PHYSICAL REVIEW VOLUME 144, NUMBER 2 15 APRIL 1966

Free-Carrier Absorption in Reduced $SrTiO_3$

W. S. Baer
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 22 November 1965)

Optical absorption in stoichiometric and reduced, semiconducting single crystals of $SrTiO_3$ has been measured in the region 0.4–5 μ at room temperature and 77°K. Reduced crystals show a rapid increase of absorption with increasing wavelength beyond 0.6 μ, characteristic of free-carrier absorption. The absorption is proportional to electron concentration and nearly independent of temperature. For wavelengths between 0.7 and 2.5 μ the absorption varies as $\lambda^{2.5}$, suggesting that longitudinal-optical-mode scattering is the dominant electron scattering mechanism at these temperatures. The magnitude of the observed free-carrier absorption is in poor agreement with that predicted from weak-coupling polaron theory but does agree with optical constants determined from recent reflectivity measurements. The validity of a weak-coupling theory is questionable in $SrTiO_3$, since the electron–longitudinal-optical-phonon coupling constant is greater than 3.

INTRODUCTION

THE electronic properties of reduced strontium titanate have been the subject of several recent investigations. As in other titanium oxides, electron transport is thought to occur via a narrow band formed from titanium 3*d* orbitals.[1] A tight-binding calculation of Kahn and Leyendecker[2] supports this conclusion and predicts six conduction-band minima at the Brillouin zone edge along the $\langle 100\rangle$ cubic axis. States at $\mathbf{k}=0$, however, probably exist only a few hundredths of an electron volt above these minima. Hall-mobility and Seebeck-coefficient measurements[3] in reduced and doped single crystals of $SrTiO_3$ confirm the existence of heavy but mobile conduction-band electrons. At sufficiently high carrier concentrations and low temperatures, the material becomes superconducting.[4]

Stoichiometric, insulating $SrTiO_3$ crystals are transparent in the visible and near infrared. Upon heating above 900°C in an oxygen-deficient atmosphere, the crystals turn blue with an associated absorption in the infrared. An earlier study[5] of optical transmission in heat-treated $SrTiO_3$ reported a broad absorption maximum near 1.4 μ, uncorrelated with any electron transport properties. This apparent absence of free-carrier absorption has led to the speculation that the band structure of $SrTiO_3$ differs significantly from that of a similar perovskite, $KTaO_3$.[6]

In this paper we present evidence that the infrared absorption in reduced single crystals of $SrTiO_3$ is due to free carriers. The wavelength dependence of the absorption suggests that electron scattering from longitudinal optical phonons is the dominant scattering mechanism at temperatures down to 77°K. Polaron effects must be included to obtain agreement with experiment. In a very recent paper,[7] Barker has discussed free-carrier contributions to the reflectivity at frequencies near the highest frequency longitudinal optical phonon in reduced $SrTiO_3$. Our experimental results at higher frequencies are in substantial agreement with his.

EXPERIMENTAL PROCEDURES AND RESULTS

$SrTiO_3$ samples for this study were cut from two boules supplied by the National Lead Company and from a small piece of a boule grown by Dr. A. Linz of MIT.[8] Samples were reduced at various temperatures above 900°C in vacuum, flowing hydrogen, or carbon monoxide; the carrier concentration and infrared absorption did not depend on the reducing atmosphere. Reduced, semiconducting crystals could be restored to the insulating state by heating them in air or oxygen above 800°C. The optical absorption was then identical to that of a stoichiometric sample. Samples could be reduced and oxidized several times without ill effect.

Electrical contacts were applied to unpolished faces with an ultrasonic soldering iron and indium enriched solder. Contact resistances were typically about 40Ω. Hall coefficient and mobility measurements were made at 296 and 77°K using conventional Hall techniques. The carrier concentration was obtained from the relation $R_H=1/Ne$. Mobilities determined at these two temperatures are in good agreement with the data of Frederickse, Thurber, and Hosler[3] for all samples used in subsequent optical studies.

