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Entropy of Formation of Vacancies in Ionic Crystals

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The effect of anharmonicity on the entropy of formation of vacancies is considered for three alkali halides. The Brauer method and Boswarva and Lidiard method have been used for evaluation of elastic displacement of the ions. It has been concluded that the anharmonic effects are small and that the Brauer method gives values in good agreement with experimental results. The Boswarva and Lidiard method gives a lower value of entropy of formation. Our findings are contrary to those of Roy and Ghosh.

I. INTRODUCTION

Theoretical investigation of the properties of a dissociated Schottky-defect pair in alkali halides usually involves the calculation of the energy and entropy of formation of these defects. Evaluation of the energy of formation has received considerable attention[1] but calculation of the entropy of formation has been done only scantily. The work in this direction was started by Theimer[2] on NaCl. His basic approach involves the calculation of the changes in the elastic spectrum of the solid due to the introduction of the defect in an otherwise perfect crystal. This ultimately reduces to the evaluation of the changes in the nearest-neighbor bond lengths of the various near and distant neighbors of the vacancy, the prerequisite for which is the knowledge of the displacements undergone by these ions owing to the presence of the vacancy.

The displacement of any ion (except the nearest-neighbor ones) can be broken into two parts[3]: the (i) electric and (ii) elastic displacement parts. Two methods are available for determining the elastic displacement part: one originally proposed by Brauer[3] and another recently proposed by Boswarva and Lidiard[4] (hereinafter referred to as BL). The general equation for the elastic displacement is

$$\vec{\xi}_{\text{elas}} = k a^2 \hat{r}/r^3 \ , \tag{1}$$

where k is the elastic strength of the vacancy and a is the interionic distance. The value of this elastic strength has been taken to be $k = \xi_{100}$ by Brauer and $k = \xi_{100} - M' a$ by BL, where

$$M' = \frac{1}{4\pi}\left(\frac{\epsilon - 1}{\epsilon}\right)\frac{2\alpha}{\alpha_{+} - \alpha_{-} + 2\alpha} \ . \tag{2}$$

α_{+} and α_{-} are, respectively, the cation and anion polarizabilities, α is the displacement polarizability, ξ_{100} is the displacement of next nearest neighbors to a vacancy, and ϵ is the static dielectric constant.

Chandra *et al.*[5] have applied Theimer's model to four alkali halide crystals and have used the Brauer term for computing elastic displacement of the various ions of the dissociated vacancy pair. Their values are in fair agreement with experimental values. The same approach was applied to evaluate the entropy of formation of the associated cation-anion vacancy defect pair.[6]

Roy and Ghosh,[7] in a recent publication, reevaluated the entropy of formation of vacancies for the KCl crystal using the previously used technique[5] of finding out the matrix elements. The main innovation in their calculation is the incorporation of anharmonic relaxation terms in the harmonic calculation of entropy in Theimer's scheme and the BL term for elastic displacement of neighbors. Their conclusion is that the BL term for elastic displacements and anharmonic corrections give a theoretical value of $6.841k$ for the entropy, which is compatible with the experimental value of $(7.1 \pm 2.3)k$. If anharmonic terms are neglected, a low value of $2.588k$ for the entropy is obtained. This result is surprising, since one would normally expect that the anharmonic effects, which are of second order, would not change the entropy values so drastically. (The inclusion of anharmonic effects is necessary for exactness.)

The main considerations which prompted us to do the present work were (i) to examine whether the anharmonic effects are so important as to change significantly the calculated value of the entropy and (ii) to determine which of the two models for the elastic displacements is more suited to this problem. In addition to these two main objectives, the other objectives were to calculate the entropy of formation for a new system, KI, and to include higher-order terms hitherto neglected in the various expansions for the entropy.

