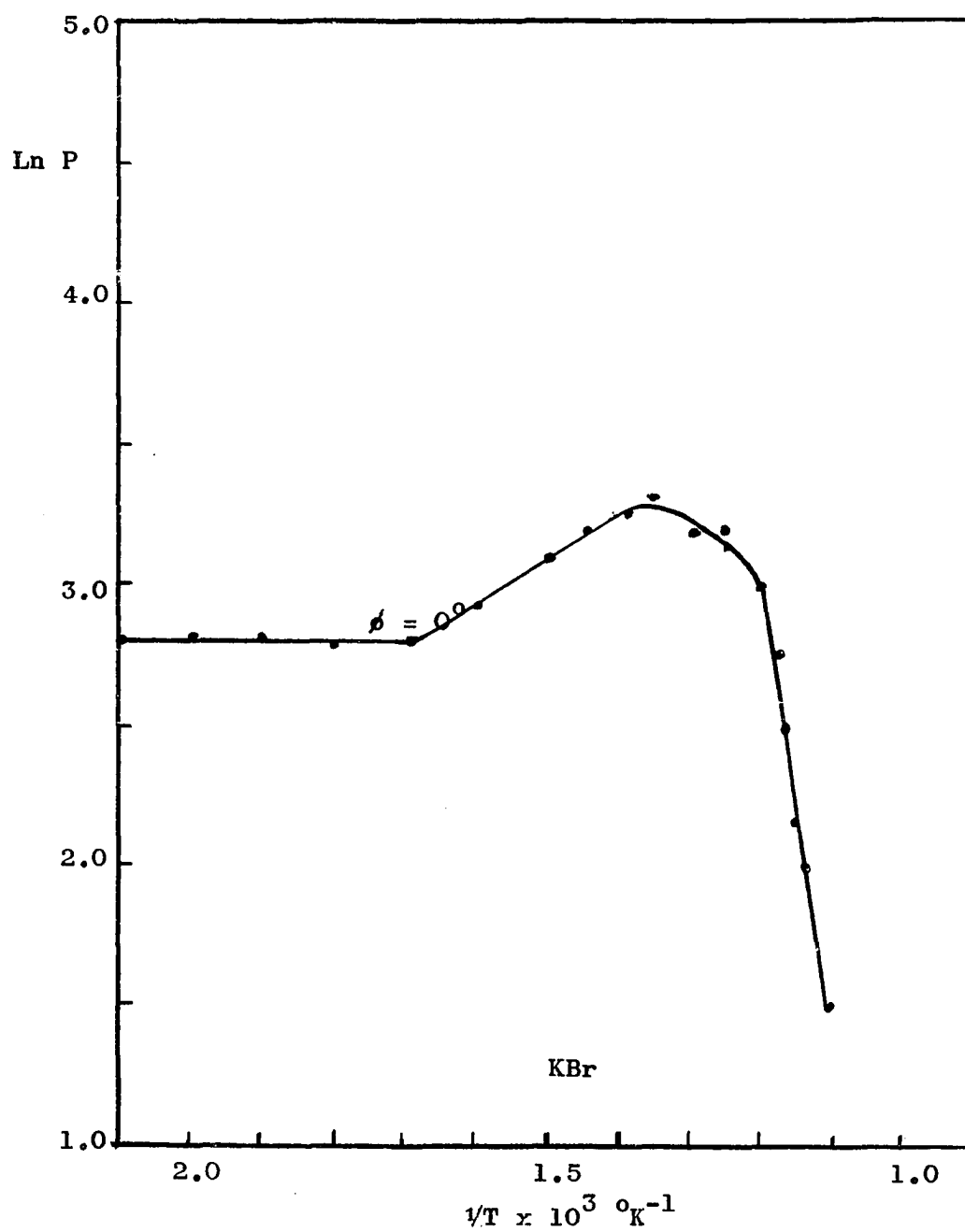


Fig. 15. Light Scattering by HAR 15 and 16 after Quench from Various Temperatures

air" quenched. Crystals HAR 4 and HAR 5 were placed in the furnace, heated to 500°C and then HAR 4 was still air quenched and HAR 5 was allowed to cool in the furnace. Both crystals showed the same increase in scattering over the room temperature value. Thus, it appears that the increase in scattering power exhibited by the crystals in the region $300^{\circ}\text{C} - 550^{\circ}\text{C}$ is most probably not due to thermal strains introduced by the quenching. We have also investigated crystals quenched from 650°C using the polarizing microscope and have found no significant quenching strains. The effect of quench treatments on potassium bromide is portrayed in Figure 15.

Since both KCl and KBr behave in a similar manner we will specify different stages of the curves from both materials by number. Stage I will consist of the flat portion of the curve and the part of the curve in which the scattering power increases with increasing temperature. Stage II will be the "leveling off" of this increase, and stage III will be the sharply decreasing section. It is interesting to note that although the graphs for KCl and KBr have the same general form the temperatures of demarcation between the various stages differ appreciably.

Discussion of Results

The scattering power, P , must be associated with the concentration of point scatterers within the "bad regions" or scattering centers of the crystal. In Chapter V equations (2) and (3) show that P is proportional to $\bar{n}^{*2}$, where $\bar{n}^*$ is the excess con-

centration of point scatterers in the bad regions. Now the point scatterers can be either vacancies or impurities in ionic crystals, and previous calculations have shown that vacancies probably provide the major contribution to the scattering.

If we assume that $\bar{n}^*$ is the excess concentration of vacancies around dislocation lines we can then evaluate the scattering in terms of point defects. N^* , the concentration of bad regions per unit volume, and V^* , the volume of the bad region, also enter the scattering formula. For stage I and stage II N^* is essentially constant as can be demonstrated by chemical etching methods. From Figure 16 it is possible to use light scattering methods to show that N^* and V^* remain constant for the temperature range under consideration. In the figure no change in the shape of the pattern of the curve scattering power versus scattering angle is apparent. The shape of this pattern is determined by both r^* , the effective radius of the dislocation, and z^* , the characteristic length of the dislocation line. Since there is no change in the scattering pattern for stages I and II we are justified in assuming that V^* is approximately constant.

A discussion of the possible physical mechanisms which cause changes in the scattering power as a function of temperature will now be undertaken. Each stage of the experimental curves will be investigated separately.

Stage I

For this region we will consider first the case for which

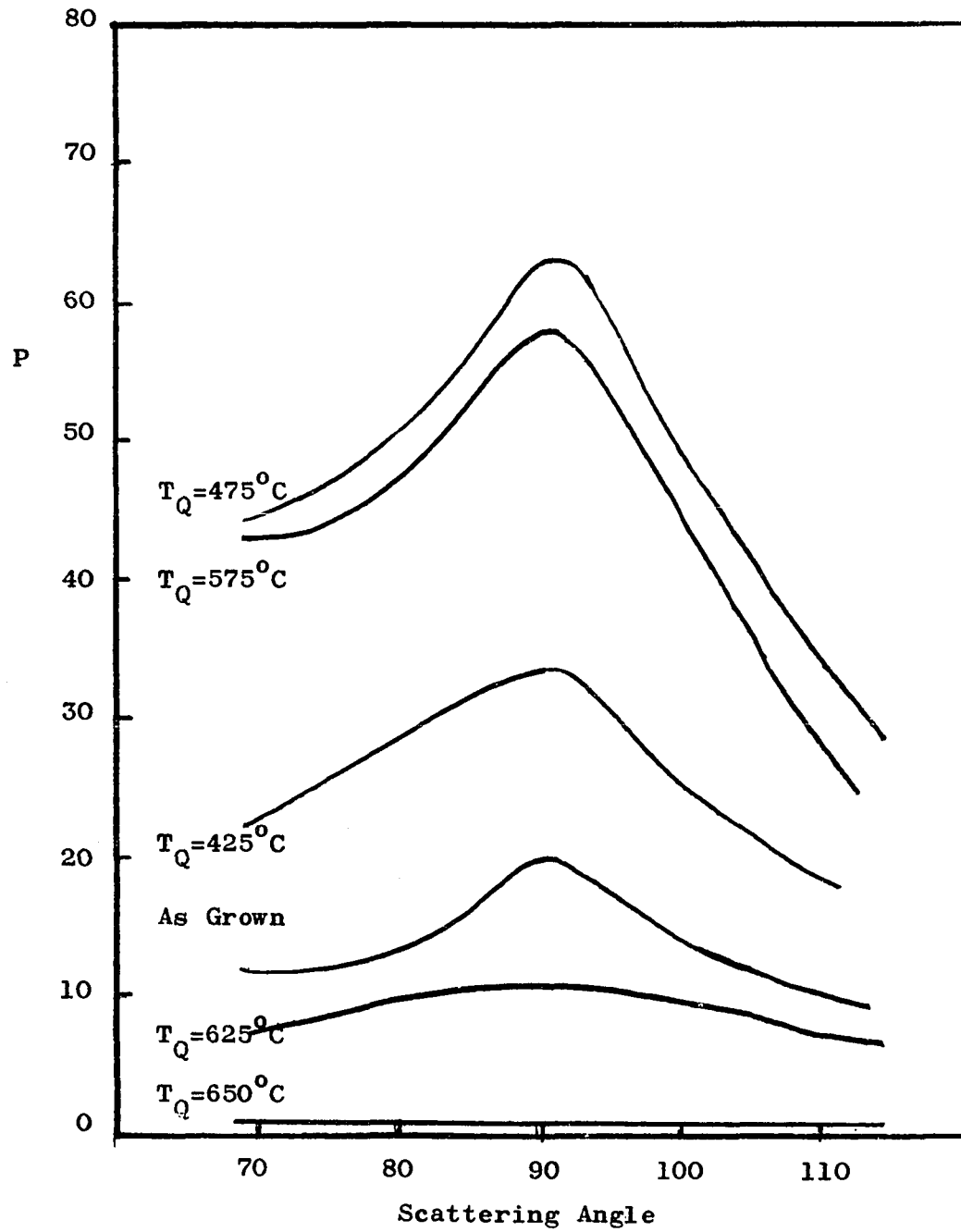


Fig. 16. Change in Scattering Peak with Temperature for HAR 5

the binding energy of a vacancy to a dislocation line is very nearly constant, e. g. negligible jog formation and very little change in the elastic strain field for temperatures up to 550°C. The number of free vacancies will be increasing with increasing temperature due to the dissociation of vacancy-divalent impurity ion complexes. Schottky defects will not enter into consideration for this stage since their density is very small, even at 550°C, when compared to the vacancy concentration due to impurity ions. In Figure 17 the concentration of Schottky defects for any particular temperature and the jump frequency of a positive-ion vacancy as a function of temperature are shown for KCl. Notice that at about 575°C the density of intrinsic vacancies becomes comparable to the density of extrinsic vacancies.

