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Entropy of Vacancies in Ionic Crystals: Application to KCl

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The entropy of formation of vacancies in KCl has been computed using the approach of Theimer. It has been concluded that the inclusion of the elastic displacement in the form proposed by Boswarva and Lidiard, together with the consideration of the effect of anharmonicity as laid down by Theimer, leads to a fair agreement with experiment when the next-nearest neighbors are also taken into account.

I. INTRODUCTION

A theoretical calculation of the entropy of formation of vacancies is of interest in different problems, e.g., the diffusion problem. It may also serve, as pointed out by Theimer,[1] to check the consistency of different theories dealing with the properties of vacancies. The entropy of formation of vacancies has been calculated by a number of workers[1-3] by following different procedures. Most of the studies have been confined to ionic crystals because of the remarkable success of the Born model of cohesion for such type of solids. Vineyard and Dienes[2] have shown that the introduction of a defect changes the elastic spectrum of the solid. Consequently, the entropy of formation of defects can be calculated from the magnitudes of such changes of frequencies in the spectrum. Stripp and Kirkwood[4] have also investigated the influence of lattice defects on the normal modes of vibration of crystals by means of the perturbation theory. Recently, Mahanty and Sachdev[5,6] have shown that the vibrational self-entropy of a point defect in a crystal can be evaluated in terms of the vibrational frequencies of two pseudomolecules whose dynamical properties can be expressed in terms of those of the region affected by the point defect in the crystal. The basic assumption in Theimer's approach is that the frequency shifts $\Delta\nu_i = \nu_i' - \nu_i$ are small. This assumption is evidently not valid for the few localized modes that may be introduced by the defect. However, for the calculation of the entropy of the dissociated vacancy pair, which depends on all the modes of the system, the error introduced by Theimer's assumption is expected to be quite small. Matthew[7] has shown that Theimer's method gives a somewhat lower value for the entropy of formation compared with the value obtained from an exact calculation. However, this method, utilizing the simple Einstein model of localized vibrations, appears to be most suitable for a detailed analysis of the different contributions to the entropy. In this method it is necessary to know the displacement of the nearest neighbors due to the creation of a vacancy. Theimer has treated a vacancy purely as an electric singularity.[3] It has been pointed out by Brauer[8] that a vacancy in the matrix of an ionic crystal should behave as an electric as well as an elastic singularity. Utilizing this concept, Chandra *et al.*[3] have found an improved agreement with the experiments by neglecting anharmonic effects. Boswarva and Lidiard[9] have pointed that the elastic term introduced by Brauer[8] overemphasizes the elastic component in the displacement of more distant ions. Recently, Hardy and Lidiard[10] have shown from the consideration of distortion dipoles that the elastic strength of the vacancy in KCl-type crystals is negligibly small and consequently the Mott-Littleton[11] procedure which considers electric displacement alone is quite justified. In view of the above discussion we have thought it worthwhile to make a detailed analysis of the situation to ascertain (i) whether the elastic displacement needs to be considered at all, and (ii) whether the anharmonic effects, as considered by Theimer,[1] have any significant influence on the entropy of formation of Schottky defects.

In the determination of the changes in the matrix elements of the force constant $\sum \Delta f_{\sigma\sigma}(k)$, only the six nearest neighbors are taken into account, although the summation extends over the whole lattice. In the present work the validity of this approximation has been checked by extending the calculations to the next-nearest neighbors and comparing their contributions with that of the nearest ones.

II. THEORY

A. General Principles

The relation between the entropy and the frequency of lattice vibrations is given by[2,12]

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

where ν_i are the normal-mode frequencies of the N cations and N anions, and ν_i' are the frequencies of the same lattice modes perturbed by a vacancy pair. For small changes of the normal-mode frequencies, S_d may be approximated by the equation

TABLE I. Constants used in the calculation.

