

rather than emit resonant radiation, unless either (or both) of the following conditions are satisfied:

- (a) The distribution is not a function of energy alone,
- (b) The resonating states do not exist above a certain energy  $\epsilon_c$ , and the distribution function satisfies the condition

$$\int_0^{\epsilon_c} d\epsilon \epsilon^2 \frac{\partial f}{\partial \epsilon} > 0.$$

Neither condition can be satisfied above  $T_0$ . Below this temperature, however, both are possibilities. The first can be satisfied if  $g$  and  $\tau$  are not functions of energy alone; this is likely to be true to a limited extent. The second condition is met if  $\epsilon_c < \hbar\omega$ ; however, the existence and the value of  $\epsilon_c$  have not yet been established.

## Self-Diffusion of the Chloride Ion in Sodium Chloride\*†

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The diffusion coefficient of  $\text{Cl}^{36}$  in NaCl has been measured in the temperature range from 520° to 740°C. Diffusion was measured in pure Harshaw crystals and in crystals containing from 0.01 to 0.1 mole percent calcium. The diffusion coefficient in pure crystals is represented by the equation  $D = 56 \exp(-2.12 \text{ ev}/kT)$   $\text{cm}^2/\text{sec}$ . The diffusion coefficient in crystals containing calcium was smaller than that measured in pure crystals by a factor of from 5 to 10, and had an activation energy of 2.5 ev. Over the range of impurity concentration employed the diffusion coefficient was insensitive to differences in calcium concentration. The results are discussed in terms of motion of free negative ion vacancies and of vacancy pairs. Possible complicating effects of dislocation lines on the diffusion coefficient are also considered.

### INTRODUCTION

THE ionic conduction process in alkali halides has been extensively studied, and the details of the ionic motion are quite well understood.<sup>1</sup> Schottky defects predominate, and the positive ion vacancy is responsible for the conductivity. The contribution of the negative ion to the conductivity is usually quite small, under 10% in most pure crystals, and essentially zero in the impurity controlled range of temperature. Kerkhoff<sup>2</sup> found that in highly purified KCl at high temperature the contribution of the negative ion to the total conductivity may be as large as 40%, but over the region of interest in most experiments it has been satisfactory to assume that the conductivity is due to the positive ion alone. For this reason early work in this field centered around the measurements of the conductivity and of the positive ion diffusion coefficient. Such studies have produced a detailed picture of the motion of a positive ion vacancy in a lattice. In contrast, although there have been several measurements of negative ion diffusion coefficients, no such detailed information on negative ion vacancies has resulted. It

has been generally assumed that the diffusion of negative ions proceeds by motion of negative ion vacancies, in analogy to the findings in the case of the positive ion, but the evidence for this is far from conclusive.

Chemla<sup>3</sup> performed the first measurements of diffusion of  $\text{Cl}^{36}$  in NaCl over a limited temperature range as a part of a survey of diffusion properties of NaCl. Laurent and Bénard<sup>4</sup> repeated these experiments, extending the range of temperature investigated. Schamp and Katz<sup>5</sup> measured the negative ion self-diffusion coefficient in NaBr. All of these measurements were made by a sectioning technique involving the removal of thin layers of crystal and measuring the amount of radioactive isotope which had penetrated from the surface. Ewles and Jain<sup>6</sup> have interpreted the time decay of conductivity in quenched samples of KCl as due to the motion of negative ion vacancies and have arrived at an expression for the diffusion coefficient of the negative ion. Recently Schamp has reported the results of diffusion measurements of the chloride ion in KCl.<sup>7</sup>

Within the last few years a group at Ottawa, Canada, under the direction of Morrison has developed a new technique for the measurement of the diffusion coefficient. They have applied this technique to the measure-

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† Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

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<sup>1</sup> For a review of this work see A. B. Lidiard, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, pp. 246-349.

<sup>2</sup> F. Kerkhoff, *Z. Physik* **130**, 449 (1951).