II. RELATION FOR ENTROPY WITH IONIC DISPLACEMENTS

The starting point is the well-known expression which relates the entropy of formation S_d in Einstein's approximation to the frequency of lattice vibrations:

$$S_d = k \sum_{i=1}^{6N} \ln \frac{\nu_i}{\nu_i'} \quad , \tag{3}$$

where ν_i are the normal-mode frequencies of the N cation and N anions, and ν_i' are the frequencies perturbed by the cation-anion Schottky pairs. Einstein's approximation neglects mode coupling. If the frequency changes $\Delta\nu = \nu_i - \nu_i'$ are small, S_d may be approximated by the equation

$$S_d = -k \sum_{i=1}^{6N} \left[\frac{\Delta\nu_i}{\nu_i} - \frac{1}{2}\left(\frac{\Delta\nu_i}{i}\right)^2 + \cdots \right]$$

$$= -\frac{k}{2} \sum_{i=1}^{6N} \left[\frac{\Delta(\nu_i^2)}{\nu_i^2} - \frac{1}{2}\left(\frac{\Delta(\nu_i^2)}{\nu_i^2}\right)^2 + \cdots \right] \quad . \tag{4}$$

The square of the normal-mode frequencies is proportional to the force constant. Hence, we get

$$S_d = -\frac{k}{2} \sum_{k\sigma} \left[\frac{\Delta f_{\sigma\sigma}(k)}{f_{\sigma\sigma}(k)} - \frac{1}{2}\left(\frac{\Delta f_{\sigma\sigma}(k)}{f_{\sigma\sigma}(k)}\right)^2 + \cdots \right] \quad . \tag{5}$$

In an ideal crystal all $f_{\sigma\sigma}(k)$ are equal; this may be written as

$$S_d = -\frac{k}{2f} \sum_{k\sigma} \left(\Delta f_{\sigma\sigma}(k) - \frac{1}{2f}[\Delta f_{\sigma\sigma}(k)]^2 + \cdots \right) \quad , \tag{6}$$

where f is any one of the $6N$ diagonal matrix elements, which are all equal in an ideal alkali halide crystal.

We assume a Born–Mayer potential $U(kl)$ for the repulsion between two ions, defined by

$$U(kl) = \beta(kl) b \exp\{[r(k) + r(l) - r(kl)]/\rho\} \quad ,$$

in which

$$\beta(++) = 1.25, \quad \beta(+-) = 1.00, \quad \beta(--) = 0.75,$$

and $r(k)$ and $r(l)$ are the ion-core radii. The force constant $f_{\sigma\sigma}(k)$ $(\sigma = x,\ y,\ z)$ for the ion k is given by

$$f_{\sigma\sigma}(k) = \sum_l \frac{\partial^2 U(kl)}{\partial x_\sigma^2(k)}$$

$$= \sum_l U(kl) \left(\frac{x_\sigma^2(kl)}{\rho^2 r^2(kl)} + \frac{x_\sigma^2(kl)}{\rho r^3(kl)} - \frac{1}{\rho r(kl)} \right) \quad , \tag{7}$$

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

where l labels the ions in the neighborhood of the 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 has, after neglecting higher-order terms

$$\sum_\sigma f_{\sigma\sigma}(k) = \frac{1}{2} f \sum_{l=1}^{6} \left(1 - \frac{\Delta r(kl)}{\rho} + \frac{1}{2} \frac{[\Delta r(kl)]^2}{\rho^2} + \cdots \right) \quad , \tag{8}$$

where

$$\Delta r(kl) = [\vec{\xi}(k) - \vec{\xi}(l)] \cdot \hat{r}(kl) \quad ; \tag{9}$$

$\hat{r}(kl)$ is a unit vector pointing from ion k to l.

III. ANHARMONIC TERMS

The effect of anharmonicity is considered as suggested by Theimer.[2] The appropriate place for its introduction is in the value of $\Delta r(kl)$. The presence of the vacancy effects the value of $\Delta r(kl)$ such that

$$\Delta^{(2)} r(kl) = \Delta^{(1)} r(kl) \pm \delta \quad , \tag{10}$$

where $\Delta^{(1)} r(kl)$ is given by Eq. (9) and δ is the anharmonicity correction factor. δ is positive or negative depending on whether it is a compression or a dilation. For the evaluation of δ, the anharmonic restoring force F_r is expanded about the field-free equilibrium distance a:

$$F_r = U(a) \left(\frac{\Delta^{(1)} r}{\rho^2} - \frac{1}{2} \frac{(\Delta^{(1)} r)^2}{\rho^3} + \cdots \right) \quad . \tag{11}$$

