

Einstein-Kanzaki model of static and dynamic lattice relaxation: Application to vacancies in metallic hydrogen[†]

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A method is proposed for calculating the formation energy of localized defects in crystalline solids with pair forces of arbitrary range. The theory is most useful in the cases of small mass or high temperature for which, in addition to the usual static relaxation, changes in the lattice vibrations make a significant contribution. Defect migration is not described however. A self-consistent Einstein approach is used, each particle in the crystal oscillating with its *own* frequency about an average position. The total free energy is minimized with respect to *all* of these frequencies and positions. This minimization is made tractable by the assumption that *large* changes in frequency and position occur only for a finite number of particles near the defect; the changes for all the other particles are treated linearly. The result is very similar to Kanzaki's \vec{k} -space "lattice statics" formalism. However, instead of being 3×3 the lattice Green's function becomes a 4×4 matrix, thereby encompassing changes in Einstein frequencies as well as particle positions. The method is applied to calculate the free energy of vacancy formation in metallic hydrogen.

I. INTRODUCTION

This paper describes a self-consistent Einstein method for calculating formation energies of localized¹ crystal defects within a k -space formalism. Changes in zero-point and/or thermal lattice vibrations are taken into account, together with static lattice relaxation. The analysis, however, is hardly more involved than that required to calculate the static relaxation alone by conventional Kanzaki² or Green's-function³ techniques. One therefore has the chance to handle quite complicated particle interactions. As an example, the case of a vacancy in metallic hydrogen will be computed using a screened proton-proton interaction which is long ranged and oscillatory. The technique is self-consistent and is expected to be valid well into the high-temperature or small-mass regimes where relaxation of lattice vibrations is important; this will be referred to as "dynamic relaxation."

To begin with, a brief account is given of some previous work relevant to this problem and necessary to place the present work in perspective.

A. Defects in "classical" crystals

These are crystals in which the thermal and/or zero-point particle vibrations are very small. An important phenomenon associated with such a classical defect is the static relaxation of the lattice to accommodate the defect. This affects every particle in the crystal; the displacements typically fall off only as the inverse square of the distance from the defect. Descriptions of this phenomenon based on the "linear lattice statics" method have been discussed by Tewary.³ In this method, one

derives a 3×3 matrix $\underline{G}(\vec{R})$ known as the "static lattice Green's function." [Its Fourier transform $G(\vec{q})$ for $\vec{q} \neq 0$ is essentially the inverse of the well-known dynamical matrix $D(\vec{q})$ which governs phonon motion.] The defect exerts a "Kanzaki force" $\vec{F}(\vec{R})$ on the lattice particles, and quantities such as the particle displacements and total strain field energy can be calculated by integrating combinations of $G(\vec{q})$ and $\vec{F}(\vec{q})$ with respect to wave number \vec{q} over a Brillouin zone. In the small \vec{q} limit, this theory reduces to the "elastic-continuum" model in which a handful of elastic constants completely specify the problem. The theory as described so far allows only for small relaxations of the lattice, but if one has very-short-ranged forces one can also treat large displacements of a few particles near the defect (as is done, for example, in the work of Benedek and Ho⁴). Here, it is desired to treat forces whose range may be many lattice spacings, so a modified version of Benedek and Ho's method will be given. (This appears to be a new departure, even in the context of "classical" crystals which are not, however, the main concern of this paper.)

A second interesting feature associated with localized defect formation is a change in the phonon spectrum. All modes are shifted slightly in frequency, and spatially localized modes may appear with frequencies discretely separated from the rest. Theories of these effects have been given by Maradudin and co-workers,⁵ and independently by Lifshitz and collaborators.⁶ At finite temperatures the change in phonon modes will contribute to the defect formation energy, but the effect is small for "classical" crystals (in the sense defined above.) In the "nonclassical" regime of higher temperatures, however, the phonon modes may be

strongly modified in a complicated fashion so that a self-consistent theory is needed. Aksenov⁷ has considered such a theory but omitted the static lattice relaxation around the defects; his method is therefore not suitable for examining defect formation energies, since relaxation may contribute a large fraction of the total formation energy.