Consider the equation which specifies the excess concentration of vacancies around a dislocation line

$$\bar{n}^* = n_{\text{bad}} - n_{\text{good}} = \phi_1 - \phi_2 + (A-D)N_1 e^{-\epsilon_0/kT} \left\{ -1 + \left(1 + 4cz_1/k e^{\epsilon_0/kT} \right)^{1/2} \right\} \quad (1)$$

where ϕ_1 and ϕ_2 are respectively the concentration of free vacancies in the bad and good regions of the crystal. The coordination number is z_1 ; c is the impurity concentration for the whole crystal; ϵ_0 is the dissociation energy of the vacancy-impurity ion complex; and N_1 is given by

$$N_1 = N_0 / 2z_1 e^{S/k} = N_0 K / 2z_1. \quad (2)$$

Where N_0 is the number of positive-ion lattice sites per cubic

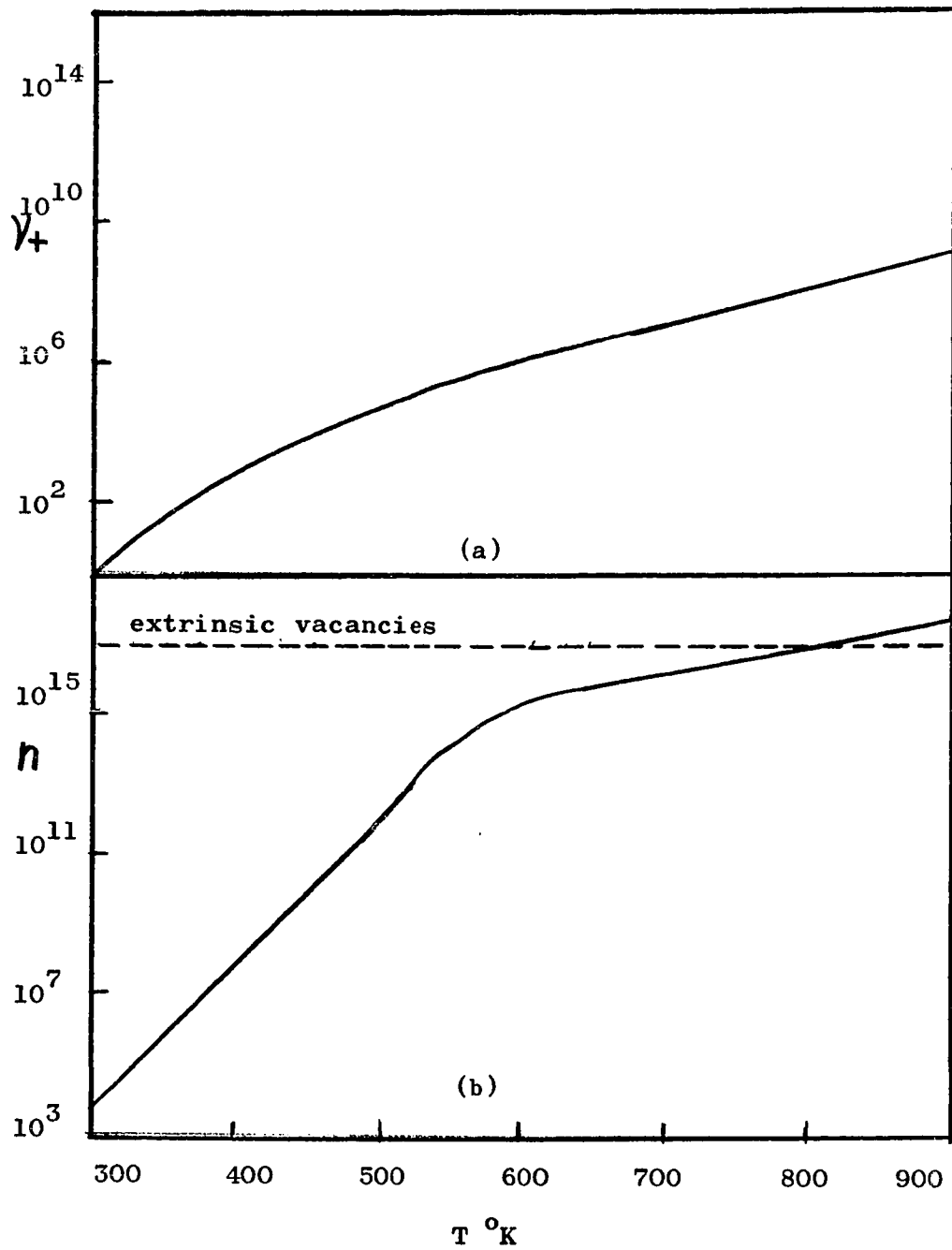


Fig. 17. Jump Frequency and Concentration of Schottky Defects in KCl

centimeter, k is Boltzmann's constant and S is the thermal entropy. The concentration of dissociated vacancies in the bad region is A and the concentration of dissociated vacancies in the good crystal is given by D . We are primarily interested in the slope, $\frac{\partial \ln P}{\partial (1/T)}$, at a temperature where $\epsilon_1 - \epsilon_2$ is small compared to the second term in $\bar{n}^*$. Thus we write

$$\frac{\partial \ln P}{\partial (1/T)} = \frac{2\epsilon_D/k(A-D)N_1 e^{-\epsilon_D/kT} \left[-X_1 + \left(1 + 4cz_1 K e^{\epsilon_D/kT}\right)^{-1/2} 2cz_1 K e^{\epsilon_D/kT} \right]}{X_2} \quad (3)$$

where

$$X_1 = \left\{ -1 + \left(1 + 4cz_1 K e^{\epsilon_D/kT}\right)^{1/2} \right\};$$

$$X_2 = (A-D)N_1 e^{-\epsilon_D/kT} X_1.$$

This reduces to the expression

$$\frac{\partial \ln P}{\partial (1/T)} = 2\epsilon_D/k \left[-1 + \frac{2cz_1 K}{e^{-\epsilon_D/kT} + 4cz_1 K - \left(e^{-2\epsilon_D/kT} + 4cz_1 K e^{-\epsilon_D/kT}\right)^{1/2}} \right] \quad (4)$$

By using the approach of Vineyard and Dienes¹ we can estimate K to be about 2.5. We will check this number shortly by means of the experimental data. With the slope of the experimental curve in stage I equal to 3.1×10^3 for KCl and by means of an iteration process, we find $\epsilon_D = .50 \pm .05$ e.v. if $c = 10^{-5}$ and $\epsilon_D = .43 \pm .05$ if $c = 10^{-4}$. These values may be compared with the value .32 e.v. found theoretically by Bassani and Fumi.² However, Bean³

¹G. H. Vineyard and G. J. Dienes, Phys. Rev. 93, 265 (1954).

²F. Bassani and F. G. Fumi, Nuovo Cim. 11, 274 (1954).

³C. Bean, Thesis, University of Illinois (1952).

has found for the system $\text{NaCl} + \text{Ca}^{++}$ that the Ca^{++} -vacancy complexes have a higher dissociation energy than Cd^{++} -vacancy, and he also found that for Ca^{++} in NaCl dissociation started above 275°C , which is lower than our results from KCl .

We can approximate K by considering the point in stage I where the scattering begins to increase. From equation (1) and previous considerations we have

$$\log_e P = 2 \log_e \left[\bar{\phi}_1 - \bar{\phi}_2 + (A-D)N_1 e^{-\epsilon_0/kT} \left\{ -1 + (1 + 4cz_1 K e^{\epsilon_0/kT})^{1/2} \right\} \right] \quad (5)$$

At $T = 610^\circ\text{K}$ the second term in (5) must be equal to the first.

Therefore,

$$\bar{\phi}_1 - \bar{\phi}_2 = \frac{(A-D)N_0}{2z_1} K e^{-\epsilon_0/kT} \left\{ -1 + (1 + 4cz_1 K e^{\epsilon_0/kT})^{1/2} \right\} \quad (6)$$

and this allows an estimate of K if we can evaluate $\bar{\phi}_1, \bar{\phi}_2, A$ and D . In the previous chapter, equation (14), we found that the scattering power can be written in terms of N^*, n^* , and V^* as

$$P' \simeq 10^{-44} N^* n^{*2} V^{*2} \quad (7)$$

and that $P' = 10^{-24} \text{cm}^{-3}$ for the "as grown" crystals. For a dislocation of length, z^* , $5 \times 10^{-4} \text{cm}$. $N^* = .2 \times 10^{10} \text{cm}^{-3}$. This comes from consideration of the linear dislocation density, $d^* \simeq 10^6 \text{cm}^{-2}$, which will be taken up in Chapter VIII. The radius of the dislocation line has been set at $1 \times 10^{-6} \text{cm}$ which gives, with z^* , $V^* = 1.5 \times 10^{-15} \text{cm}^3$. If one percent of the vacancies due to the impurity ion concentration are associated with dislocation lines

at room temperature, then for 10^{17} cm^{-3} vacancies

$$n^* = \frac{.01cN_0}{N^*V^*} = 3.3 \times 10^{20} \text{ cm}^{-3}.$$

It should be noticed that this n^* satisfies equation (7) for the N^* and V^* given above. Also note that N^* and V^* are fairly well fixed by this investigation and others: therefore, n^* can range over only a few values.