<sup>3</sup> M. Chemla, *Compt. rend.* **234**, 2601 (1952), also *Ann. phys.* **1**, 959 (1956).

<sup>4</sup> J. F. Laurent and J. Bénard, *J. Phys. Chem. Solids* **3**, 7 (1957).

<sup>5</sup> H. W. Schamp and E. Katz, *Phys. Rev.* **94**, 828 (1954).

<sup>6</sup> J. Ewles and S. C. Jain, *Proc. Roy. Soc. (London)* **A243**, 353 (1958).

<sup>7</sup> H. W. Schamp, Jr., *Bull. Am. Phys. Soc.* **5**, 48 (1960).

ment of the diffusion coefficient of  $\text{Cl}^{36}$  in NaCl and KCl.<sup>8-10</sup> This method involves the measurement of the rate of exchange of chlorine in the solid with a surrounding gas. It has enabled them to measure diffusion coefficients several orders of magnitude smaller than is possible with the more usual sectioning technique.

The results of Harrison, Morrison, and Rudham<sup>9</sup> indicate that the diffusion coefficient of Cl in NaCl exhibits a "knee" at about 500°C, remarkably similar to the "knee" in the conductivity of NaCl. They were immediately led to suggest that divalent negative ion impurities caused the number of negative ion vacancies to become fixed at this temperature, in analogy to the interpretation of this effect in the conductivity. Lidiard<sup>11</sup> pointed out that such a view was incompatible with the law of mass action in that the presence of positive divalent impurities would more than compensate for the effect of negative divalent impurities, and the excess of positive divalent impurities would "salt out" the negative ion vacancies. With this model one expects the activation energy for diffusion to increase as the temperature is lowered, which expectation is in direct opposition to the observed results. Lidiard suggested that the observations might be explained by a contribution to the diffusion at low temperatures by the motion of vacancy pairs. He also pointed out that a crucial test of this hypothesis would be the comparison of the diffusion coefficient of a pure crystal with the diffusion coefficient of a crystal containing added positive divalent impurity. The presence of the impurity should depress the concentration of negative ion vacancies, but should not affect the concentration of vacancy pairs. Morrison and Rudham<sup>12</sup> performed such experiments on KCl with a variety of doping agents and reported that the diffusion coefficient was insensitive to the presence of impurity.

The subject of vacancy pairs has long been a puzzle in the study of alkali halides. Mott and Gurney<sup>13</sup> recognized that the density of pairs might be comparable with the density of free vacancies. Seitz<sup>14</sup> estimated that the concentration of pairs should be equal to the concentration of free vacancies in NaCl at 600°C. The presence of such pairs, if mobile, would provide for a diffusion mechanism which did not transport charge, the pair being neutral, and its presence should be detected in deviations from the Einstein relation. Such deviations were in fact found,<sup>15</sup> but the

measurements of Schamp and Katz<sup>5</sup> on NaBr indicated that vacancy pairs were insufficient to explain the observed deviations. Subsequent work has ascribed these deviations to other effects. Hence, prior to the work of Morrison and Rudham there was no evidence for the existence of vacancy pairs in transport phenomena.

The present work was undertaken to investigate more fully the effect of divalent impurities on the negative ion diffusion coefficient. The system chosen for study was sodium chloride with small additions of the calcium ion. The earlier work on the diffusion coefficient in the pure material was repeated so that direct laboratory comparisons between pure and doped crystals could be made.