The optical absorption coefficients of stoichiometric $SrTiO_3$ and five reduced samples at room temperature are shown in Fig. 1. Carrier concentration and mobility data for each are given in Table I. The band edge is seen near 0.4 μ (3.1 eV). In the stoichiometric case corrections for surface reflections were made by measuring the

---

[1] F. J. Morin, Bell System Tech. J. **37**, 1047 (1958).

[2] A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A1321 (1964).

[3] H. P. R. Frederickse, W. R. Thurber, and W. R. Hosler, Phys. Rev. **134**, A442 (1964).

[4] J. F. Schooley, W. R. Hosler, and M. L. Cohen, Phys. Rev. Letters **12**, 474 (1964).

[5] H. W. Gandy, Phys. Rev. **113**, 795 (1959).

[6] S. H. Wemple, Phys. Rev. **137**, A1575 (1965).

[7] A. S. Barker, in *Proceedings of the International Colloquim on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1965).

[8] The author is grateful to S. H. Wemple of these Laboratories for providing this sample.

transmission T for two samples of different thickness t and computing the absorption coefficient A:

$$A=\ln(T_1/T_2)/(t_2-t_1). \qquad (1)$$

The reflection loss out to 4 μ agreed well with that calculated from the refractive index data of Bond.[9] A similar correction for reflection loss was made for each reduced sample.

The main feature of Fig. 1 is the monotonic increase of absorption with increasing wavelength beyond 0.6 μ for all reduced samples. The data between 0.7 and 2.5 μ for the four samples with carrier concentration $>10^{17}/\text{cm}^3$ fit a power law $A=A_0\lambda^x$ with exponents of 2.4–2.6, increasing slightly with increasing carrier concentration. Sample No. 5 with $N=8.2\times10^{16}/\text{cm}^3$ shows a smaller rise ($\sim\lambda^{2.2}$), but a reasonable fit can be obtained from the sum of a $\lambda^{2.5}$ term proportional to N and a wavelength-independent component. Except for sample No. 5, Fig. 2 shows that the absorption scales linearly with N over two orders of magnitude. It is thus convincing to conclude that the infrared absorption in reduced SrTiO$_3$ is due to free carriers.

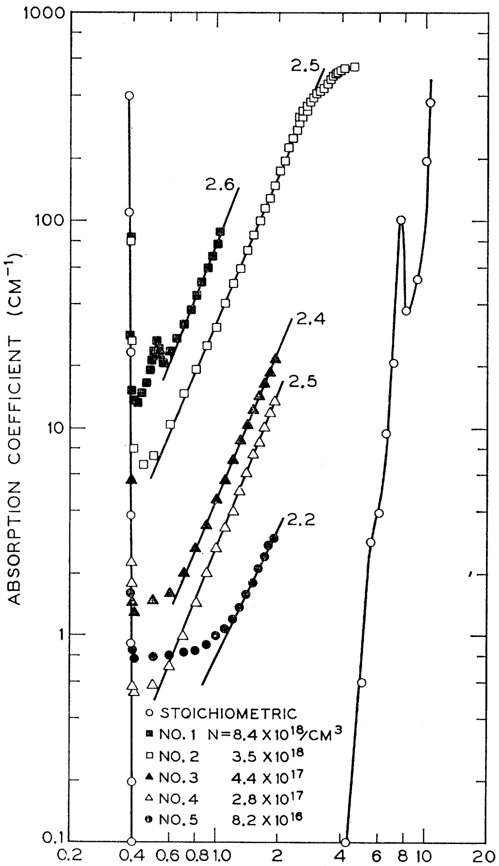

FIG. 1. Room-temperature absorption coefficient as a function of wavelength for stoichiometric SrTiO$_3$ and five reduced samples. The exponent of a power law fit, $A=A_0\lambda^x$, is indicated for each reduced sample.