This n^* means a total of 5×10^5 vacancies surrounding the dislocation. There are approximately 2.4×10^7 positive ion lattice sites around the dislocation. Therefore, one vacancy is present for every 50 ions of the same sign.

Figure 14 shows that P increases by a factor of about four in stage I. Retaining our original assumption $P \propto \bar{n}^{*2}$, this would mean that n^* increases by a factor two. There would then be 1×10^6 vacancies at the dislocation, which gives very nearly the maximum number of vacancies possible in a non-hollow dislocation. These numbers correspond extremely well with the idea of rapid diffusion along dislocation lines, and the numbers are quite consistent with all of the known properties of dislocations.

Next, we consider the data for potassium bromide with an aluminum impurity content of 10^{18} cm^{-3} . We have shown in Chapter III that aluminum most likely goes into KBr as a divalent impurity ion rather than trivalent. Therefore, we shall use the same analysis in stage I as we used for the KCl crystals.

We rewrite equation (4)

$$\frac{\partial \ln P}{\partial (1/T)} = 2\epsilon_D/k \left[-1 + \frac{2cz_1 K}{e^{-\epsilon_D/kT} + 4cz_1 K - (e^{-2\epsilon_D/kT} + 4cz_1 K e^{-\epsilon_D/kT})^{1/2}} \right] \quad (4')$$

where $c = 10^{-4}$, $z_1 = 12$, the slope is 1.87×10^3 , and we again take $K = 2.5$ as reasonable. The iteration process yields a value of $.29 \pm .05$ e.v. for ϵ_D . The theory of Bassani and Fumi for the dissociation energy of an impurity-vacancy complex shows that ϵ_D increases with the radius and polarizability of the ion. The divalent aluminum ion has a smaller polarizability and ionic radius than the calcium ion. Therefore, it should have a smaller ϵ_D than Ca^{++} .

Stage II

In Harshaw KCl and KBr the "knee" of the conductivity curves occur at 500°C and 410°C respectively as shown in Figure 18.⁴ The concentration of thermal vacancies is approximately equal to the extrinsic vacancy concentration at the knee of the conductivity curve. Figures 14 and 15 indicate that stage II starts at 500°C in KCl and 425°C in KBr. Since the dislocations are essentially "saturated" with vacancies at these temperatures any further vacancies produced by dissociation of complexes or the Schottky mechanism must pass into the bulk crystal. Thus, the scattering power will cease to increase with increasing quench temperature and will eventually decrease as the temperature is raised further.

⁴D. F. Grob, Private Communication (1958).

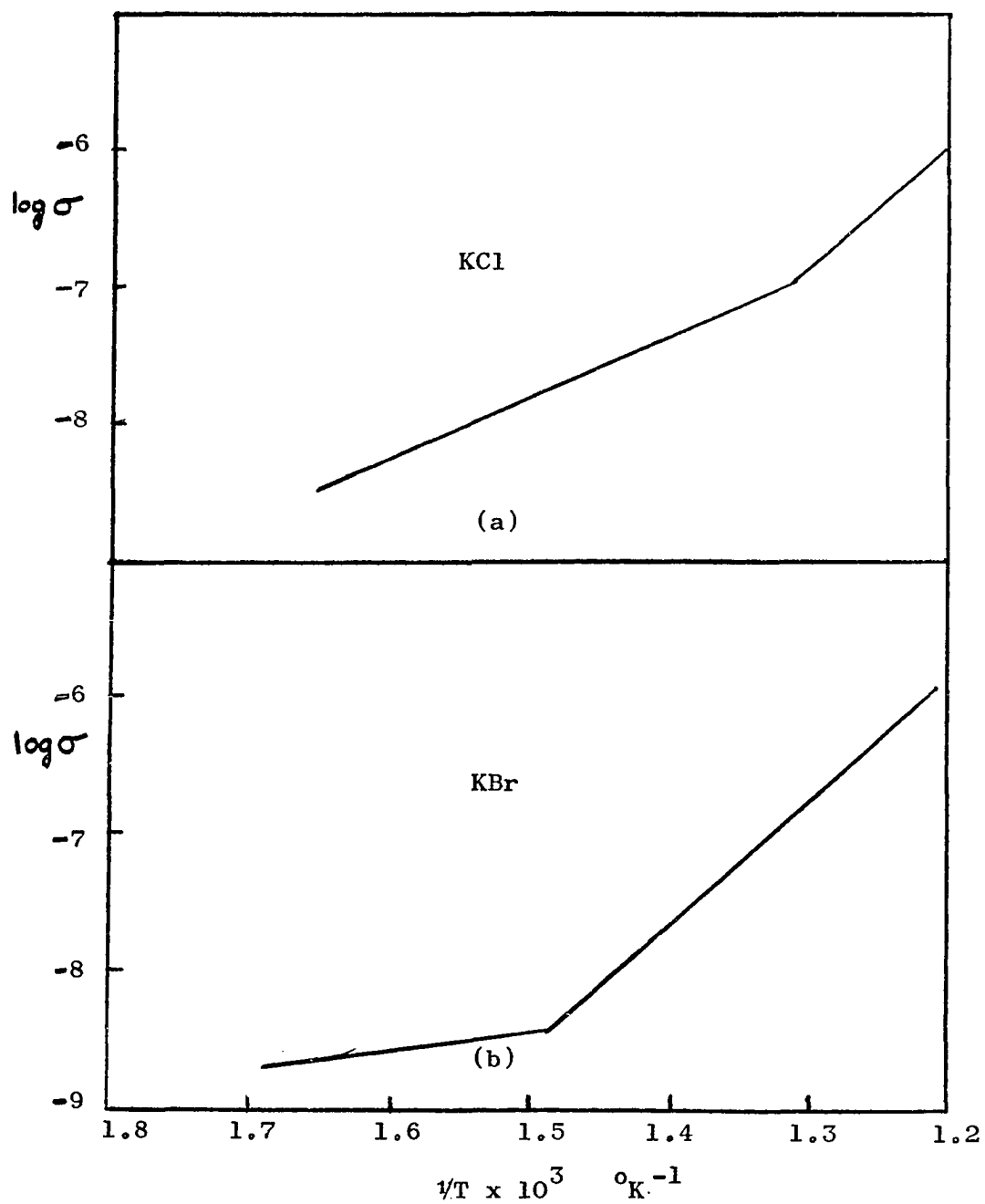


Fig. 18. Ionic Conductivity of Harshaw KCl and KBr.

Stage III

The scattering power of both KCl and KBr falls off rapidly in this range which indicates that the excess concentration of defects around the dislocation is decreasing. In other words, the number of vacancies around the dislocation lines is either constant or even decreasing while the number in the free lattice is increasing rapidly. We discuss the data for KCl and then for KBr.

First, we consider the case in which the number of vacancies around the dislocations remain constant after saturation. At saturation we have a concentration n_s at the dislocations, and about $.98cN_o$ extrinsic vacancies plus Schottky defects in the free lattice. Therefore, for stage III,

$$\bar{n}^{*2} = \left[n_s - N_2 e^{-\epsilon_f/2kT} - .98cN_o \right]^2 \quad (8)$$

where N_2 is determined by conductivity data. Then we have,

$$\ln P \propto \ln \bar{n}^{*2} = 2 \ln \left[n_s - .98cN_o - N_2 e^{-\epsilon_f/2kT} \right] \quad (9)$$

Next, take $\frac{\partial \ln P}{\partial (1/T)}$ and this gives

$$\frac{\partial (\ln P)}{\partial (1/T)} = \frac{\epsilon_f N_2 e^{-\epsilon_f/2kT}}{k \left[n_s - N_2 e^{-\epsilon_f/2kT} - .98cN_o \right]} \quad (10)$$

For a slope of 2.4×10^4 and with $n_s = 6 \times 10^{20} \text{ cm}^{-3}$ then ϵ_f is approximately .4 e.v. This value does not agree with the value 2.1 - 2.4 e.v. specified by ionic conductivity experiments and theoretical calculations.

Case two takes into account the dissociation of the vacancies from dislocations at sufficiently high temperature. Modifying equation (8) by introducing a Gibbs free energy for the vacancy-dislocation complex, we have in place of (10) for $\epsilon_f = 2.3$ e.v.

$$\frac{\partial(\ln P)}{\partial(1/T)} = \frac{2 \left[-S_2/k n_s e^{-S_2/kT} + \epsilon_f/2k N_2 e^{-\epsilon_f/2kT} \right]}{n_s e^{-S_2/kT} - .98cN_0 - N_2 e^{-\epsilon_f/2kT}} \quad (11)$$

where S_2 is the Gibbs free energy of the complex. This yields a value of .55 e.v. for S_2 . Since S_2 depends on both the thermal entropy and the configurational entropy in some unspecified manner, it is not possible to determine a precise binding energy for the vacancy to the dislocation line.

The discussion of the above two cases leads to a further interpretation of stage II. It appears that after saturation at 520°C for KCl, there is a gradual reduction in the scattering power due to the steady increase of defects of the Schottky type in the free lattice. Stage III then marks the onset of dissociation of the vacancy-dislocation system. Further support for this interpretation is found in Figure 16 in which the scattering power peaks for $\phi = 45^\circ$, which are characteristic of the dislocation with a cloud of vacancies, are increasingly smeared out above 575°C.

Lehfeldt⁵ has given the energy of formation for Schottky defects as 1.9 e.v. in KBr. Figure 15 shows a slope of 1.67×10^4

⁵W. Lehfeldt, Z. Physik 85, 717 (1933).

in stage III for KBr. From equation (11), assuming an impurity concentration of 10^{18} cm^{-3} , we obtain $S_2 = .79 \text{ e.v.}$

We have treated the scattering centers as dislocations in the theory presented thus far. It is possible, of course, that some of the scattering may come from occlusions or precipitates within the crystal. If this is the case, the scattering centers must be needle or ribbon-shaped and have some preferred orientation within the crystal to give peaks of the type shown in Chapter V. Also, the heat treatment data cannot be explained by precipitates or occlusions. Calculations using the Rayleigh-Gans scattering formula and reasonable values for the size of the precipitates show that for our experiments Harshaw KCl crystals exhibit greater scattering by dislocations than by precipitates.

