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Entropy of a point defect in an ionic crystal

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The problem of calculating the entropy of formation of a point defect in an ionic crystal is reexamined in some detail. We use two methods of calculation, which we term the embedded-crystallite and the Green-function methods. In both methods, the crystal is divided into an inner region, which contains the defect and a set of its neighbors, and an outer region. In the embedded-crystallite method, the entropy is calculated directly from the determinants of the force-constant matrices for perfect and defective crystals, restricted to the defect region. The Green-function method, which is expected to be more accurate, exploits a reformulation of the entropy expression in terms of the Green functions of the perfect crystal and the *change* of the force constants in the defect region. The principal feature of our calculations is the examination, for the first time in ionic crystals, of the convergence of the calculated entropy as the size of the defect region is increased. Associated problems, such as the correct inclusion of the long-range Coulomb contributions and the accuracy of the Green functions, have also been addressed. The model numerical calculations which we present are for the case of Frenkel (vacancy and interstitial) defects in CaF_2. The majority of the calculations have been performed with the use of a rigid-ion potential, which allows a simpler discussion of the technical problems, but we have also investigated the effect on the results of using a realistic shell model. We show that the convergence of the results is strongly affected by previously unrecognized fluctuation effects coming from the boundary of the defect region; these effects are specific to ionic crystals. It is demonstrated that the boundary effects can be eliminated with the use of a simple subtraction technique, and that the resulting entropy values can be extrapolated to infinite region size with an uncertainty of no more than a few tenths of Boltzmann's constant. It is pointed out that in a finite crystal there is a contribution to the entropy of charged defects from the structure of the physical surface; this contribution cancels out, however, for neutral sets of defects. We discuss previous work on this problem in the light of our findings.

I. INTRODUCTION

Experimental measurements of ionic conductivity and diffusion coefficients for ionic crystals are usually analyzed in terms of a defect model, in order to determine the transport mechanism.[1] If the proposed model permits a quantitative description of the data, numerical values will be obtained for the thermodynamic parameters of the defects: the energies and entropies which control their formation, migration, and association. Independent theoretical calculation of these parameters is an important field of endeavor, because it yields an atomistic interpretation of the experimental results, as well as providing a useful guide in the selection of an appropriate defect model.[2] In the last decade the calculation of defect energies has progressed to the point where the computational procedure (as distinct from the construction of interionic potentials) is now quite automatic. Available computer codes, such as the HADES program developed by Norgett[3] at Harwell, are of proven reliability and allow the routine calculation of a wide variety of defect energies.[4] The art of calculating defect entropies, by contrast, is still in a rather primitive state. In order to see this, it is enough to compare some of the recent theoretical results for the entropy of formation at constant volume of anion Frenkel defects in CaF_2. These range from the value of -1.55 given by Sahni and Jacobs[5] through the pair of estimates 4.62 and 5.41 due to Haridasan *et al.*[6] to the value of 6.4 obtained by Harding and Stoneham[7] (all in units of Boltzmann's constant k_B). It is hard to avoid the conclusion that the technical problems involved in this type of calculation have not yet been mastered. Our purpose in the present paper is to investigate these problems in some detail. We shall try to show what must be done in order to calculate entropies of formation in ionic crystals from specified interionic potentials with a precision of a few tenths of k_B, and we shall present a detailed model calculation in which this appears to have been achieved.

The high-temperature entropy of formation s_d of a defect is given, in the harmonic approximation, by[8]

$$s_d = -k_B \ln \left[\prod_i \omega_i' \bigg/ \prod_i \omega_i \right] , \tag{1}$$

where ω_i and ω_i' are the normal-mode frequencies of the perfect and the defective crystals; we omit here the contribution due to any change in the number of degrees of freedom. The earliest calculations for ionic crystals[9-11] were based on Theimer's assumption[12] that the frequency changes $\omega_i' - \omega_i$ are all very small. This assumption is now recognized to be completely unrealistic,[13] and the calculations based on it are of no more than historical interest. The more modern approaches to the problem are of three main kinds. In the first, which we shall refer to as the embedded-crystallite method, the crystal is divided into an inner region containing the defect together with a set of its neighbors and an outer region containing the remaining ions; we shall call the inner region the "defect region." The ions in the defect region are free to vibrate, but the others are held fixed. The ω_i and ω_i' of Eq. (1) are then taken to be the normal-mode frequencies of the defect region in the perfect and the defective crystals.

A second approach, which we shall call the Green-function method, was first clearly described by Mahanty,[14,15] though it is implicit in the work of Maradudin *et al.*[16] In this method the entropy formula is recast in terms of the Green functions of the the perfect lattice and the changes of the force constants caused by the introduction of the defect. As before, the crystal is divided into a defect region and an outer region, but vibrations of the ions in the outer region are now implicitly included. The sole assumption is that the force constants are changed only for ions in the defect region. If this is the case, the calculation is equivalent to one performed on the infinite crystal.

In the third approach, which we shall call the supercell method, Eq. (1) is directly applied to a periodically repeated crysallite of the perfect or the defective lattice. The frequencies ω_i and ω_i' are now those of the phonon modes at zero wave vector in the reduced Brillouin zone corresponding to the large unit cell.

The Green-function method has been applied to calculate the entropy of formation of Schottky defects in KCl (Ref. 13) and was used by Haridasan *et al.*[6] in the work referred to above on Frenkel defects in CaF_2. The supercell method was used in two rather different variants[5,7] to obtain the other results we have cited for the Frenkel entropy in CaF_2. As far as we know, the embedded-crystallite method has never been used for ionic crystals, though it has been used several times for crystals of neutral atoms.[17-20]

One of the central issues in this kind of problem is that of the convergence of the results to a limiting value as the size of the defect region is increased. In the case of defect energies, the importance of the convergence question was recognized in the very first quantitative study, made over 40 years ago by Mott and Littleton.[21] More recently, the explicit demonstration of convergence in the HADES calculations has been important evidence for their reliability.[2] Discussion of this question for the problem of entropies in ionic crystals has been conspicuously absent. However, Hatcher *et al.*[19] have recently given a thorough discussion of convergence for the entropy of formation of a vacancy in metals. That work, which uses both the embedded-crystallite and the Green-function techniques, shows that over a hundred atoms must be included in the defect region before the limiting dependence of the result on the region size becomes firmly established, and that extrapolation must be used to obtain fully satisfactory results. The calculations of Harding and Stoneham[7] on CaF_2 used a repeating cell containing only 24 ions; the Green-function calculations of Haridasan *et al.*[6] for the same system used defect region of 11 ions and 15 ions, respectively, for the vacancy and the interstitial. There are, therefore, sound reasons for questioning the reliability of these calculations.

The work to be presented in this paper consists of a detailed study of the entropy calculation for the anion vacancy and interstitial in CaF_2. The choice of this system is a natural one, in view of the previous discordant results. In order to avoid inessential complications, we use a rigid-ion model, rather than a shell model, for most of the work. Although a rigid-ion model is not fully satisfactory for realistic calculations, the particular model we use is quite adequate for studying the calculational technique. This will become clear later in the paper, when we present some results obtained with a good shell model. Our calculations are performed by both the embedded-crystallite and the Green-function techniques, using defect regions containing up to several hundred ions. We shall see that for ionic crystals in general the convergence is more complicated than for crystals of neutral atoms because of fluctation effects associated with the boundary of the defect region. A substantial part of our discussion will be concerned with the elimination of these effects. As a by-product of this discussion we shall also find that the separate entropies of vacancies or interstitials in a finite crystal contain a nontrivial contribution from the physical surface of the crystal; fortunately, this contribution cancels out when we form the Frenkel entropy. The use of large defect regions allows us to examine the convergence behavior in considerable detail and to extrapolate to infinite region size with an uncertainty of only a few tenths of k_B.

The plan of the paper is as follows. In Sec. II we summarize the basic formulas on which the work is based. Section III describes the numerical calculation of the force-constant matrix, taking full account of the long-range Coulomb potentials. Section IV presents the calculation and results for the lattice Green functions needed in our entropy calculations; here we also examine the convergence of these Green functions to the limiting elastic form at large distances, which is important later. In Sec. V we apply the techniques we have developed to the calculation of the entropies of the vacancy and the interstitial and we show how the effects associated with boundary may be dealt with. Section VI describes the extension of our methods to the shell model. In Sec. VII we summarize our findings, discuss the relative merits of the various approaches, and assess the validity of earlier results. The Appendix presents the arguments which show the existence of the contribution to the entropy of formation from physical surfaces.

II. THE ENTROPY FORMULAS

The vibrational entropy of a crystal containing N ions is, in the harmonic approximation,[8] which we assume throughout this paper,

$$S=k_B\sum_{i=1}^{3N}\left[\frac{\hbar\omega_i}{k_BT}[e^{\hbar\omega_i/k_BT}-1]^{-1}-\ln(1-e^{-\hbar\omega_i/k_BT})\right], \tag{2}$$

where the sum goes over the $3N$ normal modes, whose frequencies are ω_i; other symbols have their usual meaning. In the high-temperature limit, $k_BT \gg \hbar\omega_i$ for all i, Eq. (2) reduces to

$$S\simeq k_B\sum_{i=1}^{3N}[1-\ln(\hbar\omega_i/k_BT)], \tag{3}$$

an approximation which is generally valid for temperatures at which defect entropies are experimentally accessible. If we denote the entropies of the perfect and the defective crystals by S and S', respectively, then the entropy of formation s_d of the defect may be written

$$\begin{aligned}s_d&\equiv S'-S\\&=-k_B\ln\left[\prod_{i=1}^{3N'}\omega_i'\Big/\prod_{i=1}^{3N}\omega_i\right]\\&\quad+3k_B(N'-N)[1-\ln\hbar/k_BT)],\end{aligned} \tag{4}$$

where N and N' are the numbers of ions and ω_i, ω_i' the vibrational frequencies of the perfect and the defective crystals. The second term on the right-hand side of Eq. (4) comes from the change in the number of degrees of freedom. Our interest here will center upon the first term.