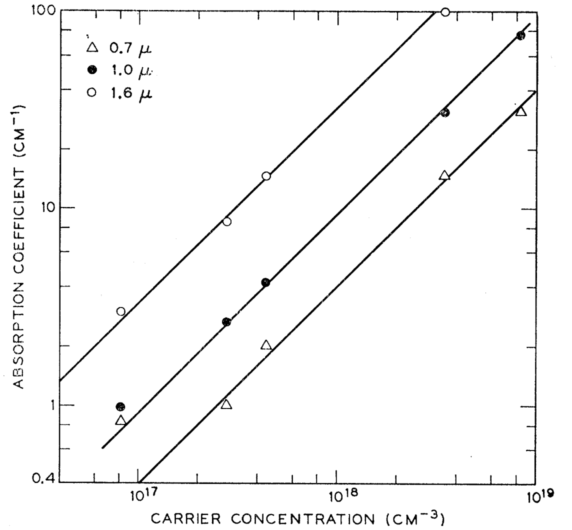

FIG. 2. Room-temperature absorption coefficient as a function of carrier concentration at three different wavelengths. The lines drawn have slopes of unity.

Figure 1 also shows an absorption peak near 0.515 μ (2.4 eV) in sample No. 1. An expanded recorder trace of this absorption is shown in Fig. 3. This peak appears to a greater or lesser extent in other reduced samples, but it cannot be correlated with carrier concentration. Its origin is still uncertain, but it may be due to excitation of an electron trapped at an oxygen vacancy, i.e., an F_1 center. F centers have been reported in BaTiO$_3$.[10]

Cooling samples Nos. 1 and 2 to liquid-nitrogen temperature does not measurably change their absorption, as shown in Fig. 4. The carrier concentration N is expected to remain constant between 300 and 77°K, since the large dielectric constant of SrTiO$_3$ ensures that carriers ionized from hydrogenic donors will remain in the conduction band down to temperatures below 1°K. Sample No. 2 does show a constant N, but the concentration of sample No. 1 appears to be 5% higher

TABLE I. Carrier concentrations and Hall mobilities of reduced SrTiO$_3$ samples.

Sample	Temp. (°K)	N (cm^{-3})	Mobility (cm^2/V sec)
1	296	8.4×10^{18}	7.2
1	77	8.7×10^{18}	230
2	296	3.5×10^{18}	5.8
2	77	3.5×10^{18}	150
3	296	4.4×10^{17}	6.4
4	296	2.8×10^{17}	5.4
5	296	8.2×10^{16}	5.8

---

[9] W. L. Bond, J. Appl. Phys. 36, 1674 (1965).

[10] P. Confova and H. Arend, Czech. J. Phys. **B11**, 416 (1961).

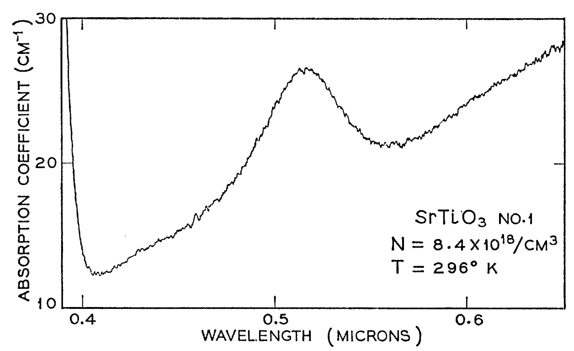

FIG. 3. Absorption near 0.5 μ in sample No. 1.

at 77°K than at 296°K. This apparent small increase in carrier concentration with decreasing temperature has been seen in other experiments[3,7] which measure the Hall effect in SrTiO$_3$ and is probably due to a change in the statistical factor r in the expression $R_H = r/Ne$ relating the Hall constant R_H to the carrier concentration N. We have taken r to be unity in calculating N for these samples, but r depends on the electron scattering mechanism involved. For scattering from longitudinal optical phonons, Devlin[11] has shown that r_{opt} is a function of the ratio of phonon to thermal energies, $\hbar\omega/kT$. Taking the highest energy longitudinal optical phonon in SrTiO$_3$ to be at 12.4 μ (0.099 eV)[12] Devlin's theory predicts that r_{opt} will be 1.16 at room temperature where these samples are nondegenerate. At 77°K, however, the samples are nearly degenerate and r will approach unity. This would account for the observed decrease in R_H.