### THEORY

In thermal equilibrium an alkali halide crystal will contain a certain number of vacant lattice sites of either sign. The number of vacancies present will be determined by two conditions, the law of mass action and the condition of electrical neutrality. The law of mass action states that

$$n_+n_- = N^2 \exp(-E_f/kT), \quad (1)$$

where  $n_+$  and  $n_-$  are the numbers of positive and negative ion vacancies, respectively,  $N$  is the number of lattice sites in either sub-lattice, and  $E_f$  is the enthalpy of a pair of separated vacancies. This expression is the direct result of the requirement that the free energy of the system be a minimum. In this and subsequent expressions we will ignore entropy changes and other terms which will alter the pre-exponential term but do not influence the exponent. The condition of electrical neutrality requires that

$$n_+ + N_i^- = n_- + N_i^+. \quad (2)$$

Here  $N_i^+$  is the number of divalent positive ions and  $N_i^-$  the number of divalent negative ions in the lattice. (Impurities of other valency will be neglected.) It is obvious from this expression that the density of vacancies of either sign will only be influenced by the difference between the two impurity concentrations. In actual practice divalent positive ions are much more soluble in alkali halides than are divalent negative ions, and the term  $N_i^-$  can usually be neglected. It will be neglected in the following discussion.

The solutions to these two equations fall into two regions. In the high-temperature region the number of thermal vacancies far exceeds the number of impurities and the impurity term can be ignored in the neutrality condition. In this region the number of positive ion vacancies equals the number of negative ion vacancies, and both have a temperature dependence characterized by an activation energy  $E_f/2$ . At low temperatures the impurities become important and the number of positive ion vacancies remains constant and the number of negative ion vacancies decreases even faster in order to satisfy (1). In this region the density of positive ion

<sup>8</sup> D. Patterson, G. S. Rose, and J. A. Morrison, *Phil. Mag.* **1**, 393 (1956).

<sup>9</sup> L. G. Harrison, J. A. Morrison, and R. Rudham, *Trans. Faraday Soc.* **54**, 106 (1958).

<sup>10</sup> L. W. Barr, I. M. Hoodless, J. A. Morrison, and R. Rudham, *Trans. Faraday Soc.* **56**, 697 (1960).

<sup>11</sup> A. B. Lidiard, *J. Phys. Chem. Solids* **6**, 298 (1958).

<sup>12</sup> J. A. Morrison and R. Rudham, *J. Phys. Chem. Solids* **6**, 402 (1958).

<sup>13</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940), p. 40.

<sup>14</sup> F. Seitz, *Revs. Modern Phys.* **18**, 384 (1946).

<sup>15</sup> D. Mapother, H. N. Crooks, and R. J. Maurer, *J. Chem. Phys.* **18**, 1231 (1950).

vacancies will be characterized by an activation energy zero, and the density of negative ion vacancies by an activation energy  $E_f$ .

In actual measurements of either conductivity or diffusion the temperature dependence of the measured quantities will contain the temperature dependence of the density of defects, which we have just discussed, and the temperature dependence of the jump probability. This will add a term of the form  $\exp(-E_m/kT)$ , where  $E_m$  is the activation energy of motion of the appropriate defect.

The number of vacancy pairs can be shown to be<sup>11</sup>

$$n_p = 6N \exp[-(E_f - E_b)/kT], \quad (3)$$

where  $E_b$  is the binding energy of the two vacancies. Since this defect is neutral it will not be influenced by the presence of aliovalent impurities and may be expected to obey a single equation of this type throughout any temperature range of interest. A diffusion process utilizing vacancy pairs will also have a term of the form  $\exp(-E_m/kT)$  in the diffusion coefficient, where this  $E_m$  is the energy of motion proper to vacancy pairs.

Since in the first approximation the density of positive ion vacancies is equal to the concentration of divalent positive ion impurities in the low-temperature region, we expect the concentration of negative ion vacancies to be proportional to the inverse of the concentration of impurities. The diffusion coefficient should also be proportional to the inverse of the concentration of impurities if the diffusion proceeds by the motion of negative ion vacancies. The diffusion coefficient should be independent of impurity concentration if vacancy pairs are the lattice defects chiefly responsible for diffusion.