In the harmonic approximation, the equation of motion of the ions may be written in the schematic form

$$(\underline{\Phi}-\omega^2\underline{M})\vec{u}=0, \tag{5}$$

where $\vec{u}$ is the column vector of the vibrational displacements, $\underline{M}$ is the (diagonal) mass matrix, and $\underline{\Phi}$ is the force-constant matrix. The product of the squared frequencies is therefore given by

$$\prod_i\omega_i^2=|\underline{\Phi}|/|\underline{M}|, \tag{6}$$

where the vertical bars indicate the determinant of a matrix. This allows us to rewrite Eq. (4) in the form[20]

$$\begin{aligned}s_d&=-\tfrac{1}{2}k_B\ln(|\underline{M}||\underline{\Phi}'|/|\underline{M}'||\underline{\Phi}|)\\&\quad+3k_B(N'-N)[1-\ln(\hbar/k_BT)],\end{aligned} \tag{7}$$

where $\underline{M}$ and $\underline{M}'$ are the mass matrices and $\underline{\Phi},\underline{\Phi}'$ the force-constant matrices for the perfect and the defective crystals. In our numerical calculations, we will be concerned with the entropies of formation of isolated vacancies and interstitials, which we denote by s_v and s_i. The explicit formulas for these cases are

$$s_v=\Delta s_v-3k_B[1-\ln(\hbar/m^{1/2}k_BT)], \tag{8}$$

$$s_i=\Delta s_i+3k_B[1-\ln(\hbar/m^{1/2}k_BT)], \tag{9}$$

where

$$\Delta s_v=-\tfrac{1}{2}k_B\ln(|\underline{\Phi}_v|/|\underline{\Phi}|), \tag{10}$$

$$\Delta s_i=-\tfrac{1}{2}k_B\ln(|\underline{\Phi}_i|/|\underline{\Phi}|). \tag{11}$$

Here m denotes the mass of the ion removed to form the vacancy, or added to form the interstitial, and $\underline{\Phi}_v,\underline{\Phi}_i$ denote the force-constant matrices for the crystal containing the vacancy and the interstitial. The last terms in Eqs. (8) and (9) for s_v and s_i will be of no interest from now on, and we shall consider only the contributions Δs_v and Δs_i, which depend solely on the force constants. However, since the matrix dimensions of $\underline{\Phi}_v$ and $\underline{\Phi}_i$ differ from that of $\underline{\Phi}$, these quantities are not properly defined unless we specify the units in which the force constants are to be expressed. In ionic crystals, it is convenient to express force constants in units of e^2/d^3, where e is the electronic charge and d is the lattice spacing; we shall assume from now on that this has been done.

The embedded-crystallite method referred to in the Introduction consists of the direct application of Eqs. (8) and (9) to a limited region of the crystal containing the defect. The approximation thus amounts to deleting those parts of the full force-constant matrices which couple ions outside the defect region either to each other or to ions within the defect region.[20]

As was pointed out by Mahanty and Sachdev,[14,15] this approximation can be avoided by reexpressing the entropy formulas in terms of the static Green functions of the perfect lattice and the *changes* in the force constants caused by the introduction of the defect. This method has been discussed in several recent papers,[6,8,13,20,23] and therefore we shall simply summarize the results we need.

Consider first the case of the vacancy. We take the full force-constant matrix $\underline{\Phi}$ for the perfect crystal and delete the three rows and columns referring to the ion which is removed to form the vacancy; call this truncated matrix $\underline{\Phi}_t$. The quantity $\delta\underline{\Phi}_v$ obtained by subtracting this from the full force-constant matrix $\underline{\Phi}_v$ of the defective crystal,

$$\delta\underline{\Phi}_v = \underline{\Phi}_v - \underline{\Phi}_t \ , \tag{12}$$

plays the role of the change of force-constant matrix. It is assumed that all elements of $\delta\underline{\Phi}_v$ are negligible, except those referring only to ions in a limited defect region. Now let $\underline{G}$ be the static Green matrix of the perfect crystal,

$$\underline{G} = \underline{\Phi}^{-1} \ , \tag{13}$$

and $\underline{g}$ be the reduced matrix obtained by deleting the rows and columns of $\underline{G}$ referring to ions outside the defect region (but not those referring to the ion at the vacancy site). Then the formula for Δs_v may be written[8,23]

$$\Delta s_v = -\tfrac{1}{2} k_B \ln(\, |\underline{g}| \, |(\underline{g}^{-1})_t + \delta\underline{\Phi}_v| \,) \ , \tag{14}$$

where $(\underline{g}^{-1})_t$ is the inverse of $\underline{g}$, truncated by deletion of the rows and columns referring to the ion at the vacancy site.

For the interstitial, the procedure is slightly different. Let the full force-constant matrix for the defective crystal be partitioned in the form

$$\underline{\Phi}_i = \begin{bmatrix} \underline{\phi}_i & \underline{a} \\ \underline{a}^T & \underline{\Phi} + \delta\underline{\Phi}_i \end{bmatrix} , \tag{15}$$

where $\delta\underline{\Phi}_i$ is the change of the force-constant matrix coupling together all the ions except the interstitial, $\underline{a}$ is the matrix of force constants coupling the interstitial to all the other ions, and $\underline{a}^T$ is the transpose of $\underline{a}$; finally, $\underline{\phi}_i$ is the 3×3 matrix referring to the interstitial alone. It is assumed that all elements of $\delta\underline{\Phi}_i$ and $\underline{a}$ are negligible except those referring to ions in a limited defect region. The entropy formula may be written in the form[8,23]

$$\Delta s_i = -\tfrac{1}{2} k_B \ln(\, |\underline{I} + \underline{g} \, \delta\underline{\Phi}_i'| \, |\underline{\phi}_i| \,) \ , \tag{16}$$

where $\underline{g}$ is, as before, the matrix $\underline{G}$ reduced by deletion of rows and columns referring to ions outside the defect region, and $\delta\underline{\Phi}_i'$ is defined as

$$\delta\underline{\Phi}_i' = \delta\underline{\Phi}_i - \underline{a}^T \underline{\phi}_i^{-1} \underline{a} \ . \tag{17}$$

The Green-function method consists of the use of Eqs. (14) and (16) to calculate the entropies of formation. These formulas follow from the original equations (10) and (11) without approximation, except for the assumption that the elements of $\delta\underline{\Phi}_v$ and $\delta\underline{\Phi}_i'$ are nonzero only in the defect region. The same is not, of course, true of the embedded-crystallite approximation, which should therefore be less accurate. Needless to say, the two methods should give the same result for large enough defect regions.

III. THE FORCE-CONSTANT MATRIX

Both the embedded-crystallite and the Green-function methods require the calculation of the force-constant matrix for ions in the defect region of the perfect and the defective lattices. The elements of the force-constant matrix for two different ions i, j are given by[16]

$$\Phi_{ij}^{\alpha\beta} = -\frac{\partial}{\partial r_i^\alpha} \frac{\partial}{\partial r_j^\beta} V_{ij}(r_{ij}), \quad i \neq j \tag{18}$$

where V_{ij} is the interionic potential for the pair of ions, $r_{ij} \equiv |\vec{r}_i - \vec{r}_j|$ is their separation, and α, β denote Cartesian components. For $i=j$, the elements are given by[16]

$$\Phi_{ii}^{\alpha\beta} = -\sum_{j\,(\neq i)} \Phi_{ij}^{\alpha\beta} \ , \tag{19}$$

where the sum goes over all other ions. The derivatives of the potential in these equations are to be evaluated at the equilibrium positions of the ions, i.e., at the fully relaxed positions, in the case of the defective lattice. It should also be noted that although we require the force-constant matrix only for ions in the defect region, the diagonal elements $\Phi_{ii}^{\alpha\beta}$ depend on the positions of ions outside this region.

The interaction potential between ions i and j is

$$V_{ij}(r)=\frac{Z_iZ_je^2}{r}+V_{ij}^s(r)\ , \tag{20}$$

where Z_i is the charge on ion i in units of the magnitude $|e|$ of the electronic charge, and V_{ij}^s is the short-range potential. The force-constant matrix is therefore the sum of Coulomb and short-range parts, which are given for $i\neq j$, by

$$\Phi_{ij}^{c,\alpha\beta}=\frac{Z_iZ_je^2}{r_{ij}^3}(\delta_{\alpha\beta}-3\hat r_{ij}^{\alpha}\hat r_{ij}^{\beta})\ , \tag{21}$$

$$\Phi_{ij}^{s,\alpha\beta}=-\delta_{\alpha\beta}\frac{V_{ij}^{s\,\prime}}{r_{ij}}-\hat r_{ij}^{\alpha}\hat r_{ij}^{\beta}\left[V_{ij}^{s\,\prime\prime}-\frac{V_{ij}^{s\,\prime}}{r_{ij}}\right]\ , \tag{22}$$

where $\hat r_{ij}$ is the unit vector from ion j to ion i and $V_{ij}^{s\,\prime}$ and $V_{ij}^{s\,\prime\prime}$ denote the first and second derivatives of V_{ij}^s with respect to the magnitude of r. If we know the equilibrium positions of the ions, the evaluation of these off-diagonal elements of the force-constant matrix for either the perfect or the defective crystal is straightforward.

The calculation of the diagonal elements $\Phi_{ii}^{\alpha\beta}$ requires more care. Consider first the short-range part $\Phi_{ii}^{s,\alpha\beta}$, given by

$$\Phi_{ii}^{s,\alpha\beta}=-\sum_{j\,(\neq i)}\Phi_{ij}^{s,\alpha\beta}\ . \tag{23}$$

This must be evaluated by taking the sum over all ions in a larger region containing the defect region; we shall call this the "extended region." Since the short-range potential falls off rapidly with distance, it will generally be sufficient to make the radius of the extended region larger than that of the defect region by a few lattice spacings.

The Coulomb sum $\Phi_{ii}^{c,\alpha\beta}$, being of infinite range, cannot be calculated in this simple way. Instead, we use the familiar Ewald strategy.[3,24] Since the ideas involved are so well known, we shall merely sketch the procedure. Note first that the elements $\Phi_{ii}^{c,\alpha\beta}$ can be expressed in terms of the electric potential $\psi_i(\vec r_i)$ at ion i due to the charges on all the other ions:

$$\Phi_{ii}^{c,\alpha\beta}=Z_i\,|\,e\,|\,\frac{\partial}{\partial r_i^{\alpha}}\frac{\partial}{\partial r_i^{\beta}}\psi_i(\vec r_i)\ . \tag{24}$$

Following the usual Ewald method, we break up the potential ψ_i into the following three contributions: (i) the potential $\psi^{(1)}$ due to a set of Gaussian charge distributions centered on the sites of the perfect lattice; (ii) the difference $\psi_i^{(2)}$ of the potentials due to the point ionic charges at their actual positions in an extended region surrounding the defect region and the above Gaussian charge distributions in the same region; (iii) the difference $\psi_i^{(3)}$, which is the same as in (ii), but for the point charges and charge distributions outside the extended region.