In equilibrium, the restoring force F_r and the external force Ee have to be equal, and one obtains δ from the equation

$$\frac{\Delta r}{\rho^2} - \frac{1}{2} \frac{(\Delta r)^2}{\rho^3} = \pm \frac{Ee}{U(a)} \quad , \tag{12}$$

with the approximate solution

$$\Delta^{(2)} r = \Delta^{(1)} r \pm [(\Delta^{(1)} r)^2/\rho] \quad . \tag{13}$$

This value of $\Delta r(kl)$, which is in fact $\Delta^{(2)} r(kl)$ if anharmonic effects are considered, is substituted

TABLE I. Values of constants used in calculations.

Constants	KCl	KBr	KI
a (Å)	3.147[a]	3.29[a]	3.53[a]
ρ (Å)	0.334[b]	0.335[a]	0.355[a]
ϵ	4.68[c]	4.78[c]	5.12[c]
α_+ (10^{-24} cm^3)	1.33[d]	1.33[d]	1.334[d]
α_- (10^{-24} cm^3)	2.96[d]	4.16[d]	6.431[d]
α (10^{-24} cm^3)	3.84[e]	7.58[e]	2.787[e]

[a] Reference 9.

[b] Reference 4.

[c] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford U.P., Oxford, England, 1940), p. 41.

[d] J. R. Tessman, A. H. Khan, and W. Shockley, Phys. Rev. 92, 890 (1953).

[e] Calculated.

TABLE II. Displacements of the nearest-neighbor ions in Å to a vacancy.

System	Cation Vacancy	Anion vacancy
KCl	0.233[a]	0.267[a]
	0.264[b]	0.276[b]
	0.277[c]	0.339[c]
	0.187[d]	0.224[d]
	0.264[e]	0.349[e]
KBr	0.266[a]	0.293[a]
	0.242[b]	0.270[b]
	0.170[d]	0.233[d]
	0.247[e]	0.364[e]
KI	0.282[a]	0.314[a]
	0.146[d]	0.251[d]
	0.223[e]	0.392[e]

[a] Present work.
[b] Reference 5.
[c] Reference 7.
[d] Reference 4.
[e] A. M. Karo and J. R. Hardy, Phys. Rev. B 3, 3418 (1971).

in Eq. (8). If the anharmonic effects are small, $\Delta^{(2)}r$, $\Delta^{(1)}r$, and Δr are all equal. The change in force constant for compression is

$$\sum_\sigma \Delta f_{\sigma\sigma}(k)=\frac{1}{2}f\sum_l\left[-\frac{\Delta^{(1)}r(kl)}{\rho}+\left(\frac{\Delta^{(1)}r(kl)}{\rho}\right)^2+\cdots\right], \qquad (14)$$

and for dilation is

$$\sum_\sigma \Delta f_{\sigma\sigma}(k)=\frac{1}{2}f\sum_l\left(-\frac{\Delta^{(1)}r(kl)}{\rho}\right). \qquad (15)$$

Roy and Ghosh[7] neglected the square term, which is justified only for dilated "bonds." Substituting the values of these quantities for compression or for dilation in Eq. (6), one can calculate the entropy of formation.

$\vec{\xi}(l)$ and $\vec{\xi}(k)$ are calculated by breaking this displacement into two parts: the (i) electric, and (ii) elastic displacements. The displacement of the six nearest neighbors is calculated by energy minimization.

IV. CHOICE OF SYSTEMS, EVALUATION OF MATRIX ELEMENTS, AND ENTROPY

For computational purposes, three crystals—KCl, KBr, and KI—having common cations were chosen. KCl was studied by the previous workers,[5,7] so our results may readily be compared with theirs; also, there is a relative abundance of experimental results on it. KBr was chosen by Chandra *et al.*,[5] but their entropy value is lower than the experimental results, so a reexamination was thought to be desirable. No theoretical calculations have been performed on the entropy of formation of vacancies for KI, and hence this choice.