Anneal Effects

Three Harshaw potassium chloride crystals which had different heat treatment histories were annealed at the same time. A comparison of scattering before and after anneal for two of the crystals is shown in Figure 19. HAR 7 was quenched from 500°C and then annealed. Notice that before anneal the peak in the scattering power for $\phi = 45^\circ$ is well defined, but that after annealing the peak has disappeared and the scattering has taken on the isotropic form prevalent in the NRL crystals. HAR 9 was quenched from 580°C , hence the smaller original peak, and then was annealed. It is interesting that after the anneal the graph for HAR 9 resembles that for HAR 7 after anneal. The third crystal,

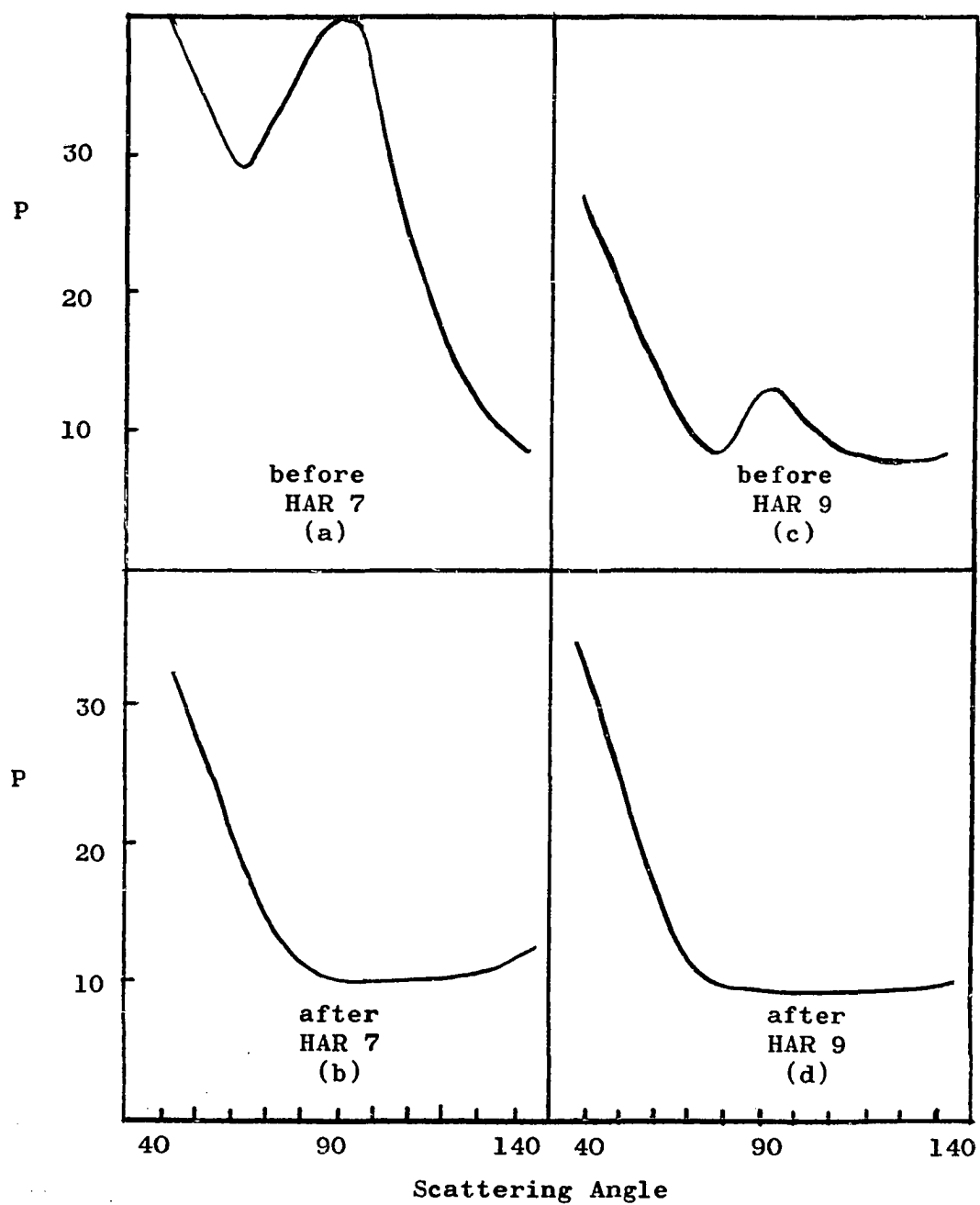


Fig. 19. Harshaw KCl Crystals Before and After Anneal

HAR 8, had been quenched from 625°C and then annealed. The peak disappeared after the quench and no apparent change in the scattering pattern was evident.

In Chapter VIII we present evidence that dislocation lines move into boundaries or arrays after the annealing treatment. Also, it is apparent from that chapter that the NRL crystals possess a large number of dislocation boundaries in the "as grown" state. Since these boundaries may have a wide range of orientations in the crystal any light scattering from them would have no crystallographic orientation dependence. This effect would also increase the effective radius of the virtual scattering center as shown in Chapter V.

CHAPTER VII

PLASTIC DEFORMATION AND HARDNESS OF POTASSIUM CHLORIDE

Three crystals of Harshaw potassium chloride were subjected to plastic deformations of 2.5%, 4.7%, and 7.7% respectively. Figures 20, 21, and 22 show the light scattering for $\phi = 0^\circ$ and $\phi = 45^\circ$, both before treatment and after deformation. As was noted in Chapter V, the forward scattering is important in determining the size and shape of the scattering center. Notice that deformation increases the scattering at all angles and that the increase in scattering for the smaller scattering angles is less than for the other scattering angles. However, the scattering peak for the orientation $\phi = 45^\circ$ is obscured due to the increase in angular range of the forward scattering. The apparent shift of the peak in the scattering pattern after deformation as shown in Figure 21(b) is probably due to misorientation of the crystal in the experiment.

Vaughan, et al.¹ have shown that there is no appreciable increase in the vacancy concentration of the crystal for deformations of less than ten percent. We have shown that if the change

¹W. H. Vaughan, W. J. Leivo and R. Smoluchowski, Phys. Rev. 110, 652 (1958).