Constants	Values	Source
r_0(Å)	3.147	Ref. 14
ρ(Å)	0.334	Ref. 9
r_+(Å)	1.51	Ref. 14
r_-(Å)	1.63	Ref. 14
b(10^{-12}erg)	0.2067	Ref. 9
$\mathcal{E}$	4.68	Ref. 12
α_+(10^{-24} cm^3)	1.33	a
α_-(10^{-24} cm^3)	2.96	a
α(10^{-24} cm^3)	3.84	b

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

[b] Calculated.

TABLE II. Displacements of the nearest neighbors to a vacancy (in Å).

Type of displacement	Cation vacancy	Anion vacancy
Electric only	0.236	0.277
Electric + elastic	0.277	0.339

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

Also, the sum of the squares of the normal-mode frequencies is equal to the trace of the dynamical matrix of the crystal, and hence approximately [1]

$$S_d \cong -\tfrac{1}{2} k \sum_{l\sigma} \frac{\Delta f_{\sigma\sigma}(l)}{f_{\sigma\sigma}(l)} \cong -\frac{k}{2f} \sum_{l\sigma} \Delta f_{\sigma\sigma}(l), \tag{3}$$

f being any one of the $6N$ diagonal matrix elements which are all equal in ideal sodium-chloride-type crystals. We designate the μth ion in the sth cell by a single symbol $l = (\mu, s)$.

We assume a Born-Mayer potential[13] $U(lm)$ for the repulsion between two ions, defined by

$$U(lm) = \beta(lm)\, b \exp\{[r(l) + r(m) - r(lm)]/\rho\}, \tag{4}$$

in which

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

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

$$f_{\sigma\sigma}(l) = \sum_m \frac{\partial^2 U(lm)}{\partial x_\sigma^2(l)} = \sum_m U(lm) \left(\frac{x_\sigma^2(lm)}{\rho^2 r^2(lm)} + \frac{x_\sigma^2(lm)}{\rho r^3(lm)} - \frac{1}{\rho r(lm)} \right), \tag{5a}$$

TABLE III. Changes $\sum_\sigma \Delta f_{\sigma\sigma}(l)$ of the diagonal element of the dynamical matrix produced by a dissociated vacancy pair in KCl when only electric displacement is considered and nearest neighbors are taken into account. Ω is the number of equivalent ions at a distance l. The changes $\Delta(1)$, $\Delta(2)$, etc., of the nearest-neighbor distances are measured in 10^{-11} cm.

$l_1l_2l_3$	Vacancy	Ω	$\Delta(1)$	$\Delta(2)$	$\Delta(3)$	$\Delta(4)$	$\Delta(5)$	$\Delta(6)$	$[\Omega\sum_\sigma \Delta f_{\sigma\sigma}(l)]_1$ Anharmonic	 Without anharmonic
100	K$^+$	6	−268	...	−33	−33	−33	−33	$1.18f_1^0$	$3.23f_1^0$
100	Cl$^-$	6	−309	...	−29	−29	−29	−29	$1.63f_1^0$	$4.29f_1^0$
110	K$^+$	12	−33	−33	26	26	69	69	$-4.46f_1^0$	$-3.75f_1^0$
110	Cl$^-$	12	−29	−29	26	26	69	69	$-4.74f_1^0$	$-4.07f_1^0$
111	K$^+$; Cl$^-$	16	26	26	26	42	42	42	$2.30f_1^0$	$2.80f_1^0$
200	K$^+$	6	−268	46	12	12	12	12	$3.13f_1^0$	$5.13f_1^0$
200	Cl$^-$	6	−309	46	12	12	12	12	$3.86f_1^0$	$6.50f_1^0$
210	K$^+$; Cl$^-$	48	69	12	−8	−8	−35	−23	$-1.01f_1^0$	$0.45f_1^0$
211	K$^+$; Cl$^-$	48	−8	−8	−42	18	18	28	$-0.86f_1^0$	$-0.17f_1^0$
220	K$^+$; Cl$^-$	24	−23	−23	5	5	20	20	$-0.29f_1^0$	$-0.08f_1^0$
221	K$^+$; Cl$^-$	48	5	18	18	−11	−17	−17	$0.58f_1^0$	$0.87f_1^0$
300	K$^+$; Cl$^-$	12	46	−22	−4	−4	−4	−4	$-0.29f_1^0$	$-0.14f_1^0$
310	K$^+$; Cl$^-$	48	−4	−35	4	4	10	20	$0.14f_1^0$	$0.52f_1^0$
311	K$^+$; Cl$^-$	48	28	4	4	−8	−8	−17	$-0.43f_1^0$	$-0.17f_1^0$
222	K$^+$; Cl$^-$	16	−11	−11	−11	12	12	12	$-0.14f_1^0$	$-0.09f_1^0$
320	K$^+$; Cl$^-$	48	20	20	−2	−2	−11	−14	$-0.14f_1^0$	$+0.03f_1^0$
321	K$^+$; Cl$^-$	96	−17	−8	−2	13	10	6	$-0.56f_1^0$	$-0.29f_1^0$