B. Localized defects in quantum crystals

A quantum crystal⁸ is one in which particle masses and interparticle forces are small, so that large zero-point excursions occur. Static relaxation of average particle positions and modification of the particle motion are both important here. The latter effect is related to changes in the phonon spectrum caused by the presence of the defect. Caron⁹ has considered an average t -matrix approach for calculation of the phonon spectrum in the presence of such defects taken as randomly distributed; his method does not appear to include the static deformations so important in calculating the formation energy. In an earlier paper,¹⁰ Caron used an Einstein model in calculating defect formation energies in metallic hydrogen at $T=0$ °K. He treated the static relaxation of only a few particles near the defect and omitted the change in Einstein frequencies as negligible. A theory permitting a change in Einstein frequency for one shell of neighbors round a metallic defect was also reported recently.¹¹ The present work generalizes these ideas and permits relaxation of *all* positions and frequencies in a tractable formalism. More complex theories permitting such universal static and dynamic relaxation have been proposed by Varma¹² and Jacobi and Zmuidzinas¹³ in terms of self-consistent phonons.¹⁴ For quantum crystals the defect causes significant changes in all the phonon modes, making perturbation theory invalid. A fully self-consistent phonon scheme is, of course, very difficult to implement here, because the defect breaks the translational symmetry so that the spatial dependence of the phonon modes should be determined variationally along with the frequencies. Varma overcomes this problem by using a trial state in which the spatial variation of the phonon modes is obtained from a classical non self-consistent theory^{5,6}; only the *frequencies* are determined self-consistently. While this enormously simplifies the algebra, the method as it stands still requires iteration of some very complicated self-consistent equations, much more involved than the ones used for self-consistent phonons in a perfect crystal.¹⁴ In fact, Varma¹² resorted to a Debye approximation in order to obtain a practical computation procedure (Jacobi and Zmuidzinas did not indicate how one would actually solve their equa-

tions). Neither method appears to deal with the difficulty that the static relaxation of the average particle positions should be calculated *self-consistently* with the changes in vibrational motion; the static relaxation is simply added after the dynamic relaxation has already been given. The Einstein theory to be given here is quite explicit and tractable in both these respects, and has been applied to the vacancy problem in metallic hydrogen. For this case, one requires a complicated long-ranged oscillatory proton-proton interaction which would render the self-consistent phonon theories^{12,13} quite unworkable without further approximation.

C. Defect migration

For sufficiently high temperature or low mass, the defect can diffuse or tunnel from site to site. The tunneling at low temperature in a quantum crystal seems to have been proposed first by Hetherington.¹⁵ Such tunneling states or "defectons" have subsequently received some theoretical attention,¹⁶ though there does not seem to be any firm experimental evidence for them. Indeed, it appears that such tunneling phenomena will be important only for *highly* quantal crystals, if at all. Defecton motion was not considered in Refs. 7, 9, 10, 11, 12, or 13, nor will it be considered here (except briefly in Sec. VI). The diffusive migration of defects near the melting temperature is probably important, however, and although this phenomenon is not attacked directly here, some suggestions are made for use of the present work as *input* to a better calculation.

Set now in the context of previous work the paper is organized as follows: In Sec. II, the self-consistent Einstein picture is presented for $T=0$ °K, and its validity is discussed. In Sec. III, a generalized "lattice statics" is derived from the $T=0$ °K Einstein model. Relaxation of the zero-point motion around a defect is included on a par with static relaxation, by introducing a 4×4 "lattice Green's function" instead of the usual 3×3 one. In Sec. IV, the generalization to nonmigratory defects at $T \neq 0$ °K is shown to be almost trivial if one uses the Gibbs-Bogoliubov inequality. In Sec. V the method is applied to calculate the free energy of vacancy formation in fcc metallic hydrogen for $0.6 \leq r_s \leq 1.5$ and $0 \leq T < 5000$ °K. Sec. VI contains further discussion, while Sec. VII gives conclusions.

II. SELF-CONSISTENT EINSTEIN MODEL AT $T=0$ °K

The model is a very simple variational one, permitting a description of an imperfect quantum crystal at zero temperature. One minimizes the total energy over a trial N -particle crystal wave function Ψ of the Hartree type,

$$\Psi(\vec{r}_1, \dots, \vec{r}_N) = \phi_1(\vec{r}_1 - \vec{x}_1) \times \phi_2(\vec{r}_2 - \vec{x}_2) \cdots \phi_N(\vec{r}_N - \vec{x}_N). \quad (1)$$

Here $\vec{r}_1, \dots, \vec{r}_N$ are the particle coordinates, and $\vec{x}_1, \dots, \vec{x}_N$ are the *average* particle positions. For a crystal without defects, the $\{\vec{x}_i\}$ lie on a perfect lattice, while for a crystal with defects they lie on a distorted lattice exhibiting a strain field as discussed in Sec. I. The localized functions $\{\phi_i\}$ represent the zero-point motion of the particles about their average positions $\{\vec{x}_i\}$; in general there will be a different function ϕ_i for each site i , except in the case of a perfect monatomic crystal.

An obvious deficiency of the Einstein trial state (1) is that it fails to correlate the zero-point motion of particles on different sites. Correspondingly, it does not describe any properties relating to the long-wavelength phonon modes. However, these modes contribute least of all to the total energy, so (1) should be a reasonable ansatz for calculating the total energy of defect formation. Indeed, the total energy will be especially well given compared with other quantities, since it is precisely the one which is stationary in the best trial state. (This point has already been noted by Varma,¹² who was concerned with thermal conductivities and spin relaxation rates for which an Einstein theory is less likely to be accurate.) One would seem to be justified in using (1) to obtain the total energy in situations for which a more complicated theory would prove intractable.