The total charge density $Q^{(1)}(\vec r)$ which gives rise to the potential $\psi^{(1)}$ is

$$Q^{(1)}(\vec r)=\sum_i Z_i\,|\,e\,|\,(\zeta/\sqrt{\pi})^3\exp(-\zeta^2\,|\,\vec r-\vec r_i^{\,0}\,|^2)\ , \tag{25}$$

where the sum goes over all sites of the perfect lattice, whose positions are $\vec r_i^{\,0}$. The choice of ζ, which specifies the width of the Gaussians, is discussed below. The potential $\psi^{(1)}$ has the periodicity of the lattice, and can be expressed as a sum over the reciprocal-lattice vectors $\vec G$:

$$\psi^{(1)}(\vec r)=\frac{4\pi\,|\,e\,|}{v_c}\sum_{\vec G\,(\neq\vec 0)}S(\vec G)G^{-2}e^{i\vec G\cdot\vec r}e^{-G^2/4\zeta^2}\ , \tag{26}$$

where the structure factors $S(\vec G)$ are given by the sum

$$S(\vec G)=\sum_{\kappa}Z_{\kappa}e^{-i\vec G\cdot\vec r_{\kappa}^{\,0}} \tag{27}$$

over ions in the primitive cell, whose volume is v_c.

The difference potential $\psi_i^{(2)}(\vec r)$ can be written down immediately,

$$\psi_i^{(2)}(\vec r)=\sum_{j\,(\neq i)}\frac{Z_j\,|\,e\,|}{|\,\vec r-\vec r_j\,|}-\sum_j\frac{Z_j\,|\,e\,|\,\mathrm{erf}(\zeta\,|\,\vec r-\vec r_j^{\,0}\,|\,)}{|\,\vec r-\vec r_j^{\,0}\,|}\ , \tag{28}$$

where the first sum goes over all ions actually present in the extended region of the perfect or the defective crystal, and the second over all regular lattice sites in the same region of the perfect crystal.

A similar formula holds for the difference $\psi_i^{(3)}$ coming from ions beyond the extended region, but this contribution can, in fact, be dropped if ζ is chosen large enough. Since the ions are distant, the error function may be replaced by unity, and $\psi_i^{(3)}$ becomes the potential due to the set of dipoles $Z_j(\vec r_j-\vec r_j^{\,0})$. In the defective lattice, the equilibrium displacements $\delta\vec r_j=\vec r_j-\vec r_j^{\,0}$ are dominated by the dielectric response of the crystal to the charge on the defect, so that the set of dipoles represents a spherically symmetric radial polarization. This polarization gives a uniform electric potential $\psi_i^{(3)}$ in the defect region, which, on differentiation with respect to position, yields no contribution in Eq. (24).

The final expression for $\Phi_{ii}^{c,\alpha\beta}$ is now obtained by inserting the formulas (26) and (28) into Eq. (24):

$$\begin{aligned}\Phi_{ii}^{c,\alpha\beta} = -\frac{4\pi Z_i e^2}{v_c} & \times \sum_{\tilde{G}\,(\neq\vec{0}\,)} S(\vec{\mathrm{G}})\frac{G^\alpha G^\beta}{G^2} e^{i\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}_i} e^{-G^2/4\zeta^2} \\ & - \sum_{j\,(\neq i)} \frac{Z_i Z_j e^2}{r_{ij}^3}(\delta_{\alpha\beta} - 3\hat{r}_{ij}^{\alpha}\hat{r}_{ij}^{\beta}) \\ & - \sum_j Z_i Z_j e^2[\delta_{\alpha\beta} t_1(\rho_{ij}) + \rho_{ij}^{\alpha}\rho_{ij}^{\beta} t_2(\rho_{ij})] , \end{aligned} \tag{29}$$

where

$$\vec{\rho}_{ij} = \vec{\mathrm{r}}_i - \vec{\mathrm{r}}_j^{\,0} \tag{30}$$

and the functions $t_1(\rho)$ and $t_2(\rho)$ are given by

$$\begin{aligned} t_1(\rho) &= \left[\frac{2\zeta\rho}{\sqrt{\pi}} e^{-\zeta^2\rho^2} - \mathrm{erf}(\zeta\rho)\right] \Big/ \rho^3 , \\ t_2(\rho) &= \left[3\,\mathrm{erf}(\zeta\rho) - \frac{2\zeta\rho}{\sqrt{\pi}}(3+2\zeta^2\rho^2)e^{-\zeta^2\rho^2}\right] \Big/ \rho^5 . \end{aligned} \tag{31}$$

The sums over j in Eq. (29) go over all ions (except i) and all regular lattice sites (without restriction) in the extended region.

In principle, the value of the Gaussian width parameter ζ is arbitrary, but in practice it is chosen so that both the reciprocal-lattice and the real-space sums can be taken to convergence without excessive computational labor.

In order to calculate the force-constant matrix for the defective crystal, we need to know the relaxed equilibrium positions of all the ions in the extended region. As in previous work,[5,6] we have used the HADES computer program[3] to obtain these positions. The principles of this program have been described before,[3] but we wish to recall the main points, for the purpose of our later discussion. In the HADES calculation, the crystal is divided into an inner region I containing the defect and an outer region II. The ions in region I are iteratively relaxed to their zero-force positions. The positions of the remaining ions are obtained, following Mott and Littleton,[21] by treating region II as a dielectric continuum. The electric polarization in region II is thus given by

$$\vec{\mathrm{P}}(\vec{\mathrm{r}}) = \frac{Z_d\,|\,e\,|}{4\pi}(1-\epsilon_0^{-1})\frac{\vec{\mathrm{r}}}{r^3} , \tag{32}$$

where Z_d is the net charge of the defect, ϵ_0 is the static dielectric constant of the bulk crystal, and $\vec{\mathrm{r}}$ is the vector distance from the defect. The ionic displacements in region II are calculated from $\vec{\mathrm{P}}$ on the assumption that the polarization is shared equally between the cation and anion sublattices.[21] For example, in the case of CaF_2, in which there is one cation of charge $+2$ and two anions of charge -1 in the unit cell, the equilibrium displacements $\delta\vec{\mathrm{r}}_+$ and $\delta\vec{\mathrm{r}}_-$ of ions in region II are given, for the rigid-ion model, by

$$\delta\vec{\mathrm{r}}_+ = -\delta\vec{\mathrm{r}}_- = \frac{Z_d v_c}{16\pi}(1-\epsilon_0^{-1})\frac{\vec{\mathrm{r}}}{r^3} . \tag{33}$$

The point we wish to emphasize is that the equilibrium positions we use in the calculation of the force constants for the defective lattice correctly allow for the dielectric response of the lattice to the charge on the defect, though they do not include the long-range elastic response. The equilibrium displacements fall off with distance as r^{-2}, cations and anions being displaced in opposite directions. As we shall see, this has important consequences for the convergence behavior of our results. It should be noted that the HADES region I has no particular relation to the defect region used in our entropy calculations.

We now give some details about our rigid-ion calculations on CaF_2. The model we use is that due to Dixon and Gillan.[25] The ions bear their full ionic charges and the short-range potentials have the normal Buckingham form:

$$V_{ij}^{s}(r) = A_{ij} e^{-r/\rho_{ij}} - C_{ij}/r^6 . \tag{34}$$

The cation-cation short-range potential is set equal to zero: $A_{++} = C_{++} = 0$, as is the cation-anion dispersion term: $C_{\pm} = 0$. The remaining parameters are given in Table I. This model has been shown to give a good account of the bulk crystal properties and of the anion defect energies of CaF_2.[25] In all the present calculations, the V_{ij}^{s} were set equal to zero for $r > 1.5d$, where d is the anion-anion nearest-neighbor separation. The HADES calculations used regions I containing 12 and 13 symmetry classes of ions for the vacancy and the interstitial,

TABLE I. Parameters of short-range interionic potentials for CaF_2 due to Dixon and Gillan (Ref. 25).

A_{+-}	674.3 eV
A_{--}	1808.0 eV
ρ_{+-}	0.336 Å
ρ_{--}	0.293 Å
C_{--}	109.1 eV Å^6

respectively. For the computation of the force-constant elements, the Gaussian width parameter was chosen so that $\zeta d = 2.2$. With this choice, it is sufficient both for the Coulomb and the short-range contributions to take the radius of the extended region to be greater than that of the defect region by $2d$ and to restrict the reciprocal-space sum to $\vec{G}$'s for which $|G|d/\pi < 6.1$, which then includes some 250 reciprocal-lattice vectors. The results to be presented were obtained with an extended region of radius $6.1d$, which includes about 1400 ions for both the vacancy and the interstitial problems. We have made test calculations to check that variation of ζ and further extension of the sums have no significant effect on the results.

IV. THE GREEN MATRIX

The elements of the Green matrix $\underline{G}$ may be expressed as an integral over wave vectors $\vec{q}$ in the first Brillouin zone by the standard formula[20,26,27]

$$G^{\alpha\beta}_{\kappa\kappa'}(\vec{r}) = \frac{v_c}{(2\pi)^3} \sum_j \int_{\mathrm{BZ}} d\vec{q}\, \frac{e^{\alpha}_{\kappa}(\vec{q},j) e^{\beta}_{\kappa'}(\vec{q},j)^*}{(m_\kappa m_{\kappa'})^{1/2} \omega(\vec{q},j)^2} \times e^{i\vec{q}\cdot\vec{r}} , \tag{35}$$

where κ,κ' designate the sublattices of the two ions concerned, whose vector separation is $\vec{r}$, m_κ is the mass of the ion on sublattice κ, and $\omega(\vec{q},j)$ and $\vec{e}_\kappa(\vec{q},j)$ are the frequency and polarization vectors of the phonon whose wave vector is $\vec{q}$ and whose branch index is j. For practical computations, the integral is replaced by a sum over the points of a uniform mesh in reciprocal space,

$$G^{\alpha\beta}_{\kappa\kappa'}(\vec{r}) \simeq \frac{1}{N} \sum_{\vec{q},j}{}' \frac{e^{\alpha}_{\kappa}(\vec{q},j) e^{\beta}_{\kappa'}(\vec{q},j)^*}{(m_\kappa m_{\kappa'})^{1/2} \omega(\vec{q},j)^2} e^{i\vec{q}\cdot\vec{r}} \tag{36}$$

where N is the number of mesh points in the Brillouin zone; the prime on the summation indicates that the Γ point $\vec{q}=0$ is to be omitted. We have used this formula to calculate the required elements of the Green matrix. In previous work,[6,8,13] we have used an alternative procedure which involves calculating the imaginary part of the frequency-dependent Green functions and then using the Kramers-Kronig relation to obtain the static quantities[20]; we now believe that this has no advantage over the direct use of Eq. (36). The phonon frequencies and polarization vectors were calculated from the interionic potentials described in the preceding section, using the standard methods of lattice vibration theory. The results we shall present are for the lattice spacing $d = 2.722$ Å, which is the zero-temperature value for $\mathrm{CaF_2}$ obtained from experiment.[28]