$$\sum_{\sigma} f_{\sigma\sigma}(l)=\sum_{m} U(lm)\left(\frac{1}{\rho^2}-\frac{2}{\rho\, r(lm)}\right), \tag{5b}$$

where m labels the ions in the neighborhood of the ion l. When only the nearest neighbors are considered ($m=1, 2, \cdots, 6$), we have for the ideal crystal

$$\textstyle\sum_{\sigma} f^0_{\sigma\sigma}(l)=3f^0 \ . \tag{6}$$

If $r(lm)$ undergoes a change by an amount $\Delta r(lm)$ in the electric field of a vacancy, one has for the displaced condition of the ions of the lattice[1]

$$\sum_{\sigma} f_{\sigma\sigma}(l)=\tfrac{1}{2}f^0\sum_{m=1}^{6}\left(1-\frac{\Delta r(lm)}{\rho}+\frac{\Delta^2 r(lm)}{\rho^2}-\cdots\right), \tag{7}$$

where

$$\Delta r(lm)=[\vec{\xi}(m)-\vec{\xi}(l)]\cdot\hat{r}(lm); \tag{8}$$

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

The contributions of the next-nearest neighbors to $\sum f_{\sigma\sigma}(l)$, can, however, be found in the following manner: Let us define

$$\textstyle\sum_{\sigma} f_{\sigma\sigma}(l)=[\sum_{\sigma} f_{\sigma\sigma}(l)]_1+[\sum_{\sigma} f_{\sigma\sigma}(l)]_2\, , \tag{9}$$

where the subscripts 1 and 2 denote contributions to $\sum_\sigma f_{\sigma\sigma}(l)$ from the nearest and next-nearest neighbors, respectively.

Thus, for an ideal crystal we have

$$\textstyle\sum_{\sigma} f^0_{\sigma\sigma}(l)=6f^0_1+6f^0_2(+)+6f^0_2(-)=3f^0\, ,$$

where

$$f^0_1=b\beta(+-)\left(\frac{1}{\rho^2}-\frac{2}{\rho r_0}\right)e^{(r_+ + r_- - r_0)/\rho}\ ,$$

$$f^0_2(+)=b\beta(++)\left(\frac{1}{\rho^2}-\frac{\sqrt{2}}{\rho r_0}\right)e^{(2r_+ - \sqrt{2}r_0)/\rho}\, , \tag{10}$$

$$f^0_2(-)=b\beta(--)\left(\frac{1}{\rho^2}-\frac{\sqrt{2}}{\rho r_0}\right)e^{(2r_- - \sqrt{2}r_0)/\rho}\ .$$