#### EXPERIMENTAL PROCEDURE

Pure crystals of sodium chloride were obtained from the Harshaw Chemical Company and were used as received. Crystals containing  $\text{CaCl}_2$  were either grown in this laboratory by the Kyropolous method or were obtained from Dr. Karl Korth, Kiel, Germany. These crystals were subjected to a standard anneal before measurements were begun. The crystals were heated to  $740^\circ\text{C}$  and held for several hours. They were cooled to room temperature at the rate of  $1^\circ\text{C}$  per minute. Samples in the form of 1-cm cubes were cleaved from the crystals. Before diffusion a fresh surface was prepared on each sample by slicing with a microtome. The microtome used in this experiment for slicing crystals has been described by Mapother, Crooks, and Maurer.<sup>15</sup> A layer approximately 2 microns thick of sodium chloride containing  $\text{Cl}^{36}$  was evaporated on the surface of each crystal. The crystals were then loaded into a Vycor holder and sealed in an atmosphere of helium. The crystals were raised rapidly (less than 2 minutes) to the diffusion temperature and held at this tempera-

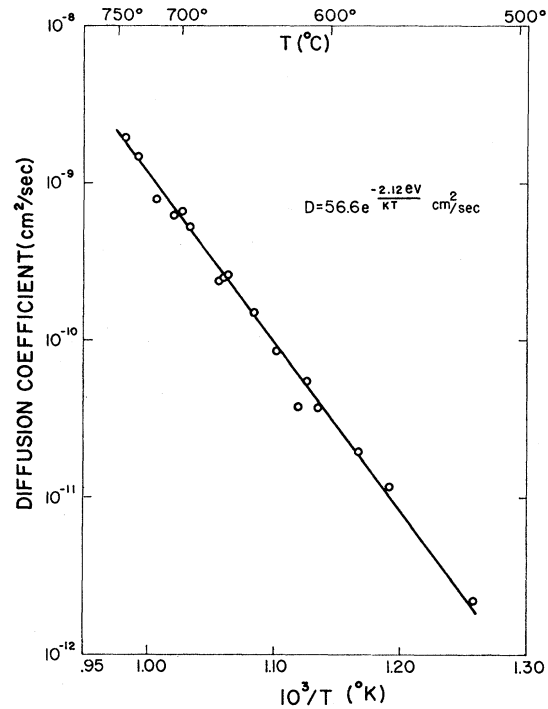


Fig. 1. Diffusion coefficient of  $\text{Cl}^{36}$  in pure NaCl as a function of temperature. The straight line has been fitted to the data by the method of least squares.

ture for a time sufficient to give a mean penetration depth of 75 microns. The time necessary varied from 3 hours to 6 weeks depending on temperature. The crystals were quickly cooled to room temperature and sectioned with the microtome. Slices of the crystal were removed by placing a piece of Scotch tape on the surface and passing the microtome knife beneath it. Between 15 and 35 slices, each approximately 5 microns thick, were removed in this manner. The thickness of the slice was measured by means of an interferometer using the mercury 5461 Å line. The activity in each slice was counted for a time sufficient to give a 1% error due to statistical fluctuations. Corrections to the data were made for the effect of the finite slice thickness, finite initial layer size, and for any misalignment.<sup>16</sup> The diffusion coefficient was calculated by making a least squares fit of the data to a Gaussian penetration curve. The temperature of the crystals during the diffusion anneal was measured by a platinum-platinum 10% rhodium thermocouple placed in thermal contact with the crystal.

#### RESULTS

The diffusion coefficient of the chlorine ion in pure sodium chloride as a function of temperature is given in Fig. 1. The parameters in the equation for  $D$  were computed by the least squares method. A comparison

<sup>16</sup> G. A. Shirn, E. S. Wajda, and H. B. Huntington, *Acta Met.* 1, 513 (1953); also see reference 5.