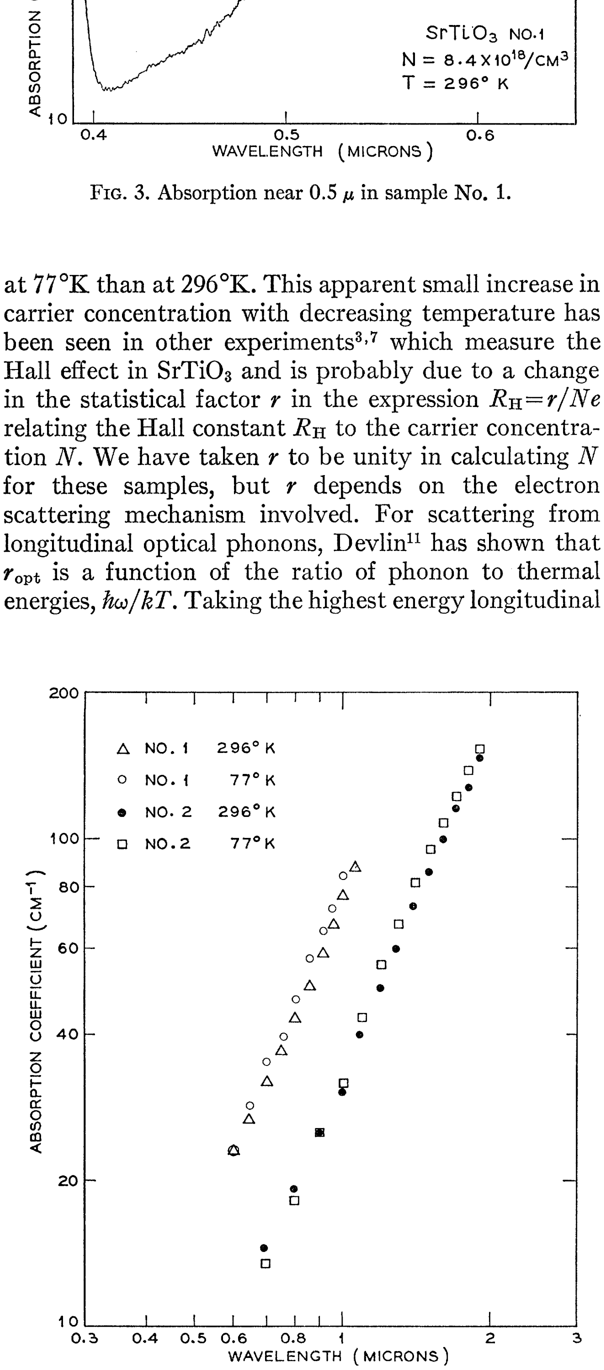

FIG. 4. Absorption coefficient as a function of wavelength for samples Nos. 1 and 2 at 296 and 77°K.

DISCUSSION

The wavelength dependence of free-carrier absorption in a semiconductor can, in principle, be used to determine the scattering mechanism(s) dominant at a given temperature. The classical Drude theory predicts a λ^2 dependence, while treatments of electron scattering from acoustical phonons,[13] longitudinal optical phonons,[14,15] and ionized impurities[14] give free-carrier absorptions varying as $\lambda^{1.5-2}$, $\lambda^{2.5}$, and λ^3, respectively. The data of Figs. 1 and 4 between 0.7 and 2.5 μ are best fitted by a $\lambda^{2.5\pm0.1}$ dependence which agrees with the longidutinal-optical-phonon scattering theory of Gurevich, Lang, and Firsov[15]:

$$A=\frac{8\pi Ne^2\alpha}{3ncm^*\omega_l}\left(\frac{\lambda}{\lambda_l}\right)^{2.5}F\left(\frac{\hbar\omega}{2kT},\frac{\hbar\omega_l}{2kT}\right). \tag{2}$$