The displacement of the six nearest neighbors of a vacancy, ξ_{100}, was calculated according to the formulation of Mott and Littleton.[8] The data of Tosi and Fumi[9] were used throughout and are given in Table I. The calculated values of the nearest-neighbor displacements for these systems are tabulated in Table II. These values for the next-neighbor displacements are different from the results of other investigators. Changes in the matrix elements of the force constants were calculated utilizing the values given in Tables I and II with and without considering the anharmonic effects. In Table III the changes in bond lengths for KI between the nearest neighbors and the corresponding changes in matrix elements are recorded. The matrix elements correspond to the Brauer elastic displacement term and show the same general features as noted by Chandra *et al.* regarding the

TABLE III. Changes $\Delta f_{\sigma\sigma}(k)$ of the diagonal elements of the dynamical matrix produced by a dissociated vacancy pair in KI, considering both electric and elastic displacements (Brauer method). n being the number of equivalent ions at a distance k. The changes Δ (1), Δ (2), etc., of the nearest-neighbor distances are measured in 10^{-11} cm.

									$n\sum_\sigma \Delta f_{\sigma\sigma}(k)$	
(k_1, k_2, k_3)	Vacancy	n	Δ (1)	Δ (2)	Δ (3)	Δ (4)	Δ (5)	Δ (6)	with anharmonic	without anharmonic
(1, 0, 0)	K^+	6	−235	•••	73	73	73	73	−2.67	−2.57
(1, 0, 0)	I^-	6	−259	•••	86	86	86	86	−2.80	−2.57
(1, 1, 0)	K^+	12	73	73	73	73	6	6	−5.34	−4.74
(1, 1, 0)	I^-	12	86	86	81	81	9	9	−6.28	−5.28
(1, 1, 1)	K^+	8	73	73	73	−45	−45	−45	−0.95	−0.60
(1, 1, 1)	I^-	8	81	81	81	−43	−43	−43	−1.31	−0.88
(2, 0, 0)	K^+	6	−235	−5	34	34	34	34	+1.74	+1.59
(2, 0, 0)	I^-	6	−259	−5	36	36	36	36	+2.06	+1.85
(2, 1, 0)	K^+	24	34	6	13	13	−49	−17	+0.09	+0.20
(2, 1, 0)	I^-	24	36	9	15	15	−53	−17	−0.02	+0.06
(2, 1, 1)	K^+	24	−45	13	13	15	15	5	−0.42	−0.41
(2, 1, 1)	I^-	24	−43	15	15	15	15	3	−0.59	−0.54

TABLE IV. Changes $\Delta f_{\sigma\sigma}(k)$ of diagonal elements of the dynamical matrix produced by a dissociated vacancy pair in KI, considering both electric and elastic displacements (BL method). n is the number of equivalent ions at a distance k. The changes Δ (1), Δ (2), etc., of the nearest-neighbor distances are measured in 10^{-11} cm.

(k_1, k_2, k_3)	Vacancy	n	Δ (1)	Δ (2)	Δ (3)	Δ (4)	Δ (5)	Δ (6)	$n\sum_\sigma \Delta f_{\sigma\sigma}(k)$ with anharmonic	$n\sum_\sigma \Delta f_{\sigma\sigma}(k)$ without anharmonic
(1, 0, 0)	K^+	6	−170	···	−29	−29	−29	−29	−0.03	−0.21
(1, 0, 0)	I^-	6	−268	···	14	14	14	14	+0.06	−0.52
(1, 1, 0)	K^+	12	−29	29	43	43	61	61	−2.59	−2.21
(1, 1, 0)	I^-	12	14	14	63	63	37	37	−3.95	−3.45
(1, 1, 1)	K^+	8	43	43	43	−43	−43	−43	+0.02	−0.18
(1, 1, 1)	I^-	8	63	63	63	−44	−44	−44	−0.59	−0.36
(2, 0, 0)	K^+	6	−170	40	9	9	9	9	+1.29	+1.16
(2, 0, 0)	I^-	6	−268	25	22	22	22	22	+2.56	+2.21
(2, 1, 0)	K^+	24	9	61	−6	−6	−49	−21	+0.32	+0.37
(2, 1, 0)	I^-	24	22	37	13	13	−35	−21	−0.63	−0.27
(2, 1, 1)	K^+	24	−43	−6	17	17	−6	24	−0.05	+0.03
(2, 1, 1)	I^-	24	−44	13	17	17	13	17	−0.07	−0.96

compression or dilatation of different bonds. Table IV gives the matrix elements when BL term for elastic displacements was used.

