Entropy of formation of a Frenkel defect in CaF_2: A Green-function calculation

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The results on the dynamics associated with an anion interstitial and with a vacancy at an anion site, discussed in our earlier work, are employed in this paper to compute the entropy of formation of a Frenkel defect in CaF_2. The interstitial and the vacancy are assumed to be far apart and hence each case is discussed separately. The symmetry coordinates of the F_{1u} representation for the interstitial and of the F_2 representation for the vacancy are chosen so as to decouple the degrees of freedom of this defect from the defect space. Then both the methods of Govindarajan *et al.* and of Mahanty and Sachdev are applied to these two defect systems to calculate the entropy of formation of an isolated interstitital and of an isolated vacancy. The entropy of formation of anion Frenkel defect in CaF_2 computed from both methods agrees well with recent experimental results.

I. INTRODUCTION

Considerable work on the defect properties of CaF_2 has been carried out in the past few years and the details are dealt with in an article by Lidiard.[1] Recently Corish *et al.*[2] have also reviewed the situation with respect to defect studies on ionic crystals. From these reviews one finds that theory and experiment give the same range of values for the formation and migration energies of defects whereas the agreement for the corresponding entropies is far less satisfactory. This disagreement may be partly due to the fact that the entropies are deduced from experimental data on conductivity and diffusion rather indirectly, while on the theoretical side the results depend on the principle and method of calculation. However, good defect models have been developed recently and this fact, along with a computer-controlled data analysis, can lead to fairly reliable experimentally deduced values for the defect entropies. Entropy calculations were first tried by a method due to Theimer[3]; his approach was followed by other workers with minor modifications. An Einstein model has also been employed in some calculations. Recently Govindarajan *et al.*[4,5] have computed the entropy of formation due to substitutional and Schottky defects in KCl using a Green-function approach which, in fact, is a generalization of the pseudomolecule procedure due to Mahanty and Sachdev.[6] In their paper Govindarajan *et al.* have briefly reviewed the earlier methods of calculation.

It has been established that the Frenkel disorder is the major defect responsible for the transport properties of CaF_2. The entropy of formation of a Frenkel defect was recently calculated by Varotsos[7] using the bulk properties such as the bulk modulus and its temperature dependence. But he neglects the temperature dependence of the lattice constant entirely. His values of the entropy of formation of a Frenkel defect is around $12k$ which is much larger than the more recent experimental result of $5.4k$ obtained by Jacobs and Ong.[8] Therefore we decided to compute the entropy of formation of Frenkel defects in CaF_2 using the Green-function formulation of Govindarajan *et al.* and the results are presented in this paper. In Sec. II we shall outline the general theory and in Sec. III apply that to an interstitial and a vacancy at the anion site in CaF_2. Section IV deals with our results followed by a discussion and possible conclusions.

II. OUTLINE OF THE THEORY

Govindarajan *et al.*[3] have shown that if we take the defect and the near neighbors of the host lattice that are directly affected by this defect to constitute

a pseudomolecule, the method of Mahanty and Sachdev[6] reduces to finding the determinant $(\underline{I}-\underline{g}\,\delta\underline{l})$ in the zero-frequency limit, where $\underline{g}$ represents the lattice Green function of the host crystal in the defect space and $\delta\underline{l}$ is the corresponding perturbation matrix which incorporates mass changes and force-constant changes that result from the introduction of the defect. The entropy of defect formation s_d is then given by

$$s_d = -\tfrac{1}{2}k \lim_{\omega\to 0} \ln\left(\left|\frac{\underline{m}}{\underline{m}'}\right| |\underline{I}-\underline{g}\,\delta\underline{l}|\right) + \cdots , \qquad (1)$$

where $\underline{m}$ and $\underline{m}'$ are diagonal mass matrices of the unperturbed and perturbed system, respectively, and the dots represent the correction term arising from the loss or gain of degrees of freedom when we have a vacancy or interstitial. The vacancy situation was handled by Govindarajan *et al.* in their calculations on KCl by truncating the $\underline{g}$ and $\delta\underline{l}$ matrices suitably to account for the loss of degrees of freedom due to the vacancy.