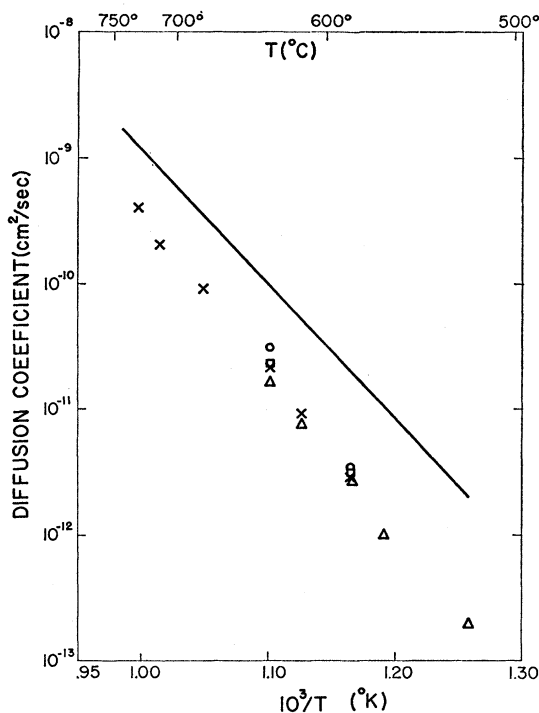


FIG. 2. Diffusion coefficient of  $\text{Cl}^{36}$  in NaCl containing Ca. The straight line from Fig. 1 representing the pure material has been added for comparison.  $\circ$   $1 \times 10^{-4}$  mole fraction calcium;  $\square$   $2 \times 10^{-4}$  mole fraction calcium;  $\times$   $5 \times 10^{-4}$  mole fraction calcium;  $\triangle$   $10 \times 10^{-4}$  mole fraction calcium.

of these parameters with those found by other investigators is given in Table I. There is reasonable agreement between our results and those of Laurent and Bénard and of Harrison, Morrison, and Rudham, especially as regards the activation energy.

The results of measurements on doped crystals are given in Fig. 2. The straight line from Fig. 1 has been included for comparison. It is seen that the effect of the calcium ion is to reduce the diffusion coefficient of the negative ion by a factor of between 5 and 10 from that of the pure crystal. Crystals of several doping concentrations are included here; it can be seen that the variation in doping concentration does not greatly influence the diffusion coefficient. A least squares curve has been fitted to points from the crystal designated  $\times$  with the result:

$$D = 1280 \exp(-2.49 \text{ ev}/kT).$$

These values are the ones included in Table I.

Figure 3 illustrates the dependence of the diffusion coefficient on calcium concentration at  $T = 584^\circ\text{C}$ . The point at the extreme left of the figure represents the "pure" Harshaw crystal. The concentration of calcium actually present in the crystals was determined by measuring the conductivity of a sample and comparing the results with the data of Bean.<sup>17</sup> Bean's results were

<sup>17</sup> C. Bean, thesis, University of Illinois, 1952 (unpublished).

extrapolated to give an effective impurity concentration for the Harshaw crystal. The value arrived at was somewhat smaller than the value  $10^{-6}$  used in the figure, so that the discrepancy between curve (a) and the experimental points is probably greater than shown here. Curve (a) shows the expected behavior for diffusion via negative ion vacancies, curve (b), the expected behavior for diffusion via vacancy pairs. Curve (c) has been drawn with the assumption that the actual dependence is that of curve (a) for small impurity concentration but becomes similar to that of curve (b) at large impurity concentrations. This will be discussed below. A similar dependence of diffusion on impurity concentration was found at  $T = 635^\circ\text{C}$  (not shown).

## DISCUSSION

The aim of these measurements is the determination of the mechanism of diffusion of the negative ion. Although one may envisage many possibilities, there are only a few which are energetically favorable. We shall attempt to interpret the data in terms of some of these models.