In the above equation, α is the electron-longitudinal-optical-phonon coupling constant, n is the refractive index at wavelength λ, c is the velocity of light, m^* is the optical effective mass, and ω_l and λ_l are the frequency and wavelength of the longitudinal optical phonon. The derivation of Eq. (2) assumes that $\omega\tau_0 = \omega/2\omega_l\alpha \gg 1$. If, in addition, as in these experiments, $\hbar\omega_l \gg kT$ and $\hbar(\omega-\omega_l)\gg kT$, Eq. (2) reduces to

$$A=(8\pi Ne^2\alpha/3ncm^*\omega_l)(\lambda/\lambda_l)^{2.5}(1-\lambda/\lambda_l)^{1/2}. \tag{3}$$

Thus the negligible change of the free-carrier absorption between 296 and 77°K also agrees with the Gurevich, Lang, and Firsov theory. For other scattering mechanisms, a stronger temperature dependence is predicted. Finally, the deviation from the $\lambda^{2.5}$ line seen in Fig. 1 for sample No. 2 beyond 2.5 μ may be ascribed to the $(1-\lambda/\lambda_l)^{1/2}$ term in Eq. (3). A similar effect has been observed in KTaO$_3$.[6]

Although the wavelength dependence and temperature independence of the free-carrier absorption are in agreement with that predicted for polar mode scattering, the absorption magnitude measured at all wavelengths and carrier concentrations is much greater than

---

[11] S. S. Devlin (to be published).

[12] D. M. Eagles, J. Phys. Chem. Solids **26**, 672 (1965); A. S. Barker, Phys. Rev. (to be published).

[13] H. J. G. Meyer, Phys. Rev. **112**, 298 (1958); R. Rosenberg and M. Lax, *ibid.* **112**, 843 (1958).

[14] S. Visvanathan, Phys. Rev. **120**, 376, 379 (1960). As the authors of Ref. 15 point out, Visvanathan's results are valid only for $\omega \gg \omega_l$.

[15] V. L. Gurevich, I. G. Lang, and Yu. A. Firsov, Fiz. Tverd. Tela **4**, 1252 (1962) [English transl.: Soviet Phys.—Solid State **4**, 918 (1962)].

that calculated from Eq. (3). Using the values $N=3.5\times10^{18}$, $\alpha=1.87(m^*/m)^{1/2}$,[12] $n=2.31$,[9] $m^*/m=2.5$,[7] $\lambda_l=12.4\ \mu$,[12] and $\lambda=1\mu$, one calculates $A\approx2$ compared with a measured A of 30. Inclusion of scattering from other longitudinal optic modes in $SrTiO_3$ increases the calculated A by about 15%. Attempts to make up the difference with other scattering mechanisms are not consistent with the observed wavelength and temperature dependence of the absorption, or the magnitude and temperature dependence of the mobility.

Our experimental values, moreover, are in good agreement with Barker's determination[7] of the free-carrier contribution to the imaginary part of the dielectric constant in reduced $SrTiO_3$ from reflectivity data. He attempts to fit his high-frequency results with the sum of a Drude term (incorporating all scattering mechanisms other than polar mode scattering) and either a "large" or a "small" polaron term to account for the electron-longitudinal-optical-phonon interaction. Since conduction in reduced $SrTiO_3$ can be described by a band picture rather than a hopping model,[3] large polaron theory is thought to apply. In addition, Holstein's criterion[16] for large polarons, that the conduction bandwidth be greater than the polaron binding energy, also holds in $SrTiO_3$ for an effective mass ratio $m^*/m<20$. The large polaron theory of Eq. (2), however, gives results an order of magnitude lower than Barker's measured values at wavelengths less than 4 μ. Turning to a small polaron theory, Barker obtains a better fit using an expression derived by Reik[17] from a perturbation treatment:

$$A=\frac{4\pi}{nc}\sigma_0\frac{\sinh(\hbar\omega/2kT)}{\hbar\omega/2kT}\exp(-\omega^2\tau^2)\,, \tag{4}$$

where σ_0 is a conductivity and τ a relaxation time not necessarily related to those at dc. Our experimental results, however, show a power-law increase of absorption with wavelength rather than an exponential rise predicted by Eq. (4). An even more important point is the temperature insensitivity of both Barker's and our results for $\hbar(\omega-\omega_l)\gg kT$, whereas Reik's theory demands an exponential temperature dependence. It is thus unlikely that a small polaron theory applies to $SrTiO_3$ under these experimental conditions.