In the case of a Frenkel defect, we shall assume that the vacancy and interstitial are far apart such that their interaction is not important. This assumption is made to make the calculations tractable, so that we can take the case of an isolated interstitial and then an isolated vacancy separately. The two results are then added to give the entropy of formation of Frenkel defect. We should admit that in so doing we are over simplifying the interactions that may exist between the interstitial and vacancy, but the neglect of defect interactions is a good starting point from which to deduce the entropy of formation. The result should be valid at temperatures up to at least 1000 K.

III. INTERSTITIAL IN CaF_2

The dynamics of an isolated interstitial have been discussed in detail in an earlier paper[9] (hereafter referred to as Paper I). There it has also been mentioned how the method of Brice[10] would give singularities in the zero-frequency limit for $|\underline{I}-\underline{g}\,\delta\underline{l}|$. On the other hand the method of Maradudin *et al.*[11] removes this difficulty by switching over the Green function of the interstitial into the $\delta\underline{l}$ part of the matrix and also, at the same time, expressing the coupling of the interstitial with the host through the coupling matrix $\underline{a}$, as defined in Paper I. The singularity in the Green function at $\omega=0$ is removed here, since the Green function of the interstitial $\gamma(\omega)$ is $m_I^{-1}(\omega^2-\omega_I^2)^{-1}$, where ω_I is the frequency of the interstitial in the otherwise frozen lattice, whereas in Brice's definition it is $1/m_I\omega^2$. Therefore we shall adopt the method of Maradudin *et al.* in the evaluation of the entropy of formation due to an interstitial.

We found that except for the F_{1u} representation, the results are identical in Brice's and Maradudin's formalisms. In those calculations for the F_{1u} representation, we had taken such a set of symmetry coordinates as to make the translational motion apparent in the $\delta\underline{l}$ matrix. However, in the present case, it would be more advantageous to obtain another set of symmetry coordinates for the F_{1u} representation by taking linear combinations such that the degrees of freedom of the interstitial can be isolated from the rest of the host lattice. This helps us to evaluate $|\underline{I}-\underline{g}\,\delta\underline{l}|$ for the F_{1u} representation for the affected host lattice, by isolating the interstitial, but at the same time including the effects of the interstitial in the host lattice. The following symmetry coordinates are employed for this purpose. The atom numbers are given in Paper I.

F_{1u} (1) x_1 ,

(2) $(x_2+x_3+x_4+x_5+x_9+x_{10}+x_{11}+x_{12})\frac{1}{\sqrt{8}}$,

(3) $(x_6+x_{13})\frac{1}{\sqrt{2}}$,

(4) $(x_{14}+x_{15}+x_7+x_8)\frac{1}{2}$,

(5) $(y_2-z_2-y_3-z_3+y_4+z_4-y_5+z_5+y_9 - z_9-y_{10}-z_{10}+y_{11}+z_{11}-y_{12}+z_{12})\frac{1}{4}$.

The remaining coordinates from [(6) to (15)] can be obtained from (1) to (5) by cyclic permutation of the corresponding (x,y,z) components. The block diagonalized form of $\delta\underline{l}$ in the notation of I for the F_{1u} representation is given below.