The calculated values of the entropy for different crystals are given in Table V together with the experimentally obtained values. In the present calculations, the contributions of the changes in the bond lengths between the next-nearest-neighbor ion have not been calculated, since their effect has been found by Roy and Ghosh to be relatively small while the scatter in experimental data is considerable. Likewise, the surface and dipole effects have also been neglected because of their insignificant contributions.[5]

TABLE V. Values of entropy of formation for a dissociated vacancy for KCl, KBr, and KI.

Systems	Method for calculating elastic displacements	Theoretically calculated values of entropy of formation (k) with anharmonic	Theoretically calculated values of entropy of formation (k) without anharmonic	Experimental values of entropy of formation (k)
KCl	Brauer method	6.58[a]	6.19[a]	7.1 ± 2.3[b]
			7.25[c]	7.54[d]
	BL method	6.84[e]	2.59[f]	8.2[g]
				5.37[h]
				9.29[i]
				9.62[j]
KBr	Brauer method	6.74[a]	5.66[a]	7.00[k]
			4.51[c]	7.30[l]
KI	Brauer method	8.23[a]	6.94[a]	8.87[m]
	BL method	2.02[a]	2.20[a]	

[a] Present work.

[b] R. W. Dreyfus and A. S. Nowick, J. Appl. Phys. Suppl. 33, 473 (1962).

[c] Reference 5.

[d] R. G. Fuller, Phys. Rev. 142, 524 (1966).

[e] This is the original value of Roy and Ghosh, which is in error. If corrections for anharmonic effects as done here are carried out, then a value 1.83k is obtained.

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V. RESULTS AND DISCUSSION

It is obvious from Table V that the calculated values of the vacancy-formation entropy in KCl, KBr, and KI are compatible with the experimental values. The anharmonic corrections increase the value of entropy in all three cases. If, instead, the BL expression is used in the computations, a very low value of entropy results. Preliminary calculations show the same trend for the KCl and KBr systems. Hence the BL term was not used in these two cases.

Inspection of Table V shows that the contribution of anharmonic effects is about 19% for KI and KBr. For KCl, the contribution is only about 6%. This proves our original assertion that the anharmonic effects do not contribute greatly to the entropy values as claimed by Roy and Ghosh (160%). The entropy value calculated by taking the BL term for the elastic displacement part of various neighbors, as has been done here for KI, also shows no enhancement even with the inclusion of anharmonic terms.

The main difficulty in this type of calculation lies in the fact that the entropy values are extremely sensitive to the displacement of next-neighbor ions. On looking into the literature one finds a large variation in these values (see Table II). In this sense this calculation is different from the energy of formation calculations. In the latter case the energy of formation is not that sensitive to the displacement of the various neighbors. This difficulty is inherent in the present model. The moment one relates the lattice-vibrational frequency modes with force constants, this difficulty crops up, since the force constants are extremely sensitive to the displacement values of the ions.

As has already been pointed out, the main shortcoming of the Einstein approximation is that it neglects mode coupling. The workers in lattice dynamics are probably not at the point where they can give a correction estimate, but a fair estimate might be in the 10–40% range.

Roy and Ghosh[7] apparently got good results because they neglected the higher-order terms involving $(\Delta r/\rho)^2$. This term could only be neglected for the bonds which show dilation as found here, and this is obviously not the case for all the bonds. The entropy value will again be reduced if the corrections for anharmonicity, as noted here, are carried out. This value for KCl from their matrix elements is $1.83k$. It is therefore concluded that anharmonic effects contribute only a small amount to the entropy value and that the BL expression for elastic displacement of ions gives the lower value of entropy. The neglect of anharmonic terms and use of the Brauer elastic displacement term by Chandra *et al.* is hence justified.

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