Thus, when we ignore the next-nearest neighbors, $f^0_2(\pm)=0$ and

$$f^0=2f^0_1\ . \tag{11}$$

In the electric field of a vacancy,

$$\sum_{\sigma} f_{\sigma\sigma}(l)=\sum_{m=1}^{6} f^0_1\left(1-\frac{\Delta r(lm)}{\rho}+\frac{1}{2}\frac{\Delta^2 r(lm)}{\rho^2}-\cdots\right)+\frac{1}{2}\sum_{n=1}^{12}[f^0_2(+)+f^0_2(-)]\times\left(1-\frac{\Delta r(ln)}{\rho}+\frac{1}{2}\frac{\Delta^2 r(ln)}{\rho^2}-\cdots\right), \tag{12}$$

where

TABLE IV. Contributions to $\sum_\sigma \Delta f_{\sigma\sigma}(l)$ from the next-nearest neighbors considering electric displacement only. Ω is the number of equivalent ions at a distance l. The changes $\Delta(1)$, $\Delta(2)$, etc., of the next-nearest-neighbor distances are measured in 10^{-11} cm.

$l_1l_2l_3$	Vacancy	Ω	$\Delta(1)$	$\Delta(2)$	$\Delta(3)$	$\Delta(4)$	$\Delta(5)$	$\Delta(6)$	$\Delta(7)$	$\Delta(8)$	$\Delta(9)$	$\Delta(10)$	$\Delta(11)$	$\Delta(12)$	$[\Omega\sum_\sigma \Delta f_{\sigma\sigma}(l)]_2$ Anharmonic	$[\Omega\sum_\sigma \Delta f_{\sigma\sigma}(l)]_2$ Without anharmonic
100	K$^+$	6	334	334	334	334	39	39	39	39	−139	−139	−139	−139	$-16.815f^0_2(-)$	$-2.573f^0_2(-)$
100	Cl$^-$	6	392	392	392	392	42	42	42	42	−167	−167	−167	−167	$-19.186f^0_2(+)$	$0.522f^0_2(+)$
110	K$^+$; Cl$^-$	12 : 12	⋯	48	−22	−22	14	14	14	14	−64	−64	−64	−64	$-4.958f^0_2(\pm)$	$-3.858f^0_2(\pm)$
111	K$^+$	8	39	39	39	−21	−21	−21	16	16	16	16	16	16	$-3.593f^0_2(-)$	$-3.326f^0_2(-)$
111	Cl$^-$	8	42	42	42	−21	−21	−21	16	16	16	16	16	16	$-3.808f^0_2(+)$	$-3.528f^0_2(+)$
200	K$^+$; Cl$^-$	6 : 6	−22	−22	−22	−22	−12	−12	−12	−12	11	11	11	11	$1.653f^0_2(\pm)$	$1.734f^0_2(\pm)$
210	K$^+$	24	−139	16	16	32	−32	16	16	−6	−6	−15	2	16	$1.437f^0_2(-)$	$3.906f^0_2(-)$
210	Cl$^-$	24	−167	16	16	32	32	16	16	−6	−6	−15	2	16	$3.449f^0_2(+)$	$6.840f^0_2(+)$
211	K$^+$	24 : 24	−12	14	14	−8	−8	12	12	10	10	−2	−2	4	$-3.162f^0_2(\pm)$	$-3.035f^0_2(\pm)$

TABLE V. The changes $\sum_\sigma \Delta f_{\sigma\sigma}(l)$ of the diagonal elements of the dynamical matrix produced by a dissociated vacancy pair in KCl, when electric as well as elastic displacement are considered and nearest neighbors are taken into account. Ω is the number of equivalent ions at a distance l. The changes $\Delta(1)$, $\Delta(2)$, etc., of the nearest-neighbor distances are measured in 10^{-11} cm.