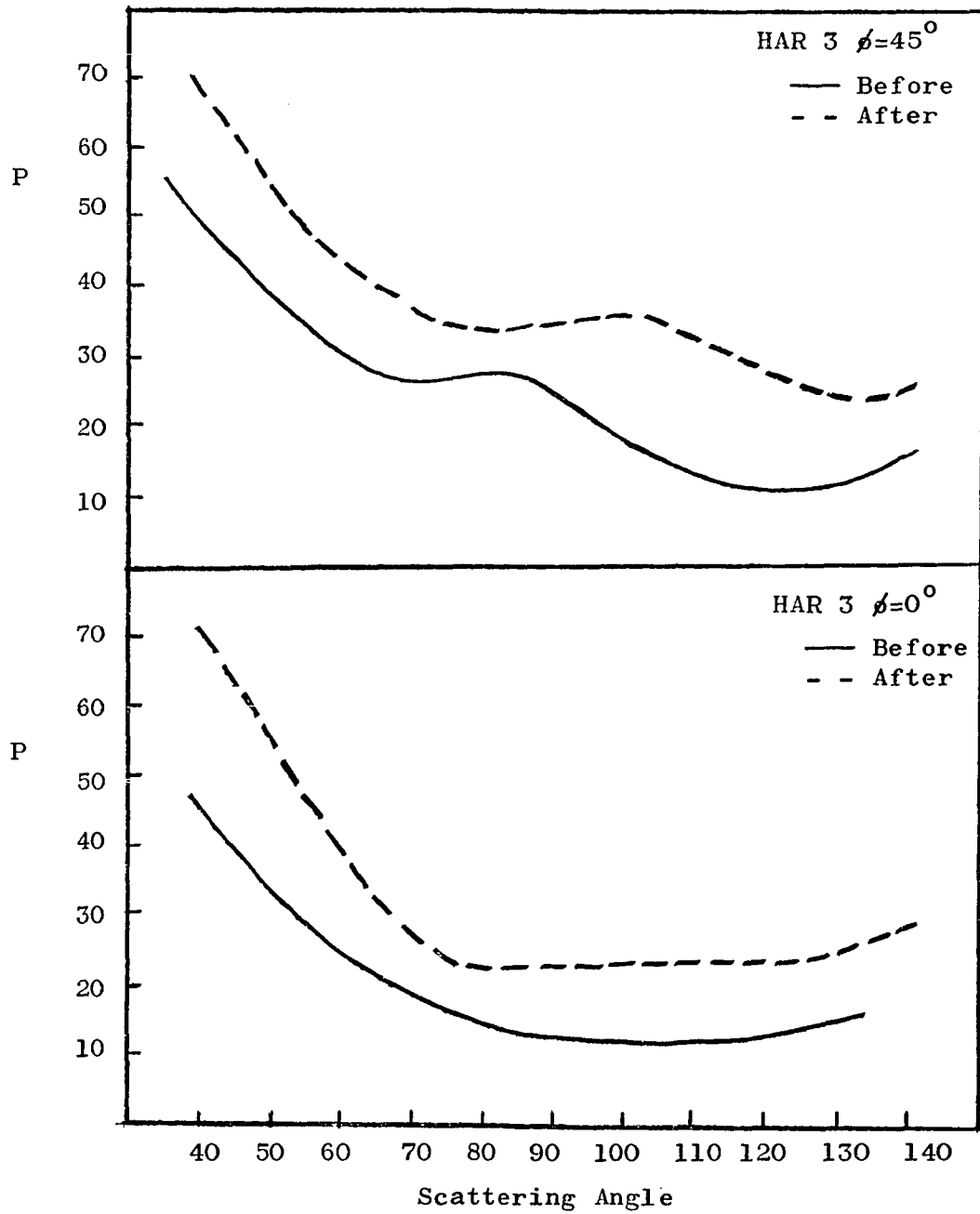


Fig. 20. Crystal HAR 3. Light Scattering Before and After 2.5% Deformation

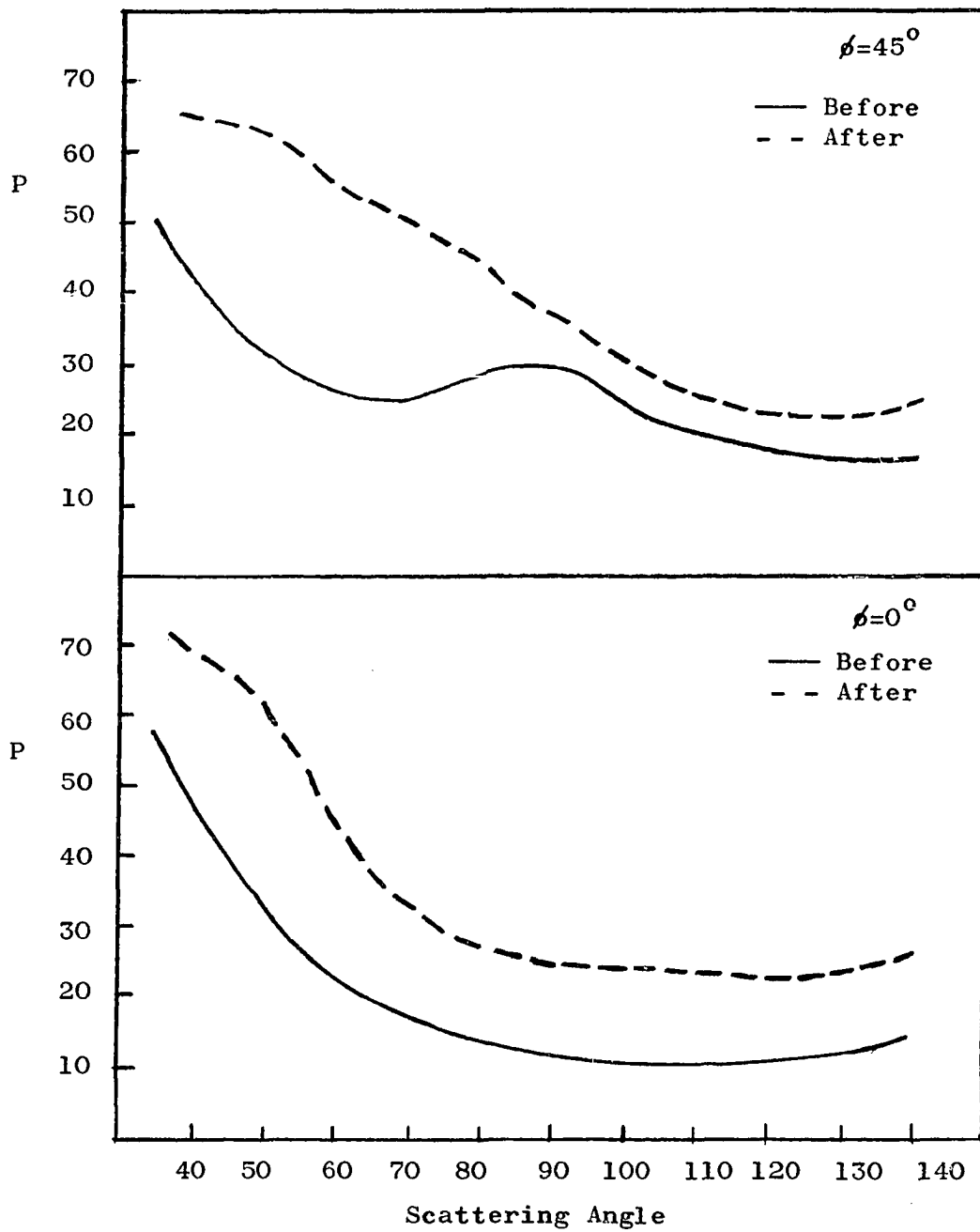


Fig. 21. Crystal HAR 10. Light Scattering Before and After 4.7% Deformation

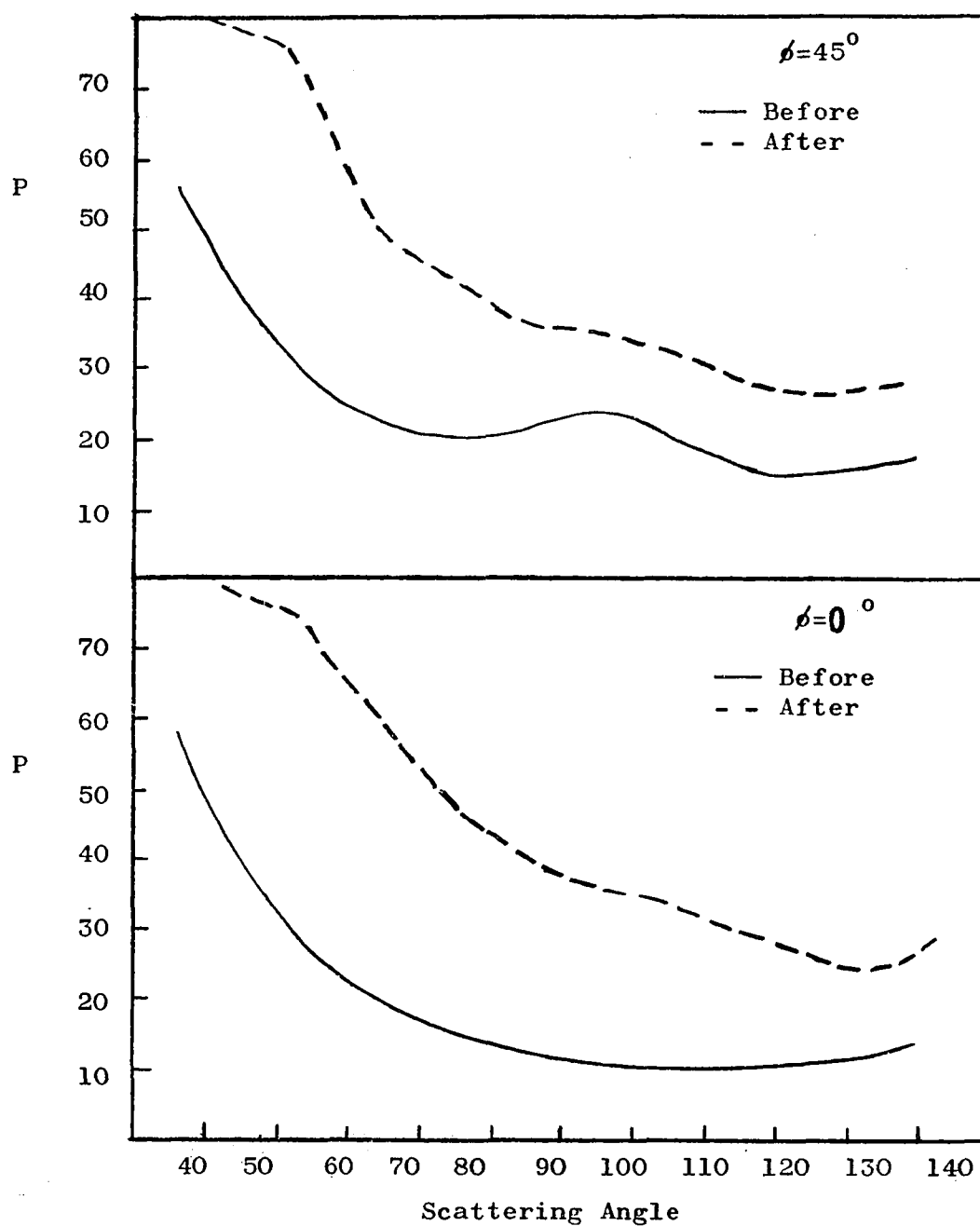


Fig. 22. Crystal HAR 11. Light Scattering Before and After 7.7% Deformation

in scattering power, P , is due strictly to an increase in the number of vacancies surrounding the dislocations, then a factor of two is approximately the maximum change in P to be expected. The increase in scattering power for the crystal deformed 7.7% is a factor of 3.1, and this apparently eliminates the possibility of vacancy concentration changes around dislocation lines as the sole mechanism.

Possible factors influencing the observed changes in the scattering are: (a) the number of dislocations in the crystal is increased, (b) the effective lengths of the dislocations are changed because of dislocations intersecting with each other, (c) the "average" width of the dislocations changes because the new dislocations will not possess a cloud of defects, (d) a large number of screw dislocations will be formed and (e) the orientations of the dislocations will be less precise due to dislocation intersections. These mechanisms are consistent with other observations which have been made, but they are not the only possible ones.

The hardness measurements show a difference between "as grown", quenched, and annealed crystals. This has been noticed many times previously, but it is satisfying to see that the crystals follow the known trend. In Table 2 we show the average of six measurements for three different crystallographic directions.

It should also be mentioned that the crystals HAR 7, HAR 8, and HAR 9 had been quenched from 500°C , 625°C , and 580°C respectively before being annealed.

TABLE 2

HARDNESS MEASUREMENTS ON HEAT TREATED KCL

Crystal	Crystallographic Test Direction			Condition
	$\langle 100 \rangle$	$\langle 010 \rangle$	$\langle 110 \rangle$	
HAR 12	70.8	71.5	72.7	As grown
HAR 11	70.3	70.7	71.9	As grown
HAR 10	71.9	71.8	72.9	As grown
HAR 5	73.4	73.0	73.5	Quenched
HAR 6	73.4	73.8	74.2	Quenched
HAR 7	67.7	67.7	69.6	Annealed
HAR 8	68.4	69.2	71.9	Annealed
HAR 9	69.7	69.4	71.3	Annealed

CHAPTER VIII

DISLOCATION ARRAYS

One of the interesting problems in defect solid state physics at this time is the movement of dislocations into grain boundaries, the demarcation lines between sections of crystalline material which are slightly misoriented with respect to each other, during plastic deformation or heat treatments of crystals. There are two possible means by which a dislocation can move, glide and climb. We will consider only edge dislocations and discuss briefly both types of movement. The direction of easy motion for any edge dislocation is restricted to the slip direction because this is the only direction in which conservative movement can occur. Conservative motion occurs when there is no change in the amount of matter associated with the dislocation. Climb is the non-conservative motion of a dislocation, and is equivalent to an increase or decrease in the area of the extra half-plane which is characteristic of the edge dislocation. In principle, climb can occur by means of an applied force, a supersaturation of vacancies, diffusion of vacancies, or a combination of these possibilities.