$$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & Y_1 & Y_2 & Y_3 & Y_4 \\ 0 & Y_2 & Y_5 & Y_6 & Y_7 \\ 0 & Y_3 & Y_6 & Y_8 & Y_9 \\ 0 & Y_4 & Y_7 & Y_9 & Y_{10} \end{pmatrix} ,$$

where

$$Y_1 = -A_1 + \frac{8A_1^2}{D_I} ,$$

$$Y_2 = \frac{4A_1A_2}{D_I} + 2\Delta A_2 ,$$

$$Y_3 = 4\sqrt{2}\,\frac{A_1B_2}{D_I} + 2\sqrt{2}\Delta A_2 ,$$

$$Y_4 = -\sqrt{2}B_1 + 8\sqrt{2}\,\frac{A_1B_1}{D_I} + \sqrt{2}\Delta B_2 ,$$

$$Y_5 = -A_2 + \frac{2A_2^2}{D_I} - 4\Delta A_2 ,$$

$$Y_6 = 2\sqrt{2}\,\frac{A_2B_2}{D_l}\,,$$

$$Y_7 = 4\sqrt{2}\,\frac{B_1A_2}{D_l} - 2\sqrt{2}\Delta B_2\,,$$

$$Y_8 = -B_2 + \frac{4B_2^2}{D_l}\,,$$

$$Y_9 = \frac{8B_1B_2}{D_l}\,,$$

$$Y_{10} = -A_1 - B_1 + \frac{16B_1^2}{D_l} + \Delta B_2 - 2\Delta A_1 - 2\Delta B_1 - 3\Delta A_2\,,$$

where

$$D_l = [M_l(\omega^2 - \omega_l^2)]^{-1}\,.$$

We note that in this block-diagonalized form, the translational motion is masked, unlike in Paper I, but we now know from the present symmetry coordinates that the first row and column correspond to the interstitial. The truncation of this row and column of $\delta\underline{l}$ in evaluating $|\underline{I} - \underline{g}\,\delta\underline{l}|$ is automatically achieved by the fact that the first row and column of the block diagonalized $\underline{g}$ is identically zero. Thus the determinant $|\underline{I} - \underline{g}\,\delta\underline{l}| = \Delta_1$, excluding the interstitial in the F_{1u} representation, is obtained from the matrices $\underline{g}$ and $\delta\underline{l}$ by excluding the first row and column in each of them. The results of Δ_l^s are computed for A_{1g} to F_{2u} using the formulas of the block diagonalization in Paper I. Finally a term $3k$ is added to account for the additional degree of freedom of the interstitial. Thus the entropy of formation of the interstitial is

$$s_d^i = \lim_{\omega\to 0}\left[-\tfrac{1}{2}k\sum_s f_s \ln\Delta_l^s(\omega) + 3k\right], \qquad (2)$$

where s represents the various irreducible representations and f_s their dimensionality. The mass factors in the entropy expression cancel.

A. Vacancy in CaF_2

The dynamics of an isolated vacancy is discussed in an earlier paper[12] (hereafter referred to as Paper II). There again we have used the symmetry coordinates for the block diagonalization to A, E, F_1, F_2', and F_2 representations. F_2' is one of the isolated modes from the 6×6 F_2 block leaving the remaining F_2 block as 5×5 in which one corresponds to the motion of the vacancy. For the F_2 block in Paper II we had used such an orthonormal set of symmetry coordinates as to make the translational motion apparent in $\delta\underline{l}$ in the zero-frequency limit. But in the present case we are interested in isolating the row and column corresponding to the vacancy motion. Accordingly, as in the interstitial case, we shall use another set of symmetry coordinates for the F_2 representation (which are in fact linear combinations of the set in Paper II) such that the row and column corresponding to the vacancy motion will become apparent in $\underline{g}$ and $\delta\underline{l}$. The following are the new set of symmetry coordinates for the F_2 representation (the same atom numbers as in Paper II are used):

F_2 (1) x_1 (vacancy),

(2) $(x_6 + x_9)\frac{1}{\sqrt{2}}$,

(3) $(x_7 + x_8 + x_{10} + x_{11})\frac{1}{2}$,

(4) $(x_2 + x_3 + x_4 + x_5)\frac{1}{2}$,

(5) $(y_2 + z_2 + y_3 - z_3 - y_4 + z_4 - y_5 - z_5)\frac{1}{\sqrt{8}}$.