In order to assess the accuracy of the results, we have made calculations for different values of the mesh length Δq, which we express in terms of π/d, the distance from the zone center to the zone boundary in the $\langle 100 \rangle$ direction. The dependence of the results on Δq is shown in Fig. 1 for three representative Green functions. As we expect, the limiting dependence is linear in Δq. From this kind of study, we conclude that for the $\vec{r}=0$ elements a mesh length of $\Delta q = 0.05$ (equivalent to 32 000 points in the zone) yields an accuracy of $\sim 2\%$. However, the accuracy becomes rapidly worse as r increases and for $r=2$ it is no better than 10%. For large separations $r \gtrsim 6$ the results are virtually meaningless. This situation is, of course, familiar from previous work on nonpolar crystals.[27]

At large separations, the lattice Green functions must tend to the elastic Green functions,[26,27] which we denote by $g^{\alpha\beta}(\vec{r})$ (these are independent of sublattice). It should be possible, then, to avoid the necessity of calculating the $G^{\alpha\beta}_{\kappa\kappa'}(\vec{r})$ for large r by replacing them by the $g^{\alpha\beta}(\vec{r})$. In order to do this confidently, we must first examine how the numerical values of these two quantities are related. It has been shown by Schober *et al.*[27] that the $g^{\alpha\beta}(\vec{r})$ are given by

$$g^{\alpha\beta}(\vec{r}) = \frac{1}{8\pi^2 r} \int_0^{2\pi} d\phi\, \gamma^{\alpha\beta}(\theta=\pi/2,\phi) , \tag{37}$$

where θ and ϕ are the polar and azimuthal angles of a unit vector $\vec{\kappa}$ with respect to the direction of $\vec{r}$; for cubic crystals (such as $\mathrm{CaF_2}$) the dependence of $\gamma^{\alpha\beta}$ on the Cartesian components κ_α of $\vec{\kappa}$ in the crystal axes is given by

$$\gamma^{\alpha\beta}(\vec{\kappa}) = \frac{\delta_{\alpha\beta}}{c_{44} + d\kappa_\alpha^2} - \frac{c\kappa_\alpha\kappa_\beta}{(c_{44}+d\kappa_\alpha^2)(c_{44}+d\kappa_\beta^2)\left[1 + c\displaystyle\sum_{\delta=1}^{3} \frac{\kappa_\delta^2}{c_{44}+d\kappa_\delta^2}\right]} , \tag{38}$$

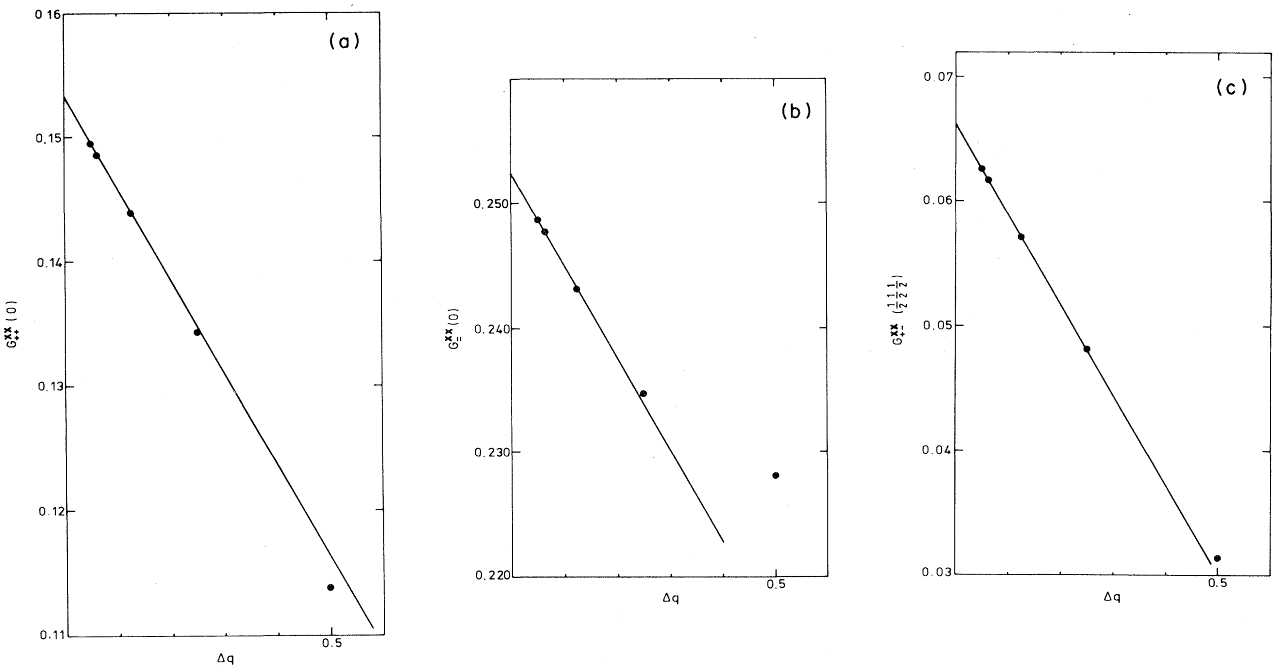

FIG. 1. Dependence of static lattice Green functions $G^{\alpha\beta}_{\kappa\kappa'}$ on the mesh length Δq used in the Brillouin-zone summation. The units of Δq are π/d (the distance in reciprocal space from the zone center Γ to the zone boundary X in the [100] direction) and the units of the Green functions are $(e^2/d^3)^{-1}$.

where c_{ij} are the usual elastic constants and d and c are

$$d=c_{11}-c_{12}-2c_{44}\ , \tag{39}$$

$$c=c_{44}+c_{12}\ . \tag{40}$$

We have evaluated the elastic Green functions from these equations, using values of the elastic constants calculated from the interionic potentials.

Since $rg^{\alpha\beta}(r)$ depends only on the direction of $\vec{r}$, it is convenient to compare this quantity with $rG^{\alpha\beta}_{\kappa\kappa'}(\vec{r})$. In making this comparison, which we present in Table II, we have used values of the lattice Green functions extrapolated to zero mesh length, $\Delta q=0$; it should be borne in mind that this extrapolation becomes rather uncertain for large r. In some directions the convergence of the lattice Green functions to their elastic counterparts is surprisingly rapid. For all the cation-anion functions listed, as well as for the cation-cation and anion-anion functions in the $\langle 111\rangle$ direction, the elastic Green functions would provide a good approximation even at the closest separation. Convergence is somewhat less rapid in the $\langle 110\rangle$ directions, but even so the lattice and elastic functions agree to $\sim 5\%$ beyond (2,2,0). Only for the $\langle 100\rangle$ direction is the convergence relatively slow.

What we have actually done in the entropy calculations is to replace the lattice Green functions by their elastic aproximation for all separations $r>2d$. As we have seen, this involves an error of only a few percent in most cases. The effect of the rather larger errors in those elements for which this is not true should be suppressed by the fact that there are relatively few of them. In addition, since the perturbation due to the defect is fairly well localized, we may expect that the accuracy of the Green functions is in any case less important at large separations.

In concluding this section we should mention that we have made extensive checks of the correctness of the Brillouin-zone results by calculating the lattice Green functions with an entirely independent method. This method exploits the fact that $G^{\alpha\beta}_{\kappa\kappa'}(\vec{r})$ is the harmonic response of the displacement of the ion κ in direction α to a unit force applied to ion κ' in direction β. The calculation consists of taking a region in the perfect crystal and applying a force to the ion at the center. All the ions in the region are then iteratively relaxed to their new equilibrium positions. This calculation can be done without difficulty for regions of radius up to $5d$. This allows the calculation of the $r=0$ Green functions to an accuracy of about 1%. Initially, we hoped that this method might provide a more economical alterna-

TABLE II. Comparison of lattice and elastic Green functions, $G_{ij}^{\alpha\beta}$ and $g^{\alpha\beta}$. Separation r is expressed in units of anion-anion nearest-neighbor separation d; Green functions are expressed in units of $(e^2/d^3)^{-1}$.

	Ion pair	Separation $\vec{r}$	rG_{ij}^{xx}	rg^{xx}
⟨100⟩ direction	$--$	(100)	0.132	
	$++$	(200)	0.064	
	$--$	(200)	0.144	
	$--$	(300)	0.129	0.084
	$--$	(400)	0.114	
	$--$	(500)	0.110	
	$--$	(600)	0.096	
⟨110⟩ direction	$++$	(110)	0.065	
	$--$	(110)	0.045	
	$++$	(220)	0.068	
	$--$	(220)	0.059	0.060
	$++$	(330)	0.064	
	$--$	(330)	0.059	
	$--$	(440)	0.059	
	$--$	(550)	0.057	
⟨111⟩ direction	$+-$	$(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.057	
	$--$	(111)	0.053	
	$+-$	$(\frac{3}{2}\frac{3}{2}\frac{3}{2})$	0.053	
	$++$	(222)	0.055	0.055
	$--$	(222)	0.053	
	$--$	(333)	0.053	
	$--$	(444)	0.053	
Other directions	$+-$	$(\frac{3}{2}\frac{1}{2}\frac{1}{2})$	0.068	0.073
	$+-$	$(\frac{3}{2}\frac{3}{2}-\frac{1}{2})$	0.061	0.059
	$+-$	$(\frac{5}{2}\frac{3}{2}\frac{1}{2})$	0.065	0.068
	$+-$	$(\frac{5}{2}\frac{3}{2}-\frac{3}{2})$	0.062	0.062
	$+-$	$(\frac{5}{2}\frac{5}{2}-\frac{1}{2})$	0.063	0.059
	$+-$	$(\frac{5}{2}\frac{5}{2}\frac{3}{2})$	0.055	0.057

tive to the Brillouin-zone technique. Unfortunately, this hope was not fulfilled. Nevertheless, the results we obtained fully confirmed the correctness of our previous calculations.

V. ENTROPY CALCULATIONS

We have used the methods described above to make numerical calculations of the entropies of formation Δs_v and Δs_i of vacancies and interstitials in CaF_2 using the rigid-ion model. Since we wish to study the convergence of the results as the size of the defect region is increased, we have made calculations for a wide range of region sizes. It turns out that in order to assess the convergence adequately, results must be obtained for regions containing up to several hundred ions. The need to store and manipulate the large matrices involved makes heavy demands on computing power unless full use is made of point-group symmetry. Standard group-theoretic techniques allow one to construct the force-constant and Green matrices directly in block-diagonal form, in which each block is associated with one of the irreducible representations of the point group. The symmetries of the vacancy and the interstitial are described by the tetrahedral group T_d and the full cubic group O_h, which have, respectively, 5 and 10 irreducible representations. The use of symmetry reduces the dimension of the matrices typically by a factor of 3 for the vacancy and a factor of 6 for the interstitial.