Free-carrier absorption has been reported in a number of polar semiconducting compounds: InP,[18] GaAs,[19] CsS,[20] ZnO,[21] and $KTaO_3$.[6] For each, polar scattering theory is most consistent with the observed wavelength, temperature, and carrier concentration dependence of the absorption. The absorption magnitudes are summarized in Table II. From the data one sees that quantitative agreement with the polar scattering theory of Gurevich *et al.* is reasonably good only for InP. The measured absorption is greater than that calculated from Eq. (3) in all cases, and, except for GaAs, the difference increases with increasing coupling constant α. This is not surprising, because Eq. (2) is derived from an expansion in powers of α and is not expected to hold for compounds with coupling constants near or greater than 1. Since α is proportional to the square root of the effective mass, a choice of $m^*/m=2.5$ from Baker's optical data[7] at 300°K results in a coupling constant of 3 for the highest frequency mode in $SrTiO_3$, while an effective mass of 16 reported by Fredericks, Thurber, and Hosler[3] gives a coupling constant near 7. It would thus be more meaningful to compare these experimental results on free-carrier absorption in $SrTiO_3$ with an intermediate coupling, high frequency polaron conductivity calculation.

TABLE II. Free-carrier absorption in polar semiconducting compounds.

Compound	m^*/m	α	N (cm^{-3})	$\lambda(\mu)$	A [Eq. (2)] (cm^{-1})	A (Observed) (cm^{-1})	Reference
InP	0.07	0.13	4×10^{17}	6	5.1	5.5	14, 18
GaAs	0.08	0.088	1.1×10^{18}	6	6.0	20	19
CdS	0.20	0.70	2.0×10^{18}	2	3.2	6	20
ZnO	0.4	1.2	1.6×10^{18}	2	9.0	26	21
$KTaO_3$	0.8	2	1.7×10^{18}	1	1.9	11	6
$SrTiO_3$	2.5	3	3.5×10^{18}	1	2	30	7, this work

[*Note added in proof.* A comparison has been made using the intermediate coupling theory of R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, Phys. Rev. **127**, 1004 (1962). For high frequencies their results require only the inclusion in Eq. (2) of a factor $(v/w)^3$, where v and w are variational parameters chosen to minimize the energy of the polaron. The ratio $(v/w)^3$ increases with increasing coupling constant: for $\alpha=3$, $(v/w)^3=2.4$, for $\alpha=5$, $(v/w)^3=6.7$ and for $\alpha=7$, $(v/w)^3=48$. A recent determination of the electron effective mass from magnetic-susceptibility measurements (H. P. R. Frederikse and G. W. Candella, Bull. Am. Phys. Soc. **11**, 108 (1966)) gives $m^*=5m_0$, so that the coupling constant will be about 4. Multiplying Eq. (2) by the factor $(v/w)^3$ will lessen the disagreement between theory and experiment, but a discrepancy of about a factor of 5 still remains.]

CONCLUSIONS

1. The infrared absorption in reduced $SrTiO_3$ is due to free carriers.

2. The wavelength dependence and temperature insensitivity of the free-carrier absorption suggests that

---

[16] T. Holstein, Ann. Phys. (N.Y.) **8**, 325 (1959).

[17] H. G. Reik, Solid State Commun. **1**, 67 (1963).

[18] R. Newman, Phys. Rev. **111**, 1518 (1958).

[19] W. G. Spitzer and J. M. Whelan, Phys. Rev. **114**, 59 (1959).

[20] W. W. Piper and D. T. F. Marple, J. Appl. Phys. **32**, 2237 (1961).