There has been much speculation concerning the climb of dislocations into grain boundaries, and it is generally accepted

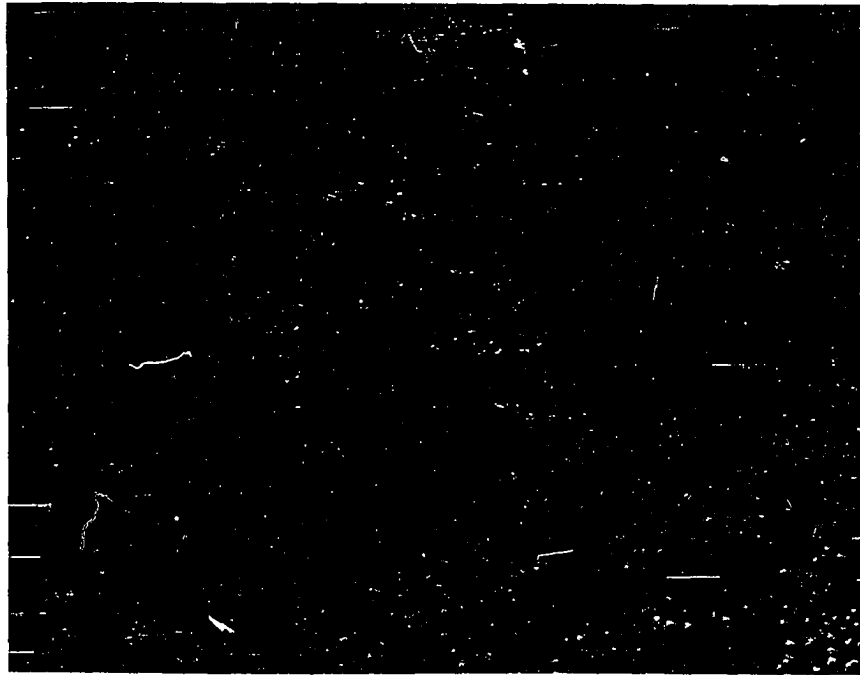
that the rate of climb depends on the jog energy, vacancy mobility, and vacancy concentration. Amelinckx¹ has observed the formation of small-angle grain boundaries by dislocations in rock salt. He observed the movement of dislocations into boundaries and a decrease in dislocation density when the crystals were held at about 700°C for at least six hours. The dislocations were detected by etch pits on the crystal surface and a careful investigation revealed a one to one correspondence between the etch pits and the dislocations. We have found a similar behaviour of the dislocations for single crystals of KCl.

A comparison of the dislocations in untreated Harshaw and NRL KCl is shown in Figure 23. Notice that before any treatments the dislocations have a rather random distribution within the crystals, except for the boundaries which are easily seen in both crystals. The untreated Harshaw crystals appear to have fewer boundaries than the NRL crystals. In the NRL crystals broad flat-bottomed pits are evident which do not have the distinctive pyramidal shape of dislocation etch pits. Pits of this type have been attributed to precipitates by Gilman.² There are more precipitate pits in the NRL crystals than in those grown by Harshaw. Table 3 shows the dislocation densities for treated and untreated KCl crystals.

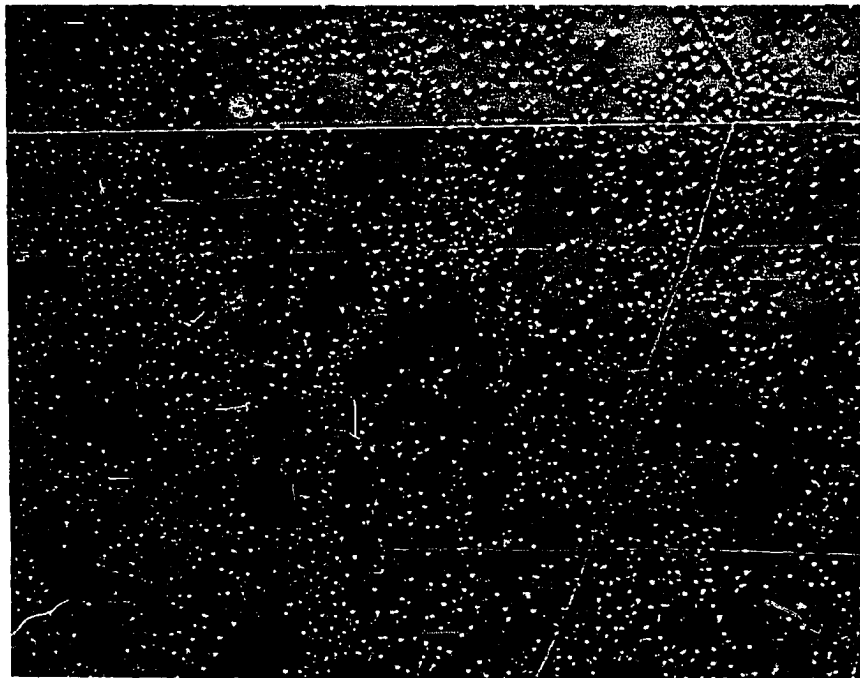
Figure 24 indicates that there is no noticeable difference

¹S. Amelinckx, *Acta Met.* 2, 848 (1954).

²J. J. Gilman, *J. App. Phys.* 30, 1584 (1959).



(a) Grown by Harshaw



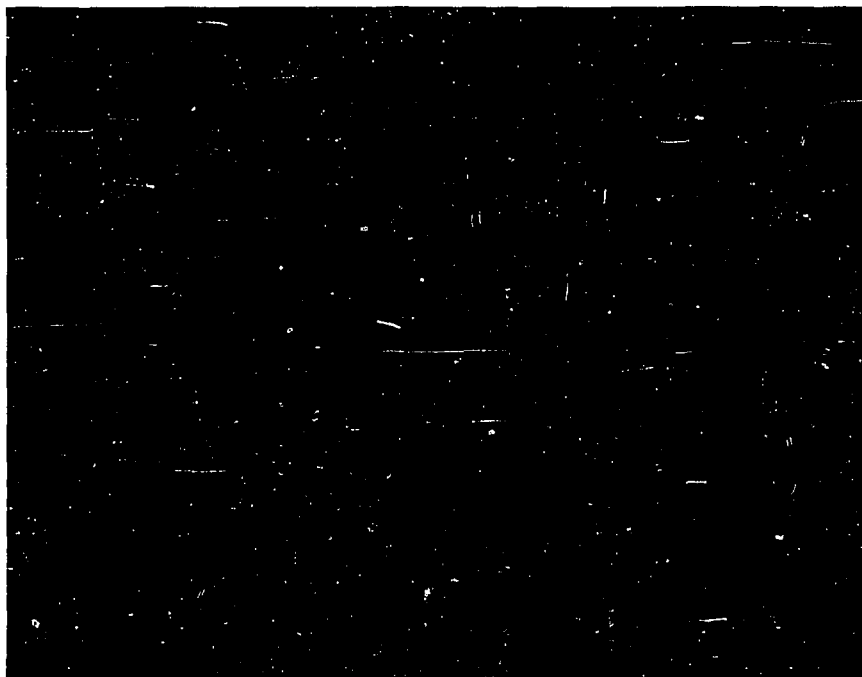
(b) Grown by Naval Research Laboratory

Fig. 23. Dislocations in Untreated KCl Crystals

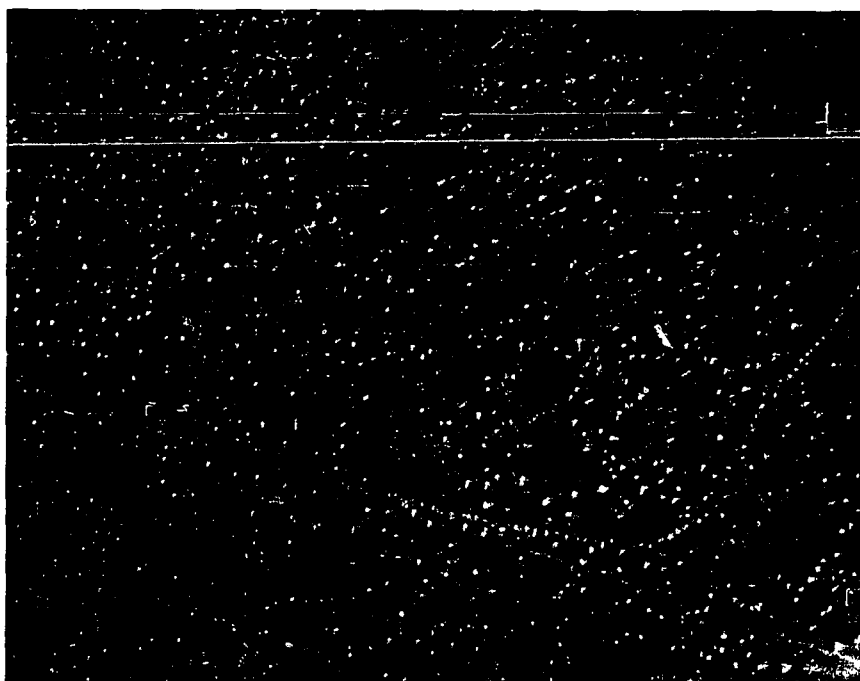
TABLE 3

DISLOCATION DENSITIES IN POTASSIUM CHLORIDE

Crystal	Treatment	Dislocation Density
NRL 13	As grown	$1.47 \times 10^6 \text{ cm}^{-2}$
NRL 14	As grown	$1.07 \times 10^6 \text{ cm}^{-2}$
HAR 1	As grown	$1.07 \times 10^6 \text{ cm}^{-2}$
HAR 12	As grown	$1.15 \times 10^6 \text{ cm}^{-2}$
HAR 5	Quenched	$1.17 \times 10^6 \text{ cm}^{-2}$
NRL 14	Quenched	$1.45 \times 10^6 \text{ cm}^{-2}$
HAR 7	Annealed	$5.20 \times 10^5 \text{ cm}^{-2}$
HAR 8	Annealed	$3.76 \times 10^5 \text{ cm}^{-2}$
NRL 13	Annealed	$5.80 \times 10^5 \text{ cm}^{-2}$



(a) Untreated NRL 14 Crystal



(b) KCl 14 after Quench from 650°C.