$l_1l_2l_3$	Vacancy	Ω	$\Delta(1)$	$\Delta(2)$	$\Delta(3)$	$\Delta(4)$	$\Delta(5)$	$\Delta(6)$	$[\Omega\sum_\sigma \Delta f_{\sigma\sigma}(l)]_1$	
									Anharmonic	Without anharmonic
100	K^+	6	-272	$\cdots$	24	24	24	24	$-2.838f_1^0$	$-0.787f_1^0$
100	Cl^-	6	-318	$\cdots$	53	53	53	53	$-4.096f_1^0$	$-1.074f_1^0$
110	K^+	12	24	24	55	55	43	43	$-8.767f_1^0$	$-8.181f_1^0$
110	Cl^-	12	53	53	67	67	32	32	$-10.922f_1^0$	$-10.027f_1^0$
111	K^+	8	55	55	55	-50	-50	-50	$-0.359f_1^0$	$0.235f_1^0$
111	Cl^-	8	67	67	67	-54	-54	-54	$-0.934f_1^0$	$-0.138f_1^0$
200	K^+	6	-272	25	26	26	26	26	$2.569f_1^0$	$4.648f_1^0$
200	Cl^-	6	-318	17	31	31	31	31	$3.180f_1^0$	$6.010f_1^0$
210	K^+	24	43	26	5	5	-48	-23	$-0.576f_1^0$	$0.006f_1^0$
210	Cl^-	24	32	31	6	6	-53	-23	$0.072f_1^0$	$0.652f_1^0$
211	K^+	24	5	5	-50	19	19	20	$-1.293f_1^0$	$-0.899f_1^0$
211	Cl^-	24	6	6	-54	19	19	18	$-1.006f_1^0$	$-0.572f_1^0$
220	K^+	12	-23	-23	11	11	16	16	$-0.287f_1^0$	$-0.190f_1^0$
220	Cl^-	12	-23	-23	13	13	15	15	$-0.359f_1^0$	$-0.260f_1^0$
221	K^+	24	11	19	19	-9	-20	-20	$0.000f_1^0$	$0.185f_1^0$
221	Cl^-	24	13	19	19	-9	-21	-21	$0.000f_1^0$	$0.199f_1^0$
300	K^+	6	25	-29	1	1	1	1	$0.000f_1^0$	$0.040f_1^0$
300	Cl^-	6	17	-32	3	3	3	3	$0.054f_1^0$	$0.090f_1^0$
310	K^+	24	1	-48	8	8	12	14	$0.359f_1^0$	$0.657f_1^0$
310	Cl^-	24	3	-53	10	10	13	12	$0.359f_1^0$	$0.718f_1^0$
311	K^+	24	20	8	8	-6	-21	-21	$-0.216f_1^0$	$-0.104f_1^0$
311	Cl^-	24	18	10	10	-6	-6	-23	$-0.216f_1^0$	$-0.095f_1^0$
222	K^+	8	-9	-9	-9	11	11	11	$-0.144f_1^0$	$-0.122f_1^0$
222	Cl^-	8	-9	-9	-9	11	11	11	$-0.144f_1^0$	$-0.122f_1^0$
320	K^+	24	16	12	1	1	-12	-17	$-0.072f_1^0$	$0.018f_1^0$
320	Cl^-	24	15	13	2	2	-12	-18	$-0.144f_1^0$	$-0.050f_1^0$
321	K^+	48	-20	-6	1	11	10	7	$-0.431f_1^0$	$-0.279f_1^0$
321	Cl^-	48	-21	-6	2	10	10	8	$-0.431f_1^0$	$-0.279f_1^0$

$$\Delta r(lm) = [\vec{\xi}(m) - \vec{\xi}(l)] \cdot \hat{r}(lm) \; ; \tag{13}$$

m and n label nearest and next-nearest neighbors, respectively. $\vec{\xi}$ is comprised of two parts: (a) The electric part is written as

$$\vec{\xi}_{\text{elec}} = M' r_0^3 \vec{r} / r^3 \, ,$$

where

$$M' = \frac{2\alpha}{\alpha_+ + \alpha_- + 2\alpha} \, \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon}\right), \tag{14}$$

α is the displacement polarizability, $\alpha_\pm$ are the electronic polarizabilities, and ϵ is the static dielectric constant. (b) The elastic displacement is taken to be

$$\vec{\xi}_{\text{elas}} = K r_0^2 \vec{r} / r^3 \, , \quad K = \xi_{100} - M' r_0 \, . \tag{15}$$

TABLE VI. Contributions to $\sum_\sigma \Delta f_{\sigma\sigma}(l)$ from the next-nearest neighbors considering electric as well as elastic displacement. Ω is the number of equivalent ions at a distance l. The changes $\Delta(1)$, $\Delta(2)$, etc. of the next-nearest-neighbor distances are measured in 10^{-11} cm.