Our results for Δs_v and Δs_i, calculated both by the crystallite and by the Green-function methods are presented in Fig. 2, where they are plotted against the reciprocal of the number of ions in the defect region. The calculations were performed for a value of the anion-anion separation d equal to 2.722 Å.[28] As we noted in Sec. II, the numerical results depend on the units used for force constants: We use units of e^2/d^3 throughout. The results are surprising and disconcerting. The fluctuations caused by changing the region size are so large that satisfactory extrapolation is quite impossible. This is true of the results obtained by both methods, but the trouble is worse for the Green-function method. Here the entropy can change by as much as $1k_B$ as we pass from one region size to the next, even for regions containing as many as 100 ions. It is clear that our attempt to master the calculation of entropies of formation will have failed unless we can tame the erratic behavior of the results.

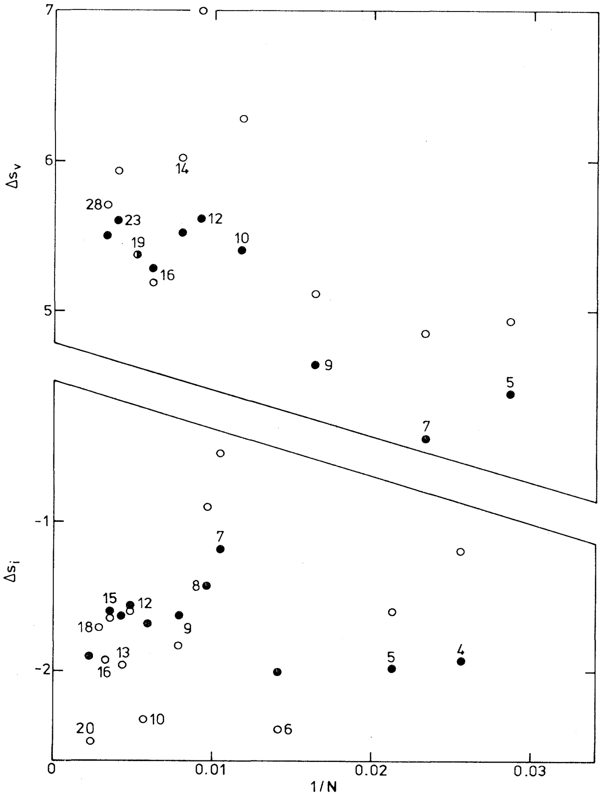

FIG. 2. Entropies Δs_v and Δs_i for vacancy and interstitial plotted against the reciprocal of N, the number of ions in the defect region. Filled and empty symbols indicate results obtained using the embedded-crystallite and the Green-function methods, respectively. Numbers attached to symbols show number of classes of equivalent ions in the defect region.

In order to understand this behavior, it is instructive to consider the entropy change caused by expanding the defect region by the addition of a single class of equivalent ions. For the interstitial, the Green-function expression for the entropy $\Delta s_i^{(n)}$ for a defect region containing n classes of ions is

$$\Delta s_i^{(n)} = -\tfrac{1}{2} k_B \ln(| \underline{I} + \underline{g}^{(n)} \delta \underline{\Phi}_i'^{(n)} | | \underline{\phi}_i |) , \tag{41}$$

where $\underline{g}^{(n)}$ and $\delta\underline{\Phi}_i'^{(n)}$ are the matrices of perfect-lattice Green functions and of force-constant changes for this defect region; the matrix $\underline{\phi}_i$ is independent of n. It may readily be shown that the change in entropy $\Delta s_i^{(n+1)} - \Delta s_i^{(n)}$ when we add an extra class is given by

$$\Delta s_i^{(n+1)} - \Delta s_i^{(n)} = -\tfrac{1}{2} k_B \ln | \underline{I} + \underline{\gamma}^{(n+1)} (\delta\underline{\Phi}_i'^{(n+1)} - \delta\underline{\Phi}_i'^{(n)}) | , \tag{42}$$

where $\underline{\gamma}^{(n+1)}$ is the Green-function matrix in the subspace appropriate to $n+1$ classes of ions of the system whose force-constant matrix is $\underline{\Phi} + \delta\underline{\Phi}_i'^{(n)}$, which we may write as

$$(\underline{\gamma}^{(n+1)})^{-1} = (\underline{g}^{(n+1)})^{-1} + \delta\underline{\Phi}'^{(n)} . \tag{43}$$

Now for large n the difference of the two $\delta\underline{\Phi}$ matrices in Eq. (42) will be small, so that we can expand the logarithm to first order to obtain

$$\Delta s_i^{(n+1)} - \Delta s_i^{(n)} \simeq -\tfrac{1}{2} k_B \operatorname{Tr}[\underline{\gamma}^{(n+1)} (\delta\underline{\Phi}_i'^{(n+1)} - \delta\underline{\Phi}_i'^{(n)})] , \tag{44}$$

where we have used the fact that the logarithm of the determinant of a matrix is equal to the trace of the logarithm.

Equation (44) allows us to study in some detail the contributions to the difference $\Delta s_i^{(n+1)} - \Delta s_i^{(n)}$ and the corresponding quantity for the vacancy. Note first that the elements in the difference of $\delta\underline{\Phi}$'s describe the coupling between ions within the extra class and between these ions and those in the original region of n classes. Inspection reveals that the largest of these elements are for the coupling of ions in the extra class with nearby ions of opposite charge in the original region. Since such pairs of ions are far from the defect, the difference between $\underline{\gamma}^{(n+1)}$ and $\underline{g}^{(n+1)}$ represented by Eq. (43) should be unimportant, and we can replace Eq. (44) by

$$\Delta s_i^{(n+1)} - \Delta s_i^{(n)} = -\tfrac{1}{2} k_B \operatorname{Tr}[\underline{g}^{(n+1)}(\delta \underline{\Phi}_i'^{(n+1)} - \delta \underline{\Phi}_i'^{(n)})] \,. \tag{45}$$

Since we know the elements of g, we can use this formula to estimate the expected changes of Δs_i as we add classes to the defect region. Our estimates suggest that the contribution from pairs of ions near the boundary accounts entirely for the irregular behavior of our results.

In the light of this, we can give a general reason why difficulties of this kind should arise for ionic crystals and not for the crystals of neutral atoms studied by Hatcher *et al.*[19] and other workers. In both neutral and ionic crystals, the equilibrium displacements fall off with distance as r^{-2}. In the neutral case, the displacements are associated solely with the elastic response, but in the ionic case they are dominated by the dielectric response, so that in the one case the radial displacements are all of the same sign, but in the other the signs are opposite for oppositely charged ions. As we have emphasized in Sec. III, the displacements used in our calculations correctly include this effect. It follows that the $\delta\underline{\Phi}$'s for nearby ions fall off as r^{-3} in the neutral case, but only as r^{-2} for ions of opposite charge in the ionic case. Since the number of ions near the boundary increases as r^2, the occurrence of convergence problems in the ionic case might possibly have been foreseen.

The key point which leads to the resolution of these problems is that the boundary effects do not depend on the presence of the defect itself, but only on the long-range distortions it causes. In particular, exactly the same effects would be found if we tried to calculate the entropy change due to a distortion of the perfect lattice, provided the distortion had the same long-range form as in the defective lattice. In order to substantiate this idea and see how to exploit it, we have made calculations for the distorted perfect lattice, which we now describe. Let us introduce in the perfect-lattice ionic displacements which are identical to those of the ions in the defective lattice. The displacements give rise to changes $\delta\underline{\Phi}$ in the force-constant matrix and hence to a change in the entropy, which is given by

$$\Delta s = -\tfrac{1}{2} k_B \ln |\underline{I} + \underline{g}\, \delta\underline{\Phi}| \,. \tag{46}$$

This can evidently be calculated numerically using the same technique as for the case of the defect. However, it is convenient to retain only that part of Δs which is linear in the displacements. This can be done by supposing all displacements to be multiplied by the same factor λ, making a power series expansion in λ:

$$\Delta s = \Delta s' \lambda + \tfrac{1}{2} \Delta s'' \lambda^2 + \cdots \tag{47}$$

and keeping only the term $\Delta s'$. If we make a similar expression for $\delta\underline{\Phi}$,

$$\delta\underline{\Phi} = \lambda \delta\underline{\Phi}' + \tfrac{1}{2} \lambda^2 \delta\underline{\Phi}'' + \cdots \,, \tag{48}$$

then $\Delta s'$ is given by

$$\Delta s' = -\tfrac{1}{2} k_B \operatorname{Tr}(\underline{g}\, \delta\underline{\Phi}') \,. \tag{49}$$

Since the displacements near the boundary are small, the boundary effects of interest will all be contained in $\Delta s'$. The main reason for keeping only the linear term will become apparent later, but we note here that the trace formula of Eq. (49) allows us to calculate $\Delta s'$ without diagonalizing, or even storing, large matrices; this means that we can go to much larger defect regions than was possible in the defect calculation. In addition, the collecting of terms in the trace can be organized in such a way that a single calculation suffices to obtain $\Delta s'$ for all sizes of defect region up to some maximum. In practice, we have avoided the explicit calculation of $\delta\underline{\Phi}'$ by evaluating $\Delta s'$ by the trace formula with the full $\delta\underline{\Phi}$ but with λ set equal to 10^{-2} and multiplying the numerical results by λ^{-1}; this procedure serves to extract the linear term $\Delta s'$ with sufficient accuracy for present purposes.

Our numerical results for $\Delta s'$ for perfect-lattice distortions corresponding to the vacancy and interstitial are shown in Fig. 3. The fluctuations of $\Delta s'$ with region size are very clear. We also find that the sign of the fluctuations is directly connected with that of the ionic charge in the last class to be added. This is expected from the analysis we have given: The $\delta\underline{\Phi}$'s for the coupling of cations in the last class with anions in previous classes will be roughly equal but opposite to those for the coupling of anions in the last class with previous cations. This suggests that the behavior of $\Delta s'$ should be paralleled by that of the net charge Q in the defect region, or better, by that of Q/r^2, since the relevant $\delta\Phi$'s fall off as r^{-2}. The comparison presented in Fig. 3 amply supports this notion.