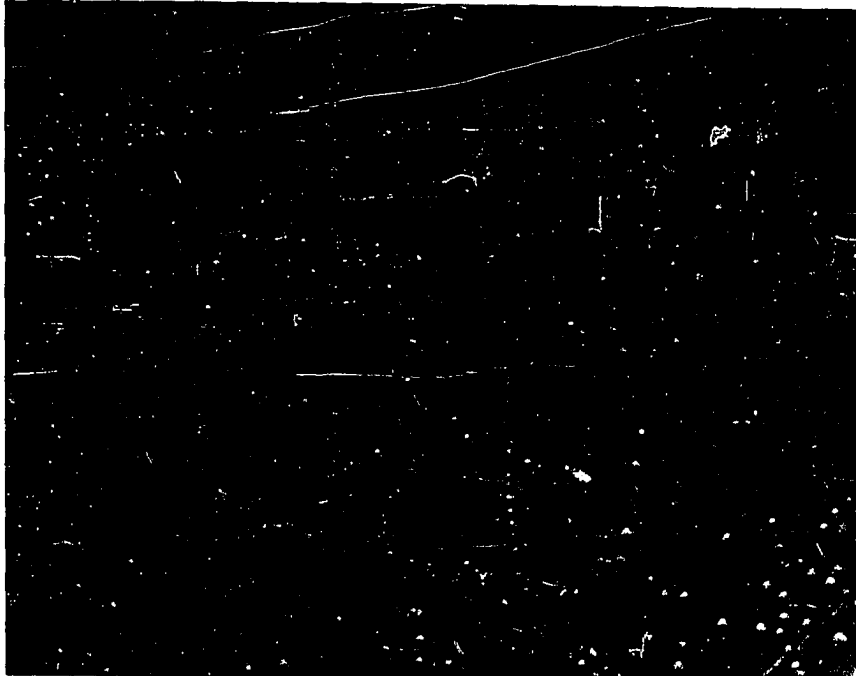
Fig. 24. Dislocations in Untreated and Quenched Kcl Crystals

in dislocation arrangement between an as grown crystal and a crystal quenched from 650°C . Before being quenched in still air the crystal was held at 650°C for two hours. Notice that the number of large flat-bottomed pits is greater for NRL 14 than for NRL 13. In all the crystals investigated thus far, no change in dislocation arrangement has occurred for crystals held at a high temperature for two hours and then quenched in still air. This result implies that two hours is not long enough for dislocations to climb an appreciable distance even when the crystals are at 750°C .

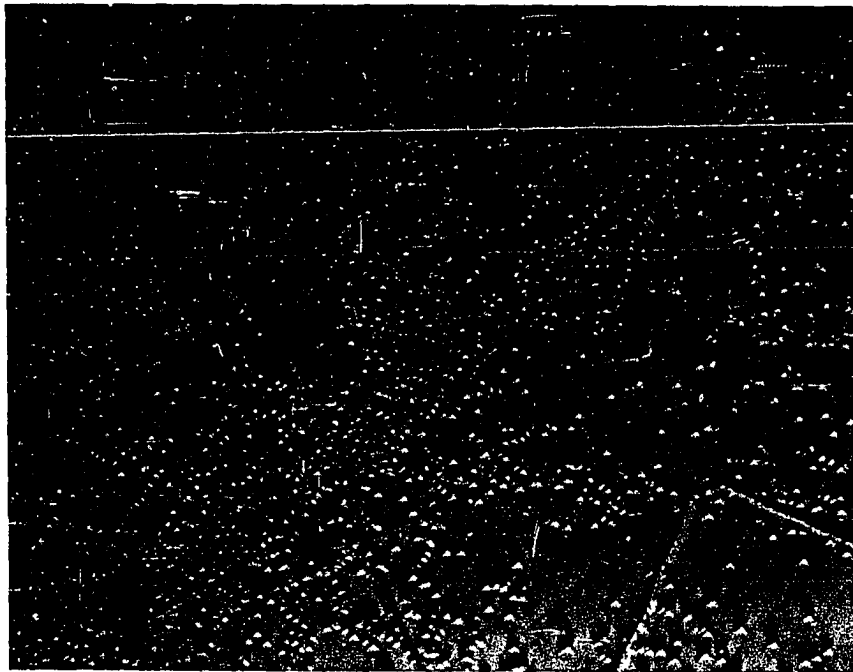
After the Harshaw and NRL crystals are held at 680°C for four hours and then cooled at the rate of 3°C/hr . a definite change in the dislocation pattern is evident. Polygonization has taken place by the movement of dislocations into boundaries as can be seen in Figure 25. Notice the number of precipitates present in the NRL crystals.

The $\langle 100 \rangle$ directions in the crystal are marked by the edge of the dislocation etch pit. In Figure 25(a) the formation of boundaries in the $\langle 110 \rangle$ directions and the $\langle 100 \rangle$ directions is apparent. Edge dislocations are along $\langle 100 \rangle$ directions in $\{110\}$ slip planes and slip in the $\langle 110 \rangle$ directions. Screw dislocations have $\langle 110 \rangle$ directions on $\{100\}$ slip planes. From these considerations it is possible to distinguish between edge and screw dislocations from the etch pits and their relative positions.

We mentioned previously that the light scattering from



(a) NRL 13 after 9 Day Anneal at 680°C .

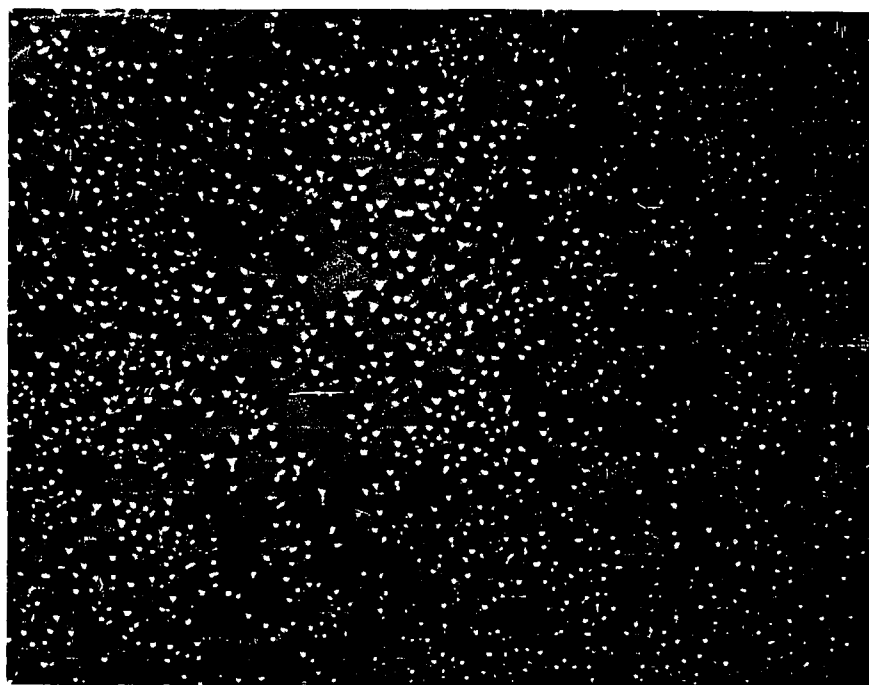


(b) NRL 14 after 9 Day Anneal at 680°C .

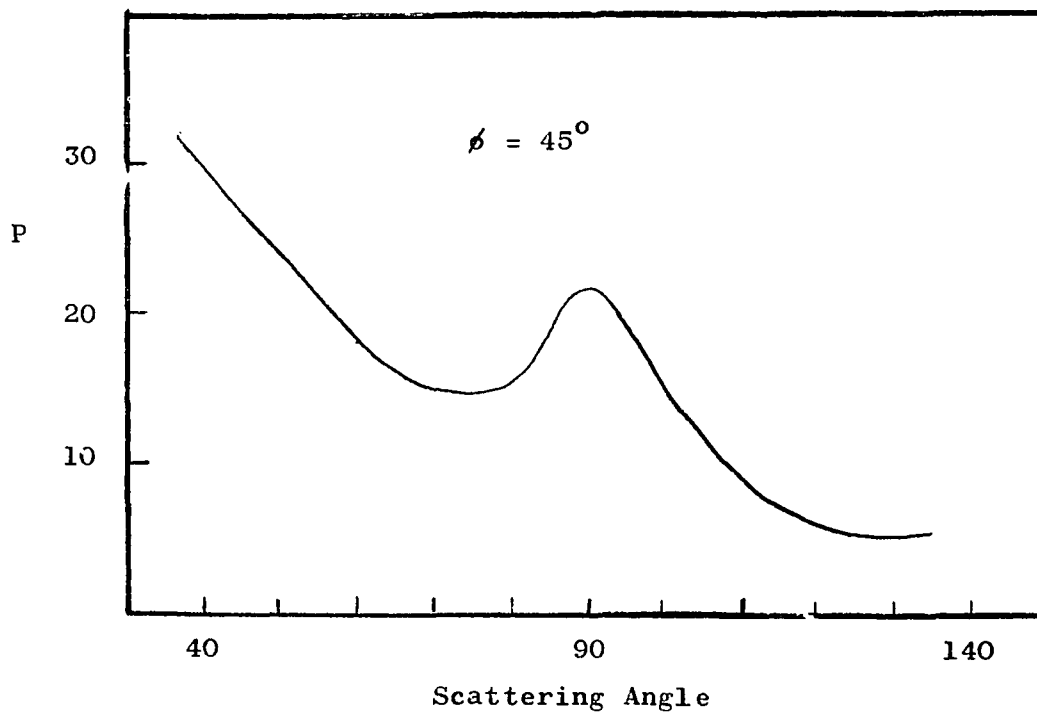
Fig. 25. Dislocation Boundaries in KCl Formed by Annealing

annealed crystals does not exhibit moving peaks which are a function of crystallographic orientation. Figures 26 and 27 compare the dislocation arrangement and the light scattering of as grown and annealed Harshaw KCl. If we note the clustering of dislocations in Figure 27(b) it seems possible that our scattering centers have changed from individual dislocations in the as grown crystals to clusters of dislocations in the annealed specimens. Assuming that this is the case the dislocation clusters, which could be sections of a grain boundary, will be oriented such as to smear the scattering peaks into the background.