$l_1l_2l_3$	Vacancy	Ω	$\Delta(1)$	$\Delta(2)$	$\Delta(3)$	$\Delta(4)$	$\Delta(5)$	$\Delta(6)$	$\Delta(7)$	$\Delta(8)$	$\Delta(9\ )$	$\Delta(10)$	$\Delta(11)$	$\Delta(12)$	$[\Omega\Sigma_\sigma \Delta f_{\sigma\sigma}(l)]_2$ Anharmonic	$[\Omega\Sigma_\sigma \Delta f_{\sigma\sigma}(l)]_2$ Without anharmonic
100	K^+	6	392	392	392	392	83	83	83	83	−139	−139	−139	−139	$-24.144f_2^0(-)$	$-4.794f_2^0(-)$
100	Cl^-	6	479	479	479	479	102	102	102	102	−169	−169	−169	−169	$-29.605f_2^0(+)$	$-0.733f_2^0(+)$
110	K^+	12	...	−8	5	5	−1	−1	−1	−1	11	11	11	11	$-13.509f_2^0(+)$	$-13.477f_2^0(+)$
111	Cl^-	12	...	−31	16	16	−8	−8	−8	−8	42	42	42	42	$-16.922f_2^0(-)$	$-16.450f_2^0(-)$
111	K^+	8	80	80	80	−46	−46	−46	35	35	35	35	35	35	$-7.473f_2^0(-)$	$-6.293f_2^0(-)$
111	Cl^-	8	100	100	100	−56	−56	−56	43	43	43	43	43	43	$-9.323f_2^0(+)$	$-7.532f_2^0(+)$
200	K^+	6	5	5	5	5	3	3	3	3	−2	−2	−2	−2	$-0.431f_2^0(+)$	$-0.427f_2^0(+)$
200	Cl^-	6	16	16	16	16	9	9	9	9	−7	−7	−7	−7	$-1.293f_2^0(-)$	$-1.252f_2^0(-)$
210	K^+	24	−139	35	35	35	35	35	34	34	−13	−13	−32	4	$-3.593f_2^0(-)$	$-0.459f_2^0(-)$
210	Cl^-	24	−169	43	43	43	43	43	35	35	−16	−16	−39	5	$-3.598f_2^0(+)$	$-0.954f_2^0(+)$
211	K^+	24	3	−1	−1	−1	−1	−1	−1	27	27	1	1	0	$-3.809f_2^0(+)$	$-3.651f_2^0(+)$
211	Cl^-	24	9	−8	−8	5	5	−6	−6	32	32	2	2	−2	$-4.096f_2^0(-)$	$-3.840f_2^0(-)$

Here K is a measure of the elastic strength of the vacancy at (000). The above relation for K has recently been suggested by Boswarva and Lidiard,[9] which ensures that the displacements predicted by (14) and (15) join smoothly to those of the nearest neighbors. Brauer,[8] who first proposed the inclusion of elastic displacements, gave a relation

$$K=\xi_{100} \tag{16}$$

which overemphasizes the elastic component in the displacement of more distant ions.[9]

B. Anharmonicity

The net effect of anharmonicity in the scheme of Theimer[1] leads to the following equations for $\sum_\sigma f_{\sigma\sigma}(l)$: (i) When only the nearest neighbors are considered, we find

$$\sum_\sigma f_{\sigma\sigma}(l)=\tfrac{1}{2}f^0\sum_{m=1}^{6}\left(1-\frac{\Delta r(lm)}{\rho}-\cdots\right). \tag{17}$$