[21] D. G. Thomas, J. Phys. Chem. Solids **10**, 47 (1959).

electron scattering from longitudinal optical phonons is the dominant scattering mechanism at 296 and 77°K.

3. The magnitude of the free-carrier absorption is in poor agreement with small coupling constant, polar scattering theory. This is not unexpected, since the electron–longitudinal optical-phonon coupling constant for the highest frequency mode in $SrTiO_3$ is between 3 and 7.

ACKNOWLEDGMENTS

The author has benefited from several discussions with A. R. Hutson, H. Scher, and A. S. Barker, Jr. Thanks are due R. E. Dietz for making available a Cary Recording Spectrophotometer at the beginning of this work, and Miss D. Dodd for absorption measurements on a stoichiometric sample. The experimental assistance of R. C. Griffith is appreciated.

PHYSICAL REVIEW VOLUME 144, NUMBER 2 15 APRIL 1966

Entropy of Vacancies in Ionic Crystals

Suresh Chandra
Physics Department, University of Gorakhpur, Gorakhpur, India

AND

Gopal Krishna Pandey and Vinai Krishna Agrawal
Physics Department, University of Allahabad, Allahabad, India

(Received 19 October 1965)

The entropy of formation of vacancies in alkali halides has been calculated by computing the changes in lattice frequencies as a result of ionic displacements produced by the creation of vancancies using the simple Einstein model. The contributions of both the electric and the elastic parts have been considered in the calculation of ionic displacements. The calculated values of entropy for LiF, NaCl, KCl, and KBr are in fair agreement with experimental values. The contributions of the surface effects and the dipole interactions to the entropy value are also discussed, and found to be negligible.

INTRODUCTION

A THEORETICAL investigation of the entropy of vacancies in ionic crystals is of interest in the study of various defect properties.[1–3] Vineyard and Dienes[4] have obtained a close relation between the entropy of formation of a defect and its influence on the lattice-vibration frequencies of the crystal. Thus, the problem of determining the specific entropy of a particular lattice defect reduces to evaluating the change in the elastic spectrum that results from the introduction of the defect. Stripp and Kirkwood[5] tried to evaluate this change by investigating the perturbations on the actual frequencies of the elastic waves caused by the defects. The mathematical difficulties are, however, formidable. The simpler Einstein model of localized vibrations has been used for calculating the entropy of defects in copper by Huntington *et al.*,[6] and in sodium chloride by Theimer.[7] In these calculations the displacement of lattice sites produced by the formation of vacancies must be known. Theimer considered the displacement of lattice sites to be purely electric and overlooked the elastic displacements. His value for sodium chloride is seriously in error both in magnitude and sign. In the present paper the entropy of vacancies for LiF, NaCl, KCl, and KBr have been obtained by taking both the electric and elastic displacements into consideration. A fair agreement of our values with the experimental values shows the importance of elastic displacement. We have also evaluated the surface effects and the dipole-interaction effects, which come out negligible in the alkali halide crystals.

ENTROPY DUE TO IONIC DISPLACEMENT

The entropy of a defect is related to the frequency of lattice vibration by[4,8]

$$S_d = k \sum_{i=1}^{6N} \ln(\nu_i/\nu_i'), \tag{1}$$

where ν_i are the normal frequencies of the N cations and N anions, and ν_i' are the frequencies perturbed by the dissociated vacancy pairs.

---

[1] S. Chandra and V. K. Agrawal, Phys. Rev. **139**, A952 (1965).

[2] A. B. Lidiard, Phys. Rev. **112**, 54 (1958).

[3] A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.

[4] G. H. Vineyard and G. J. Dienes, Phys. Rev. **93**, 265 (1954).

[5] K. F. Stripp and J. G. Kirkwood, J. Chem. Phys. **22**, 1579 (1954).

[6] H. B. Huntington, G. A. Shirn, and E. S. Wajda, Phys. Rev. **99**, 1085 (1955).

[7] O. Theimer, Phys. Rev. **112**, 1857 (1958).

[8] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1940).