If our analysis has been correct, the fluctuations in the results for the distorted perfect lattice should

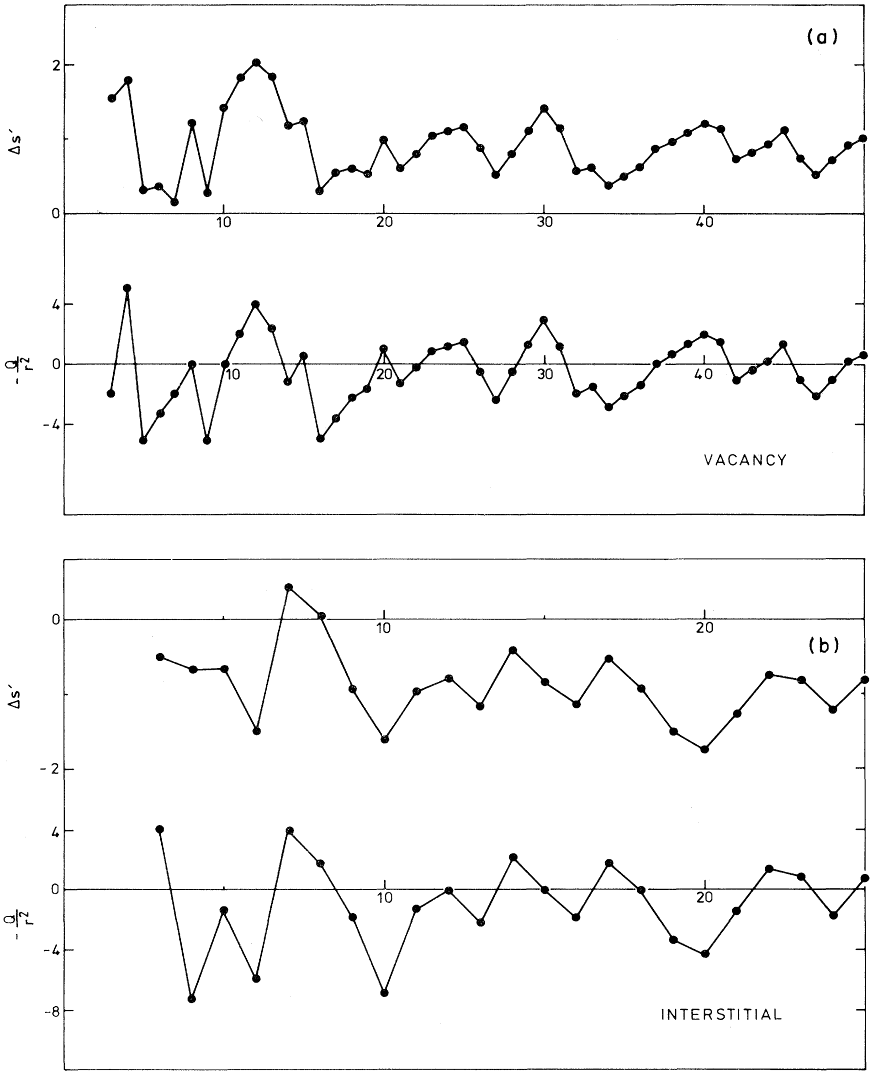

FIG. 3. Linear term $\Delta s'$ in the entropy of distorted perfect lattice corresponding to (a) vacancy and (b) interstitial, plotted against the number of classes of equivalent ions in the defect region. Also shown is the total charge Q of the ions in the defect region divided by r^2, where r is the radius to the furthest class of ions.

be almost identical to those for the defective lattice. Then the fluctuations in Δs_v and Δs_i may be largely eliminated by subtracting the appropriate $\Delta s'$; we shall write $\overline{\Delta s}_v \equiv \Delta s_v - \Delta s'$ and $\overline{\Delta s}_i \equiv \Delta s_i - \Delta s'$. This subtraction can be performed immediately for the Green-function method, using the results for $\Delta s'$ just presented. The discussion of the distorted perfect lattice may be repeated for the crystallite method, except that Δs is now given by

$$\Delta s = -\tfrac{1}{2} k_B \ln(\,|\underline{\Phi}'\,|\,/\,|\,\underline{\Phi}\,|\,)\ , \qquad (50)$$

where $\underline{\Phi}'$ and $\underline{\Phi}$ are the force-constant matrices for the defect region of the distorted and undistorted perfect lattice. As before, we have extracted the linear term $\Delta s'$ by performing the calculation with the true displacements multiplied by the factor $\lambda = 10^{-2}$, and scaling the results up by the factor λ^{-1}.

Our numerical results for $\overline{\Delta s}_v$ and $\overline{\Delta s}_i$ are shown in Fig. 4. The dramatic improvement in the regularity of their behavior is very evident. The uniformity of their dependence on N^{-1} is now sufficient to allow an extrapolation to infinite region size with an uncertainty of only $\sim \pm 0.1 k_B$. What is more, the

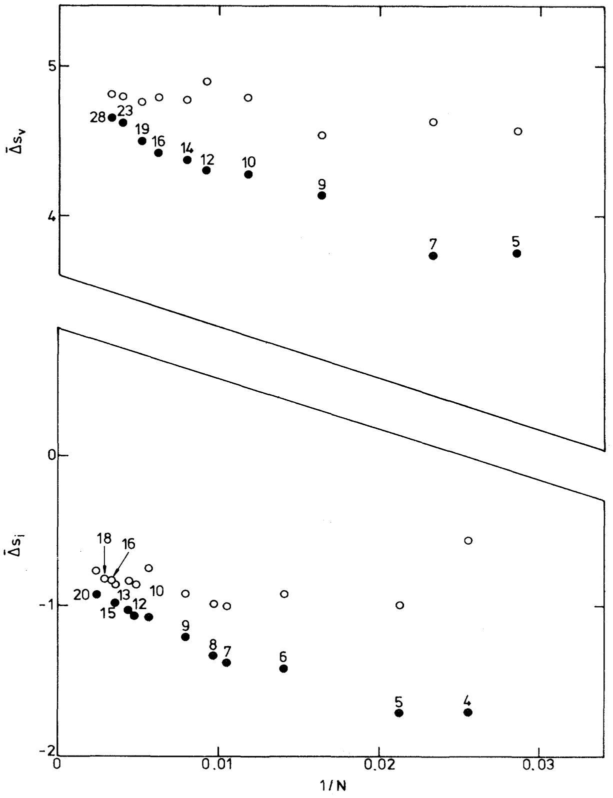

FIG. 4. Entropies $\bar{\Delta s}_v$ and $\bar{\Delta s}_i$ for vacancy and interstitial after subtraction of the corresponding distorted perfect-lattice term $\Delta s'$, plotted against the reciprocal of the number of ions in defect region. Filled and empty symbols show results of embedded-crystallite and Green-function calculations, respectively. Numbers attached to symbols show the number of classes of equivalent ions in the defect region.

crystallite and Green-function results extrapolate to the same values within this uncertainty. This agreement provides valuable confirmation of the technical correctness of the calculations; it also indicates that the errors committed in replacing lattice Green functions by elastic Green functions are not seriously influencing the final answers. On this last point, we might mention that for the vacancy and interstitial defect regions containing, respectively, 43 and 47 ions, we have repeated the calculations of Δs_v and Δs_i using calculated lattice Green functions for all separations instead of replacing them by their elastic approximation for $r > 2d$. The comparison of the results, which we show in Table III, indicates that replacement of lattice Green functions by their elastic counterparts affects the entropy values by only $\sim 0.1 k_B$.

TABLE III. Comparison of entropy results (without subtraction of $\Delta s'$) obtained by using calculated lattice Green functions for all separations and by using the elastic approximation for $r > 2d$. The defect regions contain 43 and 47 ions for the vacancy and interstitial, respectively.

	Δs_v	Δs_i
Full-lattice Green functions	4.83	−1.71
Replacement by elastic Green functions for $r > 2d$	4.85	−1.61

Although the results shown in Fig. 4 are very encouraging, it is not quite clear that we are at the end of the problems. Indeed, it might be thought that we have succeeded only in transferring the difficulties from one place to another: The subtracted quantities $\Delta s'$ are as poorly behaved as the original results, and we have no means of knowing their true limiting value; surely, at least, some correction ought to be applied to the results for $\bar{\Delta s}_v$ and $\bar{\Delta s}_i$ to compensate for the effect of the subtraction? This question is fully discussed in the Appendix, where we show that the quantities $\bar{\Delta s}_v$ and $\bar{\Delta s}_i$ correctly give the entropies of formation at constant volume for a large finite crystal, except for the omission of a contribution associated with the real surface (as opposed to the artificial boundary of the defect region). This surface term is proportional to the charge on the defect and cancels out when we add $\bar{\Delta s}_v$ and $\bar{\Delta s}_i$ to obtain the Frenkel formation entropy s_F (and, more generally, when we construct the total formation entropy for any neutral set of defects). The conclusion is, then, that the subtraction of $\Delta s'$ not only eliminates the large fluctuations but also cancels a spurious contribution associated with the use of a finite defect region in a formally infinite crystal. It would, therefore, be a mistake to attempt any correction for the effect of this subtraction.

Our extrapolated numerical results for the vacancy and interstitial entropies and the Frenkel entropy are summarized in Table IV. Their significance in relation to other theoretical and experimental results will be discussed in Sec. VII. The point we wish to emphasize here is that our aim of deriving the entropies from the interionic potentials to a precision of a few tenths of k_B appears to have been achieved.

VI. SHELL-MODEL CALCULATIONS

Rigid-ion potentials are good enough for the study of computational methods, but when it comes

TABLE IV. Extrapolated results for vacancy and interstitial entropies $\overline{\Delta s}_v$ and $\overline{\Delta s}_i$ and for the Frenkel entropy $s_F = \overline{\Delta s}_v + \overline{\Delta s}_i$ calculated using the rigid-ion and shell models for CaF_2.

	$\overline{\Delta s}_v$	$\overline{\Delta s}_i$	s_F
Rigid-ion model	4.8	−0.8	4.0
Shell model	4.0	−0.8	3.2

to calculations which are to be compared with experiment, it will always be preferable to use good shell-model potentials. We therefore wish to demonstrate here that the techniques we have developed can be extended to the shell model. There appears to us to be no essential difficulty in making shell-model calculations with either the Green-function or the embedded-crystallite methods, but we have confined ourselves to the latter, since it is simpler to use and seems from the discussion of Sec. V to be entirely satisfactory.