(ii) When the next-nearest neighbors are also considered,[1] we have

$$\sum_\sigma f_{\sigma\sigma}(l)=\sum_{m=1}^{6}f_1^0\left(1-\frac{\Delta r(lm)}{\rho}-\cdots\right)$$

$$+\frac{1}{2}\sum_{n=1}^{12}\left[f_2^0(+)+f_2^0(-)\right]\left(1-\frac{\Delta r(ln)}{\rho}-\cdots\right). \tag{18}$$

III. CALCULATION OF MATRIX ELEMENTS FOR POTASSIUM CHLORIDE

The displacement of the nearest neighbor to a vacancy, ξ_{100}, was calculated according to the Mott–Littleton scheme.[11,14] In accordance with the recommendations of Boswarva and Lidiard,[9] the data of Tosi and Fumi[15] were utilized, and these are listed in Table I. The calculated values of the nearest-neighbor displacements for different cases are recorded in Table II. Contrary to the findings of Boswarva and Lidiard,[9] we obtained an enhanced nearest-neighbor displacement when the elastic displacement was considered. Ultilizing the values given in Tables I and II, we have calculated the changes in the matrix elements of the force constants with and without considering the anharmonic effects. Tables III and IV show such values for KCl when a purely electric displacement is postulated. In Table III, the changes in bond lengths between the nearest neighbors and the corresponding changes in matrix elements are recorded, while in Table IV those between the next-nearest neighbors are recorded. Corresponding values for the case when the elastic displacements are also considered are recorded in Tables V and VI. The results shown in Tables III and V are in agreement with the findings of Theimer and Chandra *et al.*[3]

TABLE VII. Values of entropy of formation for a dissociated vacancy pair, from different considerations (see text) (nn means nearest neighbor).

Type of displacement considered	Anharmonic effects included		Anharmonic effect excluded		Experimental value
	Without next nn	With next nn	Without next nn	With next nn	
Electricity only	$0.025k$	$0.300k$	$-3.765k$	$-3.488k$	
Electric +Elastic	$6.661k$	$6.841k$	$2.428k$	$2.588k$	(7.1 ± 2.3)[a]

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

regarding the compression or dilatation of the different bonds.

The calculated values of entropy for different cases are given in Table VII together with the experimentally obtained value. In our calculation the surface and dipole effects have been neglected because of their insignificant contributions.

IV. CONCLUSIONS

(i) A pure electric displacement when the anharmonic effects are not considered leads to an entropy value with a wrong sign even when the next nearest neighbors are taken into account.

(ii) A pure electric displacement when the anharmonic effects are taken into consideration leads to an entropy value with a proper sign even when only the nearest neighbors are considered.

(iii) A combined electric and elastic displacement considering nearest neighbors alone generates a reasonable value for entropy only when anharmonic effects are incorporated; otherwise, a remarkably low value results. It may be noted here that Chandra *et al.*[3] obtained good agreement with the experiments by assuming a Brauer-type elastic displacement and neglecting the contribution due to anharmonic effects. The agreement appears to be fortuitous in view of (a) the lack of any argument as to why the anharmonic effects were neglected and (b) the inconsistency of the Brauer-type elastic displacement as pointed out by Boswarva and Lidiard.[9]

(iv) The best and most physically consistent values of the entropy can be obtained from a treatment which considers the elastic (as proposed by Boswarva and Lidiard[9]) as well as the electric displacement, together with the contribution of the anharmonic effects and the next nearest neighbors.

V. DISCUSSION

Boswarva and Lidiard[9] have recently observed that the van der Waals forces contribute significantly towards the formation energies of Schottky defects in ionic crystals. In addition, it seems that the effect of many-body forces should also be considered in these calculations. Unfortunately, owing to the uncertainties of the experimental data, which are of the order of 30% of the value, the evaluation of such a small contribution will be of theoretical interest only.

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