In order to determine when the boundaries are formed during the annealing treatment, crystals were removed at various times in the course of the anneal. It was found that crystals which had been in the oven a total of 80 hours and had cooled to 400°C showed evidence of boundary formation; whereas, those removed from the oven prior to this time gave no indication of the movement of dislocations into boundaries.



(a) Etch Pits on Untreated HAR 12 Crystal

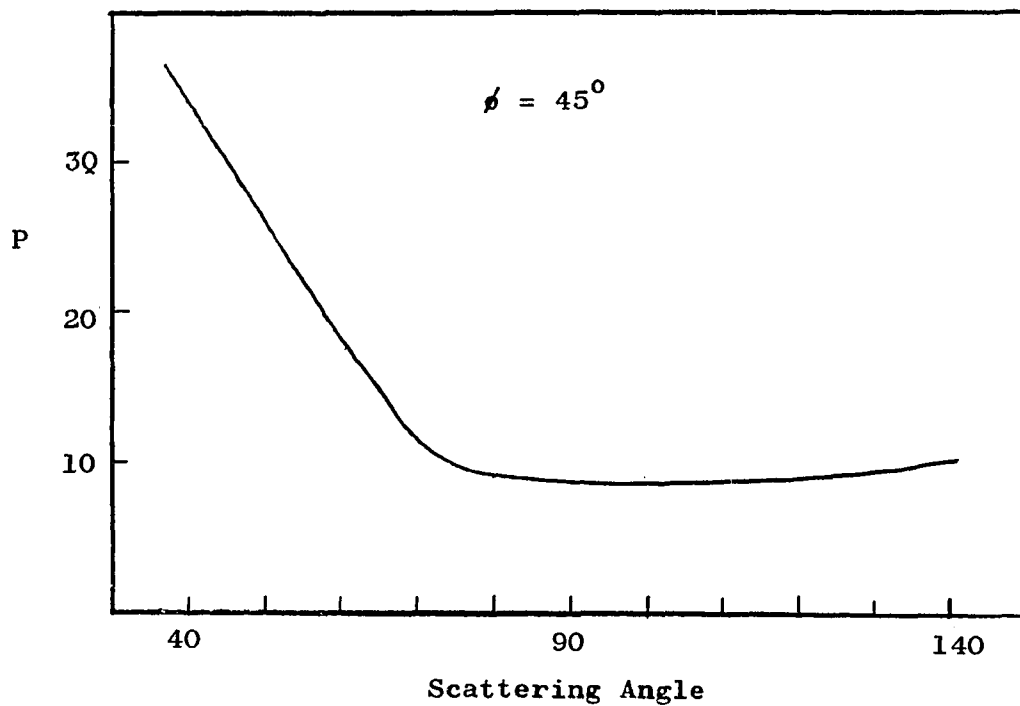


(b) Light Scattering by Untreated HAR 12 Crystal

Fig. 26. Dislocation Arrangement and Light Scattering of Untreated KCl Crystals



(a) Etch Pits on Annealed HAR 10 Crystal



(b) Light Scattering by Annealed HAR 10 Crystal

Fig. 27. Dislocation Arrangement and Light Scattering of Annealed KCl Crystals

CHAPTER IX

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

Conclusions

The more important aspects of this investigation will be presented in the same topical order as in the body of the dissertation.

There is a very marked difference in the light scattering in Harshaw crystals and crystals grown by the Naval Research Laboratory. The angular dependence of the light scattering in Harshaw potassium chloride is a function of the orientation of the crystallographic axes with respect to the incident light beam. In NRL crystals no orientational dependence of the scattering was found. A Fourier analysis of the scattering data indicates that the primary scattering centers in Harshaw crystals are cylindrical rods, oriented along the crystallographic axes, which are about 50,000 Å long and 200 Å in diameter. In the NRL crystals the scattering centers are apparently spherical in shape and have a diameter of approximately 1500 Å. Chemical etching reveals far more precipitates and dislocation boundaries in the NRL grown crystals than in the Harshaw crystals. Also, the precipitates in these crystals are probably cadmium chloride, which would cause

scattering two orders of magnitude greater than that from the calcium chloride precipitates which may be present in the Harshaw crystals! Therefore, it is most probable that the scattering in NRL crystals is due primarily to precipitates.

Light scattering techniques permit a study of the changes in the scattering centers as a result of heat treatments or deformation of the crystal. Since the scattering centers are dislocations in Harshaw KCl, it will be of particular interest to investigate them. As might be expected, the density of vacancies surrounding a dislocation line is dependent on the concentration of free vacancies in the lattice. From this consideration and the change in the light scattering as a function of temperature, we have found that the dissociation energy for calcium-vacancy complexes in KCl is 0.5 e.v. For divalent aluminum-vacancy complexes in Harshaw KBr the dissociation energy is 0.29 e.v. We have also made an estimate of $3 \times 10^{20} \text{ cm}^{-3}$ for the concentration of vacancies around an edge dislocation line in KCl. This vacancy concentration is consistent with the observed high diffusion rates found along grain boundaries. A dissociation of vacancies and the dislocation lines was observed at high temperatures, e.g. 575°C in Harshaw KCl.

The peak which exists in the angular dependent scattering of Harshaw KCl disappears when the crystals are annealed from 680°C over a nine day period. The scattering is apparently independent of crystallographic orientation after this treatment, and the

scattering pattern is similar to that of the untreated NRL crystals. This result implies a change in the scattering centers and could be attributed to a clustering of the dislocations into grain boundaries.

The scattering centers are also changed by deformation. This is very reasonable since it is known that dislocations intersect and pile up under deformation. The scattering centers are then changed from individual dislocations to groups or clusters of dislocations.

The investigation of potassium chloride crystals by chemical etching shows that the dislocations are essentially immobile, even when held at 700°C for a period of two hours. However, when the crystals are slowly cooled from 680°C at the rate of 3°C per hour the dislocations move into grain boundaries and the density of dislocations is reduced.

Suggestions for Further Work

This section will be divided into two parts. We will consider first the possible experiments which should be performed on "as grown" crystals, and then we shall consider investigations of "treated" crystals.

An investigation of an "as grown" crystal can reveal information concerning the density and arrangement of dislocations in the crystal, the size and shape of the scattering centers, and the number of scattering centers in the crystal. The following investigations on "as grown" crystals are suggested:

(1) A complete orientational dependence of the scattering from impurity doped crystals. It would be of great interest to determine experimentally whether the light scattering by NRL crystals is due to precipitates. This could be done by measuring the scattering of crystals doped with different impurities and calculating the scattering power using the Rayleigh-Gans scattering theory.

(2) A complete orientational dependence of the scattering of Harshaw NaCl and KBr. This should give information concerning dislocation orientations and the density of vacancies around dislocations in these crystals.

(3) An investigation of small angle scattering, $2\theta < 30^\circ$, for all crystals. Since precipitates with a diameter of around 1500 Å have maximum scattering power at small angles for incident light of wavelength 4358 Å, it would be possible to study both precipitates and dislocations in the same crystal.

(4) Chemical etching of the alkali halides and particularly of heavily doped crystals to determine how the number of precipitates depends on impurity concentration and growth technique.

There are a number of extremely interesting experiments to be performed on "treated" crystals. From these investigations information can be obtained on the dissociation energies for various defect complexes and the kinetics of precipitate formation. An upper limit for the number of vacancies surrounding dislocation lines can be determined. An estimate of the size of dislocation

"pile ups" can be determined, and it is possible to find the energy necessary for a dislocation to climb. The following investigations of treated crystals should be undertaken:

(1) Determination of the dissociation energy for various divalent impurity-vacancy complexes by the method used in this investigation. It may also be possible to determine the dissociation energy by finding the scattering power of the crystal at high temperatures. This would eliminate some inaccuracies inherent in the quench process.

(2) An investigation of Debye-Hückel shielding by changing the impurity concentration of the crystals. This experiment should determine if the Debye effect is important in alkali halide crystals and if the Debye-Hückel theory of electrolytes can be extended to ionic crystals.

(3) A complete orientational dependence of the scattering of crystals that have been plastically deformed. This should give information concerning the extent of dislocation pile up.

(4) An experiment to determine the difference in scattering power between "as grown" and irradiated crystals. If the crystals are heated after irradiation and the scattering power is observed as a function of temperature, we may obtain some idea of the effect of a large number of free vacancies on dislocation lines.

(5) Dislocation climb in the alkali halide crystals should be investigated by means of chemical etching. It would

be of great interest to find the lowest temperature at which climb will occur, and it may also be possible to find a temperature above which dislocation lines will not climb.

This list of possible investigations is not meant to be exhaustive: however, it does illustrate the potentiality of light scattering techniques as a tool for investigating defects in transparent crystals.

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