At this time it seems safe to limit our discussion to mechanisms involving Schottky and related defects. Theoretical arguments indicate that the existence of Frenkel defects in the negative ion lattice is extremely unlikely,<sup>18</sup> and they will not be considered further. The motion of free negative ion vacancies is an obvious choice for a diffusion mechanism. The most recent estimate of the activation energy for motion of a negative ion vacancy is contained in a paper by Guccione, Tosi, and Asdente.<sup>19</sup> They computed the energy of motion of both ions using several different forms for the repulsive potential and found that they obtained the best agreement with experiment for the positive ion when they used a Born-Mayer-Verwey potential. This potential is somewhat harder than the Born-Mayer potential more usually employed. For this potential they obtained an energy of motion of the nega-

TABLE I. Summary of experimental results of chlorine ion diffusion in NaCl. The parameters listed represent the best fit of experimental values of the diffusion coefficient to the equation  $D = D_0 \exp(-W/kT)$  in the temperature range indicated.

	Temperature range ( $^\circ\text{C}$ )	$D_0$ ( $\text{cm}^2/\text{sec}$ )	$W$ (ev)
Present work			
pure NaCl	520-745	56.6	2.12
doped NaCl	585-730	1280	2.49
Laurent and Bénard <sup>a</sup>	600-795	110	2.23
Harrison, Morrison, and Rudham <sup>b</sup>	450-690	490	2.29
Chemla <sup>c</sup>	650-760	3000	2.70

<sup>a</sup> See reference 4.

<sup>b</sup> See reference 9.

<sup>c</sup> See reference 3.

<sup>18</sup> N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).

<sup>19</sup> R. Guccione, M. P. Tosi, and M. Asdente, *J. Phys. Chem. Solids* **10**, 162 (1959).

tive ion of 1.11 ev. Using the experimental data on positive ion motion<sup>20</sup> to obtain the value of the energy of formation of a Schottky defect (2.02 ev), we conclude that the activation energy for diffusion of the negative ion should be 2.12 ev. The exact agreement of this figure with our measured value of 2.12 ev must of course be considered fortuitous, since otherwise it would imply better accuracy than can be attributed to either the experimental or the theoretical values. On the other hand the activation energy in the impure region, which should apply to our measurements on doped crystals, is predicted to be 3.13 ev. The value obtained from a series of measurements on doped crystals is 2.49 ev. Although the accuracy of this value is not so high as the value for pure crystals, the discrepancy is quite large, certainly out of the range of experimental error. In addition the behavior of the diffusion coefficient as a function of doping concentration indicates that free vacancies alone cannot explain the diffusion. The measured diffusion coefficient is about 100 times larger than one would expect on the basis of the mass action law. One view consistent with these results is that diffusion in pure crystals is dominated by free vacancies, but that in doped crystals the concentration of the free vacancies is reduced to the point where some other mechanism which is insensitive to the presence of impurity takes over.

A diffusion process involving the motion of vacancy pairs should be unaffected by the presence of divalent impurity. Since there is a large difference between the diffusion coefficient of pure and doped crystals, vacancy pairs alone cannot explain the observed results. It is possible that vacancy pairs constitute the mechanism mentioned above which dominates the diffusion process at high positive ion impurity concentrations. Qualitatively Fig. 3 agrees with this interpretation, and curve (c) has been drawn with this in mind. Under this assumption the activation energy for the doped crystals (i.e., 2.49 ev) should be that appropriate to vacancy pair diffusion. Theoretically this energy is of the form  $E_f - E_b + E_m$  where  $E_f$  is the energy to form a Schottky pair,  $E_b$  is the binding energy of the pair, and  $E_m$  is the energy to move the pair.  $E_f$  is known from measurements on the positive ion<sup>20</sup>; it is 2.02 ev. No data is available on the other terms, but both have been calculated. Fumi and Tosi<sup>21</sup> have shown that the binding energy in NaCl is 0.60 ev or less. The energy of motion has not been calculated for NaCl, but Dienes<sup>22</sup> has estimated it for KCl. He arrived at a value of 0.38 ev. However, Lidiard<sup>23</sup> has pointed out that the results of Guccione, Tosi, and Asdente<sup>19</sup> would indicate that one should use the hard potential in calculations on NaCl instead of the Born-Mayer potential employed by Dienes. In view of this Lidiard<sup>23</sup> feels it would not be