We use the shell model in its standard form,[29] in which the core and shell for each ion are coupled by an isotropic harmonic spring, the Coulomb interactions operate between the core and shell of every ion and the core and shell of every other ion, and the short-range interactions operate only between the shells on different ions. The force-constant matrices $\underline{\Psi}_{cc}$, $\underline{\Psi}_{ss}$, and $\underline{\Psi}_{cs}$ describing the coupling of cores to cores, shells to shells, and cores to shells are thus given by

$$\Psi^{\alpha\beta}_{ccij} = k_i \delta_{ij} \delta_{\alpha\beta} + \Phi^{\alpha\beta}_{ccij} \ , \tag{51a}$$

$$\Psi^{\alpha\beta}_{ssij} = k_i \delta_{ij} \delta_{\alpha\beta} + \Phi^{\alpha\beta}_{ssij} \ , \tag{51b}$$

$$\Psi^{\alpha\beta}_{csij} = -k_i \delta_{ij} \delta_{\alpha\beta} + \Phi^{\alpha\beta}_{csij} \ , \tag{51c}$$

where k_i is the core-shell spring constant for ion i and the interionic potential terms $\Phi^{\alpha\beta}_{ccij}$, etc. are given, for $i \neq j$, by

$$\Phi^{\alpha\beta}_{ccij} = \frac{X_i X_j e^2}{r^3_{ccij}} (\delta_{\alpha\beta} - 3\hat{r}^{\alpha}_{ccij} \hat{r}^{\beta}_{ccij}) \ , \tag{52a}$$

$$\Phi^{\alpha\beta}_{ssij} = \frac{Y_i Y_j e^2}{r^3_{ssij}} (\delta_{\alpha\beta} - 3\hat{r}^{\alpha}_{ssij} \hat{r}^{\beta}_{ssij}) - \delta_{\alpha\beta} \frac{V^{s'}_{ij}}{r_{ssij}} - \hat{r}^{\alpha}_{ssij} \hat{r}^{\beta}_{ssij} \left[\frac{V^{s''}_{ij} - V^{s'}_{ij}}{r_{ssij}} \right] , \tag{52b}$$

$$\Phi^{\alpha\beta}_{csij} = \frac{X_i Y_j e^2}{r^3_{csij}} (\delta_{\alpha\beta} - 3\hat{r}^{\alpha}_{csij} \hat{r}^{\beta}_{csij}) \ . \tag{52c}$$

Here X_i and Y_i are, respectively, the core and shell charge for ion i, and $\vec{r}_{ccij}$ is the separation between the core of ion i and the core of ion $\underline{j}$, etc. For $i = j$, we have

$$\Phi^{\alpha\beta}_{ccii} = -\sum_{j\,(\neq i)} (\Phi^{\alpha\beta}_{ccij} + \Phi^{\alpha\beta}_{csij}) \ , \tag{53a}$$

$$\Phi^{\alpha\beta}_{ssii} = -\sum_{j\,(\neq i)} (\Phi^{\alpha\beta}_{scij} + \Phi^{\alpha\beta}_{ssij}) \ . \tag{53b}$$

The quantities $\Phi^{\alpha\beta}_{csii}$ are zero by definition, since the interionic potentials themselves give no coupling between core and shell on the same ion.

As the cores vibrate, the shell positions adjust themselves so that the net force acting on any shell is always zero. Then the effective force-constant matrix for the cores is[30]

$$\underline{\Psi} = \underline{\Psi}_{cc} - \underline{\Psi}_{cs} \underline{\Psi}^{-1}_{ss} \underline{\Psi}_{sc} \ . \tag{54}$$

The embedded-crystallite formula for the defect entropy has exactly the same form as Eqs. (10) or (11):

$$\Delta s_d = -\tfrac{1}{2} k_B \ln(| \underline{\Psi}_d | / | \underline{\Psi} |) \ , \tag{55}$$

where d stands for v or i and $\underline{\Psi}$ and $\underline{\Psi}_d$ are the effective force-constant matrices for the perfect and the defective crystals. The calculation of the diagonal elements $\Phi^{\alpha\beta}_{ccii}$ and $\Phi^{\alpha\beta}_{ssii}$ is done exactly as for the rigid-ion calculation, by using the Ewald method for the Coulomb contributions and summing over an extended region. The value of the Gaussian width parameter ζ, and the ranges of the real and reciprocal space sums are kept the same as before. As in the previous calculations, we use group theory to exploit the symmetry.

We have performed the calculations at the lattice spacing $d = 2.722$ Å (Ref. 28) using the shell model of CaF_2 described by Catlow and Norgett[22] (model I). The equilibrium positions of the cores and shells were calculated with the HADES program, using the same sizes of region I as before.

Our numerical results for the entropy show the now expected fluctuations and we use the subtraction method to eliminate them. In calculating the linear term $\Delta s'$ in the entropy of distortion of the perfect lattice, we use the displacements in the defective crystal of both cores and shells, scaled down by the factor $\lambda = 10^{-2}$, multiplying the results as usual by λ^{-1} to obtain $\Delta s'$. The values for $\overline{\Delta s}_v$ and $\overline{\Delta s}_i$ are shown in Fig. 5, where we compare them with the rigid-ion values. The variation of the entropies with region size is qualitatively very similar for the two models. It turns out that the extrapolated results for the interstitial are essentially identical, but in the case of the vacancy the introduction of the shell model lowers the entropy of formation by $0.8k_B$. The extrapolated results are summarized in Table IV.

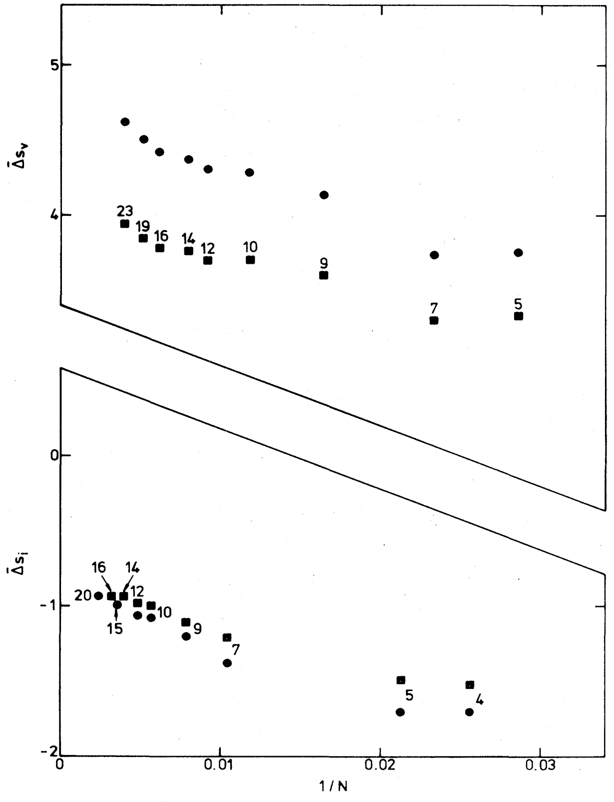

FIG. 5. Comparison of rigid-ion (circles) and shell-model (squares) results for entropies $\bar{\Delta s}_v$ and $\bar{\Delta s}_i$ of vacancy and interstitial calculated using embedded-crystallite method. Plot is against the reciprocal of the number of ions in the defect region. Numbers attached to symbols show the number of classes of equivalent ions in the defect region.

VII. DISCUSSION

We believe the main achievement of the present work has been to gain an understanding of the rather subtle technical problems involved in calculating entropies for defects in ionic crystals. We have found that the straightforward application of both the Green-function and the embedded-crystallite methods is vitiated by spurious effects associated with the surface of the defect region. These effects are peculiar to ionic crystals, since they are connected with the long-range dielectric response of the lattice to the presence of the defect. Fortunately, it has been possible to eliminate these effects by performing a fairly simple subtraction. This technique yields results which vary regularly with the size of the defect region and which can be extrapolated to give final results with a residual uncertainty of only a few tenths of k_B, which is certainly adequate for all practical purposes.

Our findings have implications for the earlier calculations of Jacobs and co-workers, which used the Green-function method.[6,8,13] Although those calculations represented an important first attempt at the problem, they cannot now be regarded as very satisfactory, for a number of reasons. Firstly, the full Coulomb contribution to the force constants was not handled correctly.[8,23] Secondly, the defect region included only first and second neighbors of the defect; the present work shows that such a small region is not adequate. Thirdly, it was not recognized that serious uncertainties can be caused by the surface fluctuations we have discussed.

We can also comment on the calculation of the Frenkel entropy for CaF_2 by Harding and Stoneham,[7] which used the supercell method. This calculation, which used exactly the same shell-model potential as we have used for the calculations of Sec. VI, yielded the result $s_F = 6.4k_B$. Since our calculations show that the correct result is $(3.2\pm0.1)k_B$, we must conclude that the method, as applied by Harding and Stoneham, is not very reliable. The reason is presumably that the repeating cell they used contained only 24 ions, which would also be inadequate in the methods we have used. It is likely, then, that the supercell method would give satisfactory results if considerably larger cell sizes could be used. The same remarks about cell size apply to the calculation of Sahni and Jacobs.[5]

Our work leads us to draw conclusions about the relative merits of the Green-function and the embedded-crystallite methods. Our results show that the Green-function method yields a better rate of convergence, at least for the system we have studied. For example, for a defect region containing about 100 ions, the Green-function method gives a Frenkel entropy which is within about $0.2k_B$ of the extrapolated result, whereas the crystallite result is still in error by about $1k_B$. Against this advantage must be set the fact that the Green-function method is very much more laborious to apply. In the present work, a large amount of both human and computer time has been spent in checking the accuracy of the many Green-function elements and in studying their convergence to the elastic Green functions. If calculations were to be made for a completely different material, it would probably be felt necessary to repeat many of these checks. The crystallite method, by contrast, is virtually automatic, apart from the need to study the convergence with respect to the size of the defect region. Its inferior rate of convergence is also not a very serious disadvantage, since there appears to be no problem in making adequate extrapolations. Our conclusion is that it will be preferable in the future to use the embedded-crystallite method. Nevertheless, for the purpose of exploring the technical problems and of establishing that our calculations are free of mistakes, we have found the Green-function method invaluable.

Finally, we comment on the comparison between our results for the Frenkel entropy of CaF_2 and the experimental value. Our results refer to the entropy of formation at constant volume, whereas the experimental values are for constant pressure. The large correction which must be added to the constant volume result to convert it to constant pressure has been discussed in previous papers.[7,23] It is shown there that this correction has a value of about $5k_B$ for CaF_2, but that this is subject to an uncertainty of at least $\pm 1k_B$. Applying this correction to our shell-model result, we arrive at a constant pressure s_F of $(8\pm 1)k_B$. This is to be compared with the most recent (and, we believe, most reliable) experimental value for CaF_2 of $5k_B$.[31] Our theoretical results, therefore, seems to be definitely too high. However, it is too early to conclude that there is a serious problem here. In the first place, there is always some uncertainty in the value of an experimental entropy that has to be derived indirectly by a model-dependent analysis. In the second place, the sensitivity of our results to the interionic potentials needs more careful study. Even the shell-model potentials we have used are unsatisfactory in one relevant respect: They predict a vacancy migration energy which is too low by a factor of 2.[22] Since this migration energy should be correlated with the force constants of the anions neighboring the vacancy, we would expect the vacancy entropy to be reduced by the use of better potentials. In the third place, the size of the correction from constant volume to constant pressure needs to be reexamined. We hope to return to these matters in a future paper.

