

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 SrTiO₃ is between 3 and 7.

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Entropy of Vacancies in Ionic Crystals

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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 vacancies 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 Dienes⁴ 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 Kirkwood⁵ 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}

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

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.

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

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

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

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

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

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

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

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

If the frequency changes $\Delta\nu_i = \nu'_i - \nu_i$ are small, S_d may be approximated as

$$S_d \cong -k \sum_{i=1}^{6N} (\Delta\nu_i/\nu_i) \cong -\frac{1}{2}k \sum_{i=1}^{6N} (\Delta(\nu_i^2)/\nu_i^2). \quad (2)$$

It is seen from the simple lattice-vibration theory of crystals with two kinds of atoms (like alkali halides) that the squares of the normal-mode frequencies are proportional to the force constant. Hence one gets

TABLE I. Displacement of the ions (in Å) due to vacancy.

Substance	Cation vacancy	Anion vacancy
LiF	0.208	0.245
NaCl	0.230	0.278
KCl	0.264	0.276
KBr	0.242	0.270

approximately

$$S_d \cong -\frac{1}{2}k \sum_{i=1}^{6N} (\Delta f_{ii}/f_{ii}). \quad (3)$$

Since in an ideal crystal all f_{ii} are equal, this can be written as

$$S_d \cong -(k/2f) \sum_{i=1}^{6N} \Delta f_{ii}, \quad (4)$$

where f is any one of the $6N$ diagonal matrix elements, which are all equal in an ideal crystal. Theimer got a similar expression by following a different argument, which appears to be erroneous. Going from his second equation to his third involves the following steps: The sum of the quotients is replaced by the quotient of sums, then the trace relation is used, and then the quotient of the sums is replaced by the sum of quotients. This does not seem to be justified.

Assuming a Born-Mayer potential U between the two ions, the force constant $f_{\sigma\sigma}(k)$ ($\sigma = x, y, z$) for the

TABLE II. Values of the constants used in the calculation.

Constants	LiF	NaCl	KCl	KBr
a (Å)	2.014 ^a	2.81 ^b	3.14 ^b	3.29 ^b
ρ (Å)	0.299 ^a	0.345 ^b	0.345 ^b	0.345 ^b
ϵ	9.27 ^b	5.62 ^b	4.68 ^b	4.78 ^b
α_+ (10^{-24} cm ³)	0.029 ^b	0.41 ^c	1.33 ^c	1.33 ^c
α_- (10^{-24} cm ³)	1.04 ^b	2.96 ^c	2.96 ^c	4.16 ^c
α (10^{-24} cm ³)	2.02 ^d	4.27 ^d	3.84 ^d	7.58 ^d

^a M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids 25, 45 (1964).

^b Reference 8.

^c J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. 92, 890 (1953).

^d Calculated.

TABLE III. The changes $\Delta f_{\sigma\sigma}(k)$ of the diagonal elements of the dynamical matrix produced by a dissociated vacancy pair in KCl, considering both electric and elastic displacements (Theimer's notation).

($k_1 k_2 k_3$)	Vacancy	n	$\Delta(1)$	$\Delta(2)$	$\Delta(3)$	$\Delta(4)$	$\Delta(5)$	$\Delta(6)$	$n \sum_{\sigma} \Delta f_{\sigma\sigma}(k)$
(100)	K ⁺	6	-229	...	56	56	56	56	-2.13 f
(100)	Cl ⁻	6	-238	...	60	60	60	60	-2.11 f
(110)	K ⁺	12	56	56	75	75	20	20	-4.79 f
(110)	Cl ⁻	12	60	60	77	77	19	19	-4.93 f
(111)	K ⁺	8	75	75	75	-19	-19	-19	-1.65 f
(111)	Cl ⁻	8	77	77	77	-53	-53	-53	-0.79 f
(200)	K ⁺	6	-229	9	35	35	35	35	1.41 f
(200)	Cl ⁻	6	-238	7	36	36	36	36	1.54 f
(210)	K ⁺	24	35	20	-54	-22	24	24	-0.63 f
(210)	Cl ⁻	24	36	19	-54	-22	11	11	0.23 f
(211)	K ⁺	24	24	24	1	1	-19	-21	-0.25 f
(211)	Cl ⁻	24	11	11	18	18	-53	12	-0.40 f
									$n \sum_{k\sigma} \Delta f_{\sigma\sigma}(k) = -14.5f$
									$S_d = 7.25k$

ion k is given by

$$f_{\sigma\sigma}(k) = \frac{\partial^2 U}{\partial x_{\sigma}^2(k)} = \sum_l U(kl) \left[\frac{x_{\sigma}^2(kl)}{\rho^2 r^2(kl)} + \frac{x_{\sigma}^2(kl)}{\rho r^3(kl)} - \frac{1}{\rho r(kl)} \right], \quad (5)$$

$$\sum_l f_{\sigma\sigma}(k) = \sum_l U(kl) \left[\frac{1}{\rho^2} - \frac{2}{\rho r(kl)} \right],$$

TABLE IV. The changes $\Delta f_{\sigma\sigma}(k)$ of the diagonal elements of the dynamical matrix produced by a dissociated vacancy pair in KCl, considering electric displacement only (Theimer's notation).