The others from [(6) to (15)] can be obtained from (1) through (5) by cyclic permutations of the corresponding (x,y,z) components. The block diagonalized $\delta\underline{l}$ is

$$\begin{pmatrix} D_1 & \sqrt{2}\Delta A_2 & 2\Delta B_2 & 2\Delta A_1 & -\sqrt{8}\Delta B_1 \\ \sqrt{2}\Delta A_2 & \Delta G_1 & 0 & \sqrt{2}\Delta C_1 & 2\Delta D_1 \\ 2\Delta B_2 & 0 & \Delta H_1 & 2\Delta C_1 & 0 \\ 2\Delta A_1 & \sqrt{2}\Delta C_1 & 2\Delta C_1 & \Delta E_1 & -\sqrt{2}\Delta F_1 \\ -\sqrt{8}\Delta B_1 & 2\Delta D_1 & 0 & -\sqrt{2}\Delta F_1 & \Delta E_1 + \Delta F_1 \end{pmatrix}.$$

The first row and column in both $\underline{g}$ and $\delta\underline{l}$ here correspond clearly to the vacancy motion and these are deleted in computing Δ_1 arising from the F_2 representation. The remaining Δ_l^s for other irreduci-

TABLE I. Δ_l^s for interstitial in CaF_2.[a]

Model	Δ_l^s for:							
	A_{1g}	E_g	F_{1g}	A_{2u}	E_u	F_{2u}	F_{2g}	F_{1u}
1	1.374	2.508	0.644	0.965	1.034	0.561	0.381	3.281
2	1.225	2.307	0.704	0.987	1.264	0.531	0.491	3.106
3	1.383	2.589	0.727	1.265	1.312	0.629	0.638	3.109

[a] s_d^i [from Eq. (2)] $= 3.10k$ [model (i)]; $= 2.67k$ [model (ii)]; $= 1.64k$ [model (iii)]. In model (i), both the long-range and the short-range part of the force-constant changes are taken into account. In model (ii), only the short-range part is taken into account.

ble representations A, E, F_1, and F_2' are calculated using the block-diagonalized form of $\underline{g}$ and $\delta\underline{l}$ given in Paper II. The entropy of formation of the vacancy can then be written

$$s_d^v = \lim_{\omega \to 0} \left[-\frac{1}{2} k \sum_s f_s \ln \Delta_1^s \right] . \tag{3}$$

Unlike the case of the interstitial we do not have to remove again another $3k$ from s_d^v since the vacancy degree of freedom is already eliminated from the calculation. Again the mass factors in the entropy expression cancel.

IV. RESULTS

The parameters accounting for the force-constant changes, and how they are determined, are discussed in Papers I and II. The method of evaluating the Green functions has also been discussed there. Using these data the Δ_1^s for $\omega \to 0$ are evaluated for the interstitial case and vacancy case as discussed in Sec. III. The results obtained for interstitials are given in the Table I for the various irreducible representations. The Δ_1^s calculated for the various irreducible representations for the vacancy are given in Table II. For the set (3) the determinant for F_2 became negative and hence that set was not used in the estimation of entropy of formation. s_d^v calculated from set (1) in Eq. (3) gives a value of $2.31k$ whereas from set (2) it is $1.95k$. The values of s_d^i were $3.20k$ from set (1), $2.78k$ from set (2), and $1.75k$ from set (3).

Since the models (i) and (ii) and sets (1) and (2) correspond, the entropy of formation and anion Frenkel defect calculated from these data is $5.41k$ for model (i) and $4.62k$ for model (ii).

TABLE II. Δ_1^s for the anion vacancy in CaF_2.[a]

Model	Δ_1^s for:				
	A	E	F_1	F_2'	F_2
1	1.283	0.482	0.614	1.222	0.428
2	1.269	0.541	0.730	1.222	0.423
3	0.928	0.537	0.740	1.024	−0.039

[a] s_d^v [from Eq. (3)] $= 2.31k$ [model (i)]; $= 1.95k$ [model (ii)]. In model (i), for the force-constant changes among first-neighbor host atoms, both the long-range and short-range contributions are taken. In model (ii), only the short-range contributions are retained.