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APPENDIX: THE SURFACE CONTRIBUTION

The calculations performed in this paper refer implicitly to an infinite crystal, since there is no mention of any physical surfaces. Real crystals are of finite size and have surfaces, so we need to ask what is the relation between entropies of defect formation in finite and in infinite crystals. This discussion has a bearing on the subtraction we have used to eliminate the fluctuations associated with the boundary of the defect region. We shall be able to decide whether any correction is needed to compensate for this subtraction.

We begin by showing that the entropy of formation of a single-charged defect in a finite crystal contains a contribution which depends on the detailed properties of the surface. This rather unexpected fact may be demonstrated by a simple and general argument. Let us take an ionic crystal in thermal equilibrium and let us change the charge on one of the ions by an infinitesimal amount δq, the change being made reversibly at constant temperature and volume. Since any external forces at the surface do no work, the change in the Helmholtz free energy δF is just the work done in bringing up the extra charge from infinity to the ion in question:

$$\delta F = \delta q \langle \psi \rangle \ , \tag{A1}$$

where $\langle \psi \rangle$ is the thermal average of the electric potential at the ion. The associated entropy change is

$$\delta S = -\partial F/\partial T = -\delta q\, \partial \langle \psi \rangle / \partial T \ , \tag{A2}$$

the temperature derivative being taken at constant volume. There will, in general, be a contribution to $\langle \psi \rangle$ from the surface: Since the cations and anions at the surface have different equilibrium relaxations from the perfect-lattice positions[32] there must be an electrical double layer at the surface, and this will give rise to an electric potential in the interior of the crystal. Since the strength of the double layer will generally be temperature dependent, it follows from Eq. (A2) that there is a genuine surface contribution to δS. It should be noted that for a given strength of the double layer, the potential in the interior does not depend on the size of the crystal, so that the contribution to δS exists even for crystals of macroscopic size. It does, however, depend on the crystallographic nature of the surfaces and on the shape of the crystal and the position of the ion with respect to the surface (except for a spherical crystal). Since a defect can be formed by a sequence of infinitesimal changes, it follows that the entropy of formation contains a surface contribution which is given by

$$\Delta s^{\sigma} = -q \partial \langle \psi^{\sigma} \rangle / \partial T \ , \tag{A3}$$

where q is the net charge on the defect and $\langle \psi^\sigma \rangle$ is the surface electric potential at the position of the defect.

The temperature dependence of $\langle \psi^\sigma \rangle$ is evidently a consequence of anharmonicity, since it stems from the variation with temperature of the mean positions of the ions at the surface. It might be thought, then, that the contribution Δs^σ, although real, is irrelevant to the calculations of this paper, which treat lattice vibrations as harmonic. This is not the case, as we now show. Let the displacement of ion i from its zero-temperature equilibrium position be denoted by $\vec{\eta}_i$. Then the difference between $\langle \psi^\sigma \rangle$ and its value at zero temperature is

$$\Delta \langle \psi^\sigma \rangle = -\sum_i{}^{\sigma} q_i \langle \vec{\eta}_i \rangle \cdot \vec{r}_i / r_i^3 , \tag{A4}$$

where $\langle \vec{\eta}_i \rangle$ is the thermal average of the displacement, q_i is the charge, and $\vec{r}_i$ is the position of ion i with respect to the defect; the sum $\sum^\sigma$ goes only over ions near the surface. It follows that

$$\Delta s^\sigma = q \sum_i{}^{\sigma} q_i (\partial \langle \vec{\eta}_i \rangle / \partial T) \cdot \vec{r}_i / r_i^3 . \tag{A5}$$

Now the quantity $\vec{f}_i \equiv q q_i \vec{r}_i / r_i^3$ is just the electrostatic force exerted by the defect on ion i, and we can write

$$\Delta s^\sigma = \sum_i{}^{\sigma} \vec{f}_i \partial \langle \vec{\eta}_i \rangle / \partial T . \tag{A6}$$

Consider now the effect on the entropy of a crystal of introducing a set of small external forces $\vec{f}_i$, again at constant temperature and volume. These forces may be represented by adding to the Hamiltonian a term equal to

$$\Delta H = -\sum_i \vec{f}_i \cdot \vec{\eta}_i , \tag{A7}$$

so that the work done (i.e., the change in free energy) is

$$\delta F = -\sum_i \vec{f}_i \cdot \langle \vec{\eta}_i \rangle . \tag{A8}$$

Then the entropy change is

$$\delta S = \sum_i \vec{f}_i \cdot \partial \langle \vec{\eta}_i \rangle / \partial T . \tag{A9}$$

One contribution to this is the change of surface entropy δS^σ:

$$\delta S^\sigma = \sum_i{}^{\sigma} \vec{f}_i \cdot \partial \langle \vec{\eta}_i \rangle / \partial T , \tag{A10}$$

which is identical to Eq. (A6). This gives us a clear physical interpretation of the surface contribution to the entropy of defect formation: It is the change of surface entropy caused by the electrostatic forces exerted by the defect on the surface ions, forces which may be regarded as "external."

The physical reason for this change of surface entropy is clear: The effect of the forces is to change the equilibrium positions of the ions at the surface; the change of positions entails a change in the force constants and hence a change in the entropy, even when calculated in the harmonic approximation. From this it is plain that the surface contribution does fall within the scope of our harmonic calculations. If we had done for the finite crystal what we have done for the infinite crystal, that is performed harmonic entropy calculations for the fully relaxed defective and nondefective systems and taken the difference, we would have picked up a surface contribution of exactly the kind we have described.

We can now give a partial answer to our question about the relation between the entropies of formation in finite and infinite crystals by saying that the result for the infinite crystal omits a surface contribution which is present for the real finite crystal. It is clear that this omission does not matter for most applications. The only property of the defect which enters the surface contribution is its net charge, so that if we are concerned with the sum of the entropies for oppositely charged defects (e.g., Schottky and Frenkel pairs) the surface terms cancel out. However, there are situations where the individual entropies are required, for example in the analysis of the thermopower of ionic crystals.[33] In such cases, the techniques developed in the present paper would not suffice, and the surface contribution would have to be considered separately.

We now wish to complete the answer to our question by considering the formation entropy in a finite crystal when the surface term is removed. Recall that for the infinite crystal we calculate the limit for a large defect region of the defect entropy Δs minus the entropy $\Delta s'$ calculated for the distorted perfect lattice; as before, we write $\overline{\Delta s} \equiv \Delta s - \Delta s'$. Now consider the same calculation done for the finite crystal. We denote by Δs_{fin} the total entropy of formation (including the surface contribution) for the finite crystal, and by $\Delta s'_{\text{fin}}$ the entropy change for the nondefective finite crystal caused by the distortions present in the defective crystal, keeping as usual only the term linear in the distortions; we then write $\overline{\Delta s}_{\text{fin}} \equiv \Delta s_{\text{fin}} - \Delta s'_{\text{fin}}$. We shall argue that (i) $\overline{\Delta s}$ and $\overline{\Delta s}_{\text{fin}}$ are the same if the size of the defect region in the infinite crystal and the size of the finite crystal are large; (ii) the quantity $\Delta s'_{\text{fin}}$ is exactly the surface contribution with nothing else added. This will allow us to conclude that the $\overline{\Delta s}$ we have calculated is the entropy of formation for the finite crystal, with the surface contribution omitted,

$$\overline{\Delta}s = \Delta s_{\rm fin} - \Delta s^{\sigma} \; . \tag{A11}$$

The correctness of assertion (i) is almost self-evident, since the effect of the subtractions $\Delta s'$ and $\Delta s'_{\rm fin}$ is to cancel contributions to the entropy from regions far from the defect (and, in particular, from regions near the surface). However, a full proof would be tedious and we shall merely sketch an argument which could be elaborated if necessary. Let us suppose the finite crystal to be divided into two regions by a boundary which encloses the defect and which is distant on the atomic scale from both the defect and the surface. For the outer region, the deviation $\delta\Phi$ of the force-constant matrix from that of the perfect crystal can be assumed linear in the ionic displacements, since these are very small. Since they are also identical for the defective crystal and for the distorted perfect lattice, the $\delta\Phi$'s are also identical, except insofar as they depend on the presence of the defect in the inner region. To this extent, then, the contributions to $\Delta s_{\rm fin}$ and $\Delta s'_{\rm fin}$ from the outer region cancel exactly. The only difference between the $\delta\Phi$'s which need to be considered here is that due to the *charge* on the defect which introduces a difference between the on-site elements of the two $\delta\Phi$'s which falls off only as r^{-3}. However, this difference is traceless in the Cartesian components and so does not contribute to this order in r^{-1}, except perhaps for ions near the surface. This means that the difference of the $\delta\Phi$'s contributes to order at most r^{-4} for ions in bulk and r^{-3} for ions near the surface of the outer region, so that the contribution to $\overline{\Delta}s_{\rm fin}$ from this region is negligible for a large crystal. On the other hand, the contribution to $\overline{\Delta}s_{\rm fin}$ from the inner region is the same as $\overline{\Delta}s$ for the infinite crystal, since the vibrational properties of the inner region will be unaffected by the presence of the distant surface. We thus arrive at assertion (i): $\overline{\Delta}s = \overline{\Delta}s_{\rm fin}$.

Now consider assertion (ii), that $\Delta s'_{\rm fin} = \Delta s^{\sigma}$. The small displacements in the perfect lattice may be assumed to be produced by a set of small external forces $\vec{f}_i$. But we already know the effect on the entropy of such forces: It is given by Eq. (A9). But the derivative $\partial\langle \vec{\eta}_i \rangle/\partial T$, being taken at constant volume, is zero for all the ions in the bulk: The mean position of an ion in the bulk of a perfect crystal is independent of temperature at constant volume. It follows that the sum can be restricted to ions near the surface:

$$\Delta s'_{\rm fin} = \sum_i{}^{\sigma} \vec{f}_i \cdot \partial\langle \vec{\eta}_i \rangle/\partial T = \Delta s^{\sigma} \; ,$$

since the external forces necessary to maintain the distortion near the surface must be exactly the quantities $qq_i \vec{r}_i/r_i^3$ appearing in Δs^{σ}. This demonstrates the assertion.

In summary, we have shown that the entropy of formation $\overline{\Delta}s$ calculated in the body of the paper is equal to the entropy of formation at constant volume $\Delta s_{\rm fin}$ for a finite crystal with the omission of the contribution Δs^{σ} coming from the (real) surface. Note that there is no correction to compensate for the subtraction $\Delta s'$. Note also where the condition of constant volume enters: In the present scheme it enters in the discussion of $\Delta s'_{\rm fin}$, where it allows us to set $\partial\langle \vec{\eta}_i \rangle/\partial T = 0$ for the ions of the bulk.

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