($k_1 k_2 k_3$)	Vacancy	n	$\Delta(1)$	$\Delta(2)$	$\Delta(3)$	$\Delta(4)$	$\Delta(5)$	$\Delta(6)$	$n \sum_{\sigma} \Delta f_{\sigma\sigma}(k)$
(100)	K ⁺	6	-295	...	-29	-29	-29	-29	1.71 f
(100)	Cl ⁻	6	-307	...	-28	-28	-28	-28	1.87 f
(110)	K ⁺	12	-29	-29	26	26	67	67	-1.92 f
(110)	Cl ⁻	12	-28	-28	26	26	67	67	-1.96 f
(111)	K ⁺	8	26	26	26	-39	-39	-39	0.56 f
(111)	Cl ⁻	8	26	26	26	-39	-39	-39	0.56 f
(200)	K ⁺	6	-295	45	12	12	12	12	2.88 f
(200)	Cl ⁻	6	-307	45	12	12	12	12	3.08 f
(210)	K ⁺	24	67	-8	-8	-22	12	-31	-0.035 f
(210)	Cl ⁻	24	67	-8	-8	-22	12	-31	-0.035 f
(211)	K ⁺	24	-39	-8	-8	16	16	27	0.145 f
(211)	Cl ⁻	24	-39	-8	-8	16	16	27	0.145 f
									$n \sum_{k\sigma} \Delta f_{\sigma\sigma}(k) = 7.00f$
									$S_d = -3.50k$

where l labels the ions in the neighborhood of ion k . The presence of the vacancy destroys this equality of the force constants and the ions undergo displacements. If $r(kl)$ changes by an amount $\Delta r(kl)$, one has⁷

$$\sum_l f_{\sigma\sigma}(k) = \frac{1}{2}f \sum_{l=1}^6 [1 - \Delta r(kl)/\rho + \frac{1}{2}\Delta^2 r(kl)/\rho^2 + \dots], \quad (6)$$

TABLE V. Values of entropy for formation of a dissociated vacancy pair.

Substance	Calculated value of entropy considering both electric and elastic displacements	Calculated value of entropy considering electric displacement only	Value from experimental data
LiF	6.14 <i>k</i>	-5.22 <i>k</i>	6.20 <i>k</i> ^a
NaCl	5.84 <i>k</i>	-2.35 <i>k</i> -0.085 <i>k</i> ^b	(6.2±1.8) <i>k</i> ^c 3.3 <i>k</i> ^d
KCl	7.25 <i>k</i>	-3.50 <i>k</i>	(7.1±2.3) <i>k</i> ^e
KBr	4.51 <i>k</i>	-3.45 <i>k</i>	≈7 <i>k</i> ^e

^a Y. Haven, Rec. Trav. Chim. 69, 1259, 1471 (1950).

^b Value calculated by Theimer using Fumi and Tosi's value of nearest-neighbor displacement.

^c R. W. Dreyfus and A. S. Nowick, J. Appl. Phys. Suppl. 33, 473 (1962).

^d H. Etzel and R. Maurer, J. Chem. Phys. 18, 1003 (1950).

^e N. A. Economou and P. V. Sastry, Phys. Status Solidi 6, 135 (1964).

where

$$\Delta r(kl) = [\xi(l) - \xi(k)] \cdot \mathbf{1}(kl)$$

and $\mathbf{1}(kl)$ is a unit vector from ion k to ion l .

Theimer considered the displacement ξ to be purely electric. But the total displacement of the ions excepting the nearest neighbors will consist of two parts,

(i) electric displacement

$$\xi_{\text{elec}} = M'a / (h^2 + k^2 + l^2), \quad (7)$$

and (ii) elastic displacement

$$\xi_{\text{elas}} = \xi_{100} / (h^2 + k^2 + l^2), \quad (8)$$

where (h, k, l) are the coordinates of the ion, taking the vacancy to be the point $(0, 0, 0)$.

The calculated values of ξ_{100} , which is the displacement of a nearest neighbor to a vacancy, using the well-known expressions,³ are given in Table I. The values of the constants used in the calculations are given in Table II. Using these, the change in the matrix elements of the force constant can be obtained. Table III shows a typical set of such values for KCl when both the electric and the elastic displacements were considered. Table IV shows the matrix elements without elastic displacement. It is obvious from Table III that bonds (100) and (200), (111) and (211), (210) and (310), and (210) and (220) are compressed, while the rest of the bonds are dilated. This property is common in all four crystals.

The calculated values of entropy, taking (i) only electric displacement and (ii) both electric and elastic displacements into consideration, are given in Table V

for LiF, NaCl, KCl, and KBr. The available experimental values are also given for comparison.

SURFACE EFFECTS

The contribution of surface effects to the entropy is approximately given by the expression⁶

$$(\partial S / \partial V)_T = (\partial P / \partial T)_V = K\beta,$$

where K is the bulk modulus and β is the thermal coefficient of expansion. For metals where both K and β are large, this may make a significant contribution. But for alkali halides, K and β are fairly low. Hence, the surface effects contribute negligibly to the entropy of formation.

DIPOLE EFFECTS

The vacancy induces dipoles in its neighbors. The force constant will be modified because of the dipole-interaction energy, which is given by

$$E_{\text{dipole}} = \{\mathbf{u}_1 \cdot \mathbf{u}_2 - 3(\mathbf{u}_1 \cdot \mathbf{r}_0)(\mathbf{u}_2 \cdot \mathbf{r}_0)\} / r^3.$$

The interaction energy also turns out to be small in comparison with the more predominant repulsive energy terms in the case of alkali halides. Its contribution to the entropy is only $-0.08k$ for KCl.

DISCUSSION

From inspection of Table V, it is obvious that our values are in fair agreement with the experimental values. Thus, it appears that the elastic displacements produced by the formation of vacancies make important contributions to their entropy values. The apparent discrepancy between Theimer's theoretical and experimental values is removed. The neighbors of the cation and anion vacancies have to be treated separately because of the different elastic displacements undergone by them. Though we have considered the effect of some far neighbors also, actually the next nearest neighbors contribute most significantly to the trace of the dynamical matrix, as is evident from Table III. The contributions due to the surface effects and dipole effects are negligible in these cases also.

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