V. DISCUSSION

The result computed can be compared with the experimentally deduced value of $5.4k$ for the entropy of formation of a Frenkel defect (Jacobs and Ong[8]). The earlier experimental work of Ure[13] on the conductivity in CaF_2 had given a value for the entropy of formation of the Frenkel defect of $13.5k$ but the later value is to be preferred.[8] The calculation of Varotsos[7] using bulk properties, however, give a much higher value than ours, comparable with Ure's, but he did not take the temperature dependence of the lattice parameter into account in his calculations. The Δ_1^s given in Tables I and II at $\omega = 0$ for the irreducible representations agree very well with the asymptotic limits of Δ_1^s at $\omega \to 0$ computed in Papers I and II for all representations except for F_{1u}, in the case of interstitial, and for F_2 in the case of vacancy, where we have eliminated the defect degrees of freedom in the present calculations. In order to cross check our computed results we have employed the 45×45 $\underline{g}$ and $\delta\underline{l}$ matrices given in Paper I and the 33×33 matrices given in Paper II without block diagonalization to compute the corresponding entropies of formation using the Mahanty and Sachdev procedure[6] as used by Govindarajan *et al.*[5] for their vacancy calculation in KCl. These results, as is to be expected, are in striking agreement with the values reported above. Thus our present computed results are consistent in the two equivalent formulations. To our knowledge no calculation on the entropy of formation of an interstitial has been carried out for a similar system but for the vacancy, Nardelli and Terzi[14] have estimated the entropy of formation in an argon crystal allowing for elastic relaxations around the vacancy. They obtained a result of $2.74k$. Our values reported here are also in the same range. However, one should bear in mind that in the argon crystal, anharmonicity for the zero-point motion plays a considerable role in determining these thermodynamic properties.

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[1] A. B. Lidiard, in *Crystals with Flourite-Structures,* edited by W. Hayes (Clarendon, Oxford, 1974).

[2] J. Corish, P. W. M. Jacobs, and S. Radhakrishna, in *Surface and Defect Properties of Solids,* edited by J. M. Thomas and M. W. Roberts (Chemical Soc., London, 1977), Vol. VI, Chap. V.

[3]O. Theimer, Phys. Rev. 112, 1857 (1958).
[4]J. Govindarajan, P. W. M. Jacobs, and M. A. Nerenberg, J. Phys. C 9, 3911 (1976).
[5]J. Govindarajan, P. W. M. Jacobs, and M. A. Nerenberg, J. Phys. C 10, 1809 (1977).
[6]J. Mahanty and M. Sachdev, J. Phys. C 3, 773 (1970).
[7]P. Varotsos, Phys. Rev. 13, 938 (1976).
[8]P. W. M. Jacobs and H. Ong, J. Phys. (Paris) 38, C7-331 (1976).
[9]T. M. Haridasan, J. Govindarajan, M. A. Nerenberg, and P. W. M. Jacobs, Phys. Rev. B 20, 3462 (1979) (second preceding paper; Paper I).
[10]D. K. Brice, Phys. Rev. 140, A1211 (1965).
[11]A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, *Theory of Lattice Dynamics in the Harmonic Approximation,* 2nd ed. (Academic, New York, 1971).
[12]T. M. Haridasan, J. Govindarajan, M. A. Nerenberg, and P. W. M. Jacobs, Phys. Rev. B 20, 3474 (1979) (preceding paper; Paper II).
[13]R. W. Ure, J. Chem. Phys. 26, 1363 (1957).
[14]G. F. Nardelli and N. Terzi, J. Phys. Chem. Solids 25, 815 (1964).