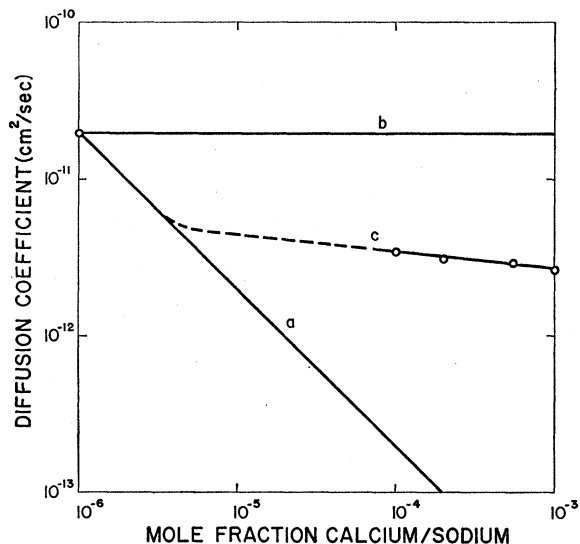


FIG. 3. Diffusion coefficient of Cl<sup>36</sup> in NaCl as a function of calcium content.  $T = 584^\circ\text{C}$ . The point on the extreme left represents the pure Harshaw material. (a) Prediction of mass action law for free vacancy motion; (b) Prediction for diffusion via vacancy pairs; (c) Experimental points.

unreasonable to expect the energy of motion of the pair to be nearly as large as that of an isolated vacancy. Using the values of Tosi and Fumi for the binding energy we may use our data to calculate an energy of motion of the vacancy pair. This turns out to be 1.07 ev, only slightly smaller than that calculated for a free negative ion vacancy. Lidiard<sup>24</sup> also has made some calculations of the density of vacancies and of vacancy pairs for various impurity concentrations. Comparing his results with ours, it can be seen that the density of vacancy pairs is of the right order of magnitude with respect to the density of vacancies to explain our results *if the energy of motion of negative ion vacancies is not much different from that of vacancy pairs*. It would be desirable to repeat the calculation of Dienes on the energy of motion of a vacancy pair using the Born-Mayer-Verwey form of the repulsive potential as employed by Guccione, Tosi, and Asdente. At present, however, all one can say is that the hypothesis that the diffusion in doped crystals is due to the motion of vacancy pairs seems fairly reasonable. This explanation has the virtue that it explains why the effect of vacancy pairs has not been observed in positive ion diffusion measurements. Vacancy pairs do not influence the positive ion self-diffusion coefficient because of the large activation energy for motion of a pair.

Recently there has appeared some evidence that chlorine ion diffusion is sensitive to the presence of dislocations. Barr *et al.*<sup>10</sup> have repeated the low-temperature measurements of Harrison, Morrison, and Rudham<sup>9</sup> and have found that the diffusion coefficient

<sup>20</sup> H. W. Etzel and R. J. Maurer, *J. Chem. Phys.* **18**, 1003 (1950).

<sup>21</sup> M. P. Tosi and F. G. Fumi, *Nuovo cimento* **1**, 95 (1958).

<sup>22</sup> G. J. Dienes, *J. Chem. Phys.* **16**, 620 (1948).

<sup>23</sup> A. B. Lidiard (private communication).

<sup>24</sup> A. B. Lidiard and K. Tharmalingam, *Discussions Faraday Soc.* **56**, 64 (1960).

may be reduced by suitably annealing the specimen. They have correlated this decrease with a decrease in the dislocation density as determined by etching. These results offer no serious problem to the interpretation of the present data because these effects were found at temperatures below those used in the present work. However, if we are to believe the interpretation based on vacancy pairs advanced above, this means that at sufficiently low temperatures the diffusing species with which they were dealing was a vacancy pair and not a free vacancy as they have supposed. This in turn means that their arguments concerning the effect of a charged dislocation line on the diffusion are inapplicable, and one must look for some interaction of dislocations with vacancy pairs which increases either their number or their mobility. Such an interaction can only depend indirectly on the charge of the dislocation line since the vacancy pair is uncharged. On the other hand these results suggest that the difference in diffusion coefficient between pure and doped crystals reported here may be (at least partially) the result of a difference in the dislocation content between the two types of crystals.

