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CALCULATION OF DEFECT ENTROPIES IN IONIC CRYSTALS IN THE QUASIHARMONIC APPROXIMATION : APPLICATION TO FLUORITES

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1. Outline of Theory The dynamical matrix for a crystal containing an interstitial can be written in the form

$$\tilde{L} = \begin{vmatrix} L & -\delta L & A \\ A^T & & \Lambda \end{vmatrix} \quad (1)$$

where L is the dynamical matrix of the perfect crystal, Λ is that part of L that refers exclusively to the interstitial and A is the matrix that connects the interstitial coordinates with those of the rest of the lattice. A^T is the transpose of A . δL is the matrix that describes the force constant changes which occur because of the relaxations of the lattice ions due to the presence of the interstitial. The Green matrix $\bar{G} = \tilde{L}^{-1}$ may also be written in partitioned form like that in (1), whence it may be shown that the determinant of $\bar{G}$ is

$$|\bar{G}| = |I - G \delta L'| |G| |\Lambda|^{-1} \quad (2)$$

where $\delta L' = \delta L + A \Lambda^{-1} A^T$ and I is the $3N \times 3N$ unit matrix, N being the number of atoms in the crystal. Since static lattice calculations show that relaxations of the lattice ions are small except for the first and second neighbours, the non-zero elements of δL will be restricted to a small sub-space comprising these n ions that are perturbed appreciably by the interstitial. It then follows that

$$|I - G \delta L'| = |I - g \delta l'| \quad (3)$$

where I on the RS of (3) is now the $3n \times 3n$ unit matrix.

$$\delta l' = \delta l + \Lambda^{-1} a^T \quad (4)$$

where

$$A = \begin{vmatrix} 0 \\ a \end{vmatrix} \quad (5)$$

and the dimensions of the matrix a are $3n \times 3$.

The entropy change associated with the introduction of an anion from ∞ into an interstitial position in the high-temperature approximation may then be written in the form

$$s_i = -\frac{1}{2} k \ln \lim_{\omega \rightarrow 0} |I - g \delta l'| + 3k \{1 - \ln (\hbar \omega_i / kT)\} \quad (6)$$

where ω_i is the hypothetical frequency of vibration of an interstitial in a lattice in which all the host-lattice ions are frozen at their (perfect lattice) equilibrium positions. In similar fashion the dynamical matrix of a crystal with a vacancy is

$$\tilde{L}_v = L_t - \delta l \quad (7)$$

where L_t is the dynamical matrix L of the crystal without a vacancy, truncated by removing the three rows and columns belonging to the ion which is no longer present. δL is the matrix of force constant changed due to the relaxations of the ions caused by the vacancy. It includes as well the changes in the "self-terms" of the ions because of the removal from these sums the contributions due to the ion which has now been removed. By partitioning $\bar{L}_v$, and also the perfect crystal dynamical matrix L , into blocks such that one of the diagonal blocks of $\bar{L}_v$ represents the 'defect space' (that is those ions that are perturbed by the presence of the vacancy - in practice this means its first and second neighbours) and the corresponding block of L represents the defect space-to-be (including the ion that will become a vacancy) it may be shown that the entropy change associated with the removal of a lattice anion to ∞ is

$$s_v = -\frac{1}{2}k \ln \lim_{\omega \rightarrow 0} \{ m_-^3 |g_v| | (g_v^{-1})_t - \delta L | (kT/h)^6 \} - 3k \quad (8)$$

The entropy of formation of a Frenkel defect is thus given by

$$\begin{aligned} s_F &= s_i + s_v \\ &= -\frac{1}{2}k \ln \lim_{\omega \rightarrow 0} \{ |g_v| | (g_v^{-1})_t - \delta L | | I - g \delta L' | m_-^3 \omega_I^6 \} \end{aligned} \quad (9)$$

In these expressions m_- is the mass of an anion, g_v is the perfect-lattice Green matrix for the defect space-to-be and $(g_v^{-1})_t$ is the truncated version of the reciprocal of g_v (that is, with the 3 rows and columns deleted that correspond to the ion which is to be removed when the vacancy is found). We may not multiply out the first product of determinants in (9) since the operations of truncation and inversion do not, in general, commute.

2. Calculation The necessary Green functions were evaluated using shell model parameters fitted to the experimental phonon dispersion. These parameters were taken from the work of Elcombe and Pryor¹ and Elcombe². For the calculation of δL we require the coordinates of the ions in the imperfect crystal which were obtained from the HADES program.³ The changes in the short-range interaction were restricted to second neighbours, but in the calculation of the self-terms in the δL matrix, it was necessary to ensure that each ion had its full complement of first and second neighbours, even though these neighbours might lie outside the defect space. The short-range force constants were calculated using the two-body central potential of Catlow, Norgett and Ross⁴. The change in the coulomb interaction was calculated only between the ion at the origin (which later became the site of the vacancy) and its first and second neighbours (Benedek⁵). The defect space comprising the interstitial and its first and second neighbours consisted of 15 ions, but 95 ions had to be taken into account while calculating the diagonal terms of δL . The change in the coulomb force between the interstitial and only its first and second neighbours was included. Additionally, the presence of the interstitial is felt through the terms $a \Lambda^{-1} a^T$, where Λ^{-1} was calculated from the self term of the interstitial.

The calculation is a quasiharmonic one in that the actual lattice parameter at each T was used in determining the relaxations of the ions. The Green matrix at, each T was obtained by a scaling procedure⁶. This calculation yields an entropy of

Frenkel defect formation at constant volume, s_F^v . For comparison with experiment we need the corresponding entropy at constant pressure s^p . Since to first order in v^p , the volume change on forming a Frenkel defect at constant pressure, the Gibbs energy change g^p is equal to the Helmholtz energy change f^v , s^p is related to by s^v by

$$s^p - s^v = - \left(\frac{\partial f^v}{\partial v} \right) \beta^p v \quad (10)$$

where v is the volume per molecule ($=2r_o^3$, r_o being the $F^- F^-$ nn distance) and β^p the expansivity. Since both the energy and entropy of defect formation at constant volume u^v and s^v are determined by our calculations, f^v and s^p may be found and compared with experimental values.

3. Results

CaF ₂	T/K	300	1000	1500	
	s ^v /k	0.73	2.88	5.30	
	s ^p /k	8.83	13.30	18.42	
SrF ₂	T/K	300	600	900	(1200) ^a
	s ^v /k	4.49	3.64	3.34	(2.97)
	s ^p /k	5.74	5.68	5.28	(4.15)

^aBased on extrapolated values.

For CaF₂⁸ the mean calculated value of s^p in the range 550 - 1000 K is $\sim 10k$, and the experimental value of s^p is about 5 k.⁸ For SrF₂ s^p (expt) = 4.1 k in the range $\sim 570 - 1100$ K, and the calculated value of s^p is about 5 k. The quasiharmonic calculation depends critically on a knowledge of the temperature dependence of the lattice constant.

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