Dislocations might be expected to augment the diffusion coefficient by providing easy paths for the diffusing species, and such a process need not result in a deviation from bulk kinetics, as Hart<sup>25</sup> has shown. It is possible that the presence of the calcium ion alters the equilibrium dislocation density, thereby affecting the diffusion coefficient. This field is still in its infancy, and further work, both experimental and theoretical, is needed to understand the effect of dislocations.

#### ACKNOWLEDGMENTS

It is a pleasure to acknowledge the guidance and assistance of Professor R. J. Maurer throughout the course of this work. I wish to thank Professor J. A. Morrison for stimulating correspondence and for the privilege of reading his manuscript prior to publication. I also wish to thank Professor A. B. Lidiard for his correspondence and for supplying me with the results of his calculations. The support afforded by a National Science Foundation Fellowship held during the course of this investigation is gratefully acknowledged.

<sup>25</sup> E. W. Hart, *Acta Met.* **5**, 597 (1957).

## Magnetic Susceptibility of *p*-Type Ge

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(Received May 26, 1960)

The magnetic susceptibility of *p*-type Ge has been measured for a range of extrinsic carrier densities extending from  $5 \times 10^{17} \text{ cm}^{-3}$  to  $5 \times 10^{20} \text{ cm}^{-3}$ . Measurements were made in the temperature range 300°K to 1.3°K. The degenerate hole susceptibility was determined from the data. At the lower carrier densities, the data depart appreciably from the Landau-Peierls value; above  $10^{20} \text{ cm}^{-3}$  the data exhibit features due to the population of the split-off band. From the experimental results, it is estimated that the Fermi level touches the minimum of the split-off band at a carrier density of  $1.3 \times 10^{20} \text{ cm}^{-3}$ . A qualitative discussion is given of the factors determining the susceptibility including band degeneracy and spin-orbit coupling; a detailed quantitative analysis is not attempted.

#### INTRODUCTION

THIS paper describes an investigation of the static magnetic susceptibility of extrinsic holes in Ge. This investigation is similar to our earlier magnetic studies of electrons in Ge<sup>1</sup> and InSb.<sup>2</sup> The purpose of the work is to compare the experimentally observed carrier susceptibility with theoretical expectations and thereby obtain information concerning the band structure. A study of *p*-type Ge was undertaken because the valence band not only departs from a simple parabolic

form in the experimentally attainable range<sup>3,4</sup> but also, at the highest carrier densities, it was expected that carriers would occupy the band "split-off" by spin-orbit coupling.<sup>3,4</sup> Band degeneracy and spin-orbit interactions are expected to be important in determining the susceptibility of the holes. An investigation of carrier susceptibility in this case seemed a worthwhile extension of our previous studies of the susceptibility in a parabolic band (*n*-type Ge<sup>1</sup>) and in a nondegenerate nonparabolic band (*n*-type InSb<sup>2</sup>). Studies of this kind on relatively simple and understood systems are desirable if static susceptibility measurements are to be used for the investigation of materials with poorly known band

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<sup>1</sup> R. Bowers, *Phys. Rev.* **108**, 683 (1957).

<sup>2</sup> R. Bowers and Y. Yafet, *Phys. Rev.* **115**, 1165 (1959). Y. Yafet, *Phys. Rev.* **115**, 1172 (1959).

<sup>3</sup> G. Dresselhaus, A. F. Kip, and C. Kittel, *Phys. Rev.* **98**, 386 (1955).

<sup>4</sup> E. O. Kane, *J. Chem. Phys. Solids* **1**, 83 (1956).