For simplicity of exposition in this paper the Hamiltonian operator \hat{H} will be assumed to include only two-body forces

$$\hat{H} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2M_i} + \frac{1}{2} \sum_{i \neq j}^N V(\hat{r}_i - \hat{r}_j), \quad (2)$$

where \hat{r}_i and \hat{p}_i are position and momentum operators for the i th particle. For metals, it may be necessary to include effective volume-dependent and many-body forces acting between the ions whose coordinates appear explicitly in (2). The theory can be generalized in surprisingly compact form to include n -body forces; this work will be described shortly.¹⁷

The expectation value of the Hamiltonian (2) in the trial state (1) is

$$\begin{aligned} \langle \hat{H} \rangle &= \langle \hat{T} \rangle + \langle \hat{V} \rangle \\ &= \sum_{i=1}^N t_i + \frac{1}{2} \sum_{i \neq j}^N U\{\phi_i, \vec{x}_i; \phi_j, \vec{x}_j\}, \end{aligned} \quad (3)$$

where

$$t_i = \frac{\hbar^2}{2M_i} \int d^3x |\nabla \phi_i(\vec{x})|^2 \quad (4)$$

and

$$\begin{aligned} U\{\phi_1, \vec{x}_1; \phi_2, \vec{x}_2\} &= \int d^3y_1 d^3y_2 |\phi_1(\vec{y}_1)|^2 \\ &\quad \times |\phi_2(\vec{y}_2)|^2 V(\vec{x}_1 + \vec{y}_1 - \vec{x}_2 - \vec{y}_2). \end{aligned} \quad (5)$$

One can regard U as an effective "smeared" pair potential acting between point particles at \vec{x}_1 and \vec{x}_2 . If the $\{U\}$ do not fall off rapidly with particle separation $|\vec{x}_i - \vec{x}_j|$ it may be convenient to convert to a k -space representation. Defining Fourier-transformed pair potentials $V(\vec{k})$ and particle-density distributions f by the relations

$$V(\vec{r}) = \frac{1}{\Omega} \sum_{\vec{k}} V(\vec{k}) e^{i\vec{k} \cdot \vec{r}}, \quad (6)$$

and

$$|\phi_i(\vec{x})|^2 = \frac{1}{\Omega} \sum_{\vec{k}} f_i(\vec{k}) e^{i\vec{k} \cdot \vec{x}}, \quad (7)$$

one obtains from (5),

$$\begin{aligned} U\{\phi_i, \vec{x}_i; \phi_j, \vec{x}_j\} &= \frac{1}{\Omega} \sum_{\vec{k}} f_i(\vec{k}) f_j(\vec{k}) V(-\vec{k}) \\ &\quad \times e^{i\vec{k} \cdot (\vec{x}_j - \vec{x}_i)}. \end{aligned} \quad (8)$$

Here Ω is the volume and the sum $\sum_{\vec{k}}$ becomes an infinite integral $\Omega(2\pi)^{-3} \int d^3k$ in the thermodynamic limit.

For a *perfect monatomic crystal*, the local wave functions ϕ_i are all the same and the average positions \vec{x}_i are the perfect lattice sites \vec{R}_i . Thus, using the identity

$$\sum_{i=1}^N e^{-i\vec{k} \cdot \vec{R}_i} = N \delta_{\vec{k}, \vec{g}} S(\vec{g}), \quad (9)$$

one obtains from (8) the result for the total potential energy in (3),

$$\begin{aligned} \langle \hat{V} \rangle &= \frac{N}{2} \left(\frac{N}{\Omega} \sum_{\vec{g}} f^2(\vec{g}) V(\vec{g}) S(\vec{g}) \right. \\ &\quad \left. - \frac{1}{(2\pi)^3} \int d^3k f^2(\vec{k}) V(\vec{k}) \right). \end{aligned} \quad (10)$$

Here the $\{\vec{g}\}$ are the reciprocal-lattice vectors and $S(\vec{g})$ is the structure factor of the unit cell [$S(\vec{g}) = 1$ for primitive Bravais lattices].

So far nothing has been said about the form of the local functions $\phi_i(\vec{x})$. For classical solids (those with very little particle motion) a good choice for ϕ is a Gaussian. In fact, the standard Einstein model of a perfect crystal is obtained by choosing ϕ_i to be the (Gaussian) harmonic oscillator function which solves the one-particle Schrödinger equation in the spherically averaged harmonic potential set up at each site i by the other $(N-1)$ par-

ticles perfectly localized on their lattice sites. The present work is intended for *moderately* non-classical crystals for which a Gaussian should remain a reasonable trial function¹⁸; however, in contrast to the classical Einstein model described above, this will be a “*self-consistent*” harmonic Einstein model in which the total energy is minimized with respect to all the harmonic frequencies. The localized trial wave functions are then generalized Gaussians

$$\phi_i(\vec{y}) = \left(\frac{M_i}{\pi\hbar}\right)^{3/4} (\det \underline{\omega}_i)^{1/4} \exp\left(\frac{-M_i \vec{y} \cdot \underline{\omega}_i \cdot \vec{y}}{2\hbar}\right), \quad (11)$$

where M_i is the particle mass. If the 3×3 frequency matrix $\underline{\omega}_i$ is of the form

$$\underline{\omega}_i = \text{diag}(\omega_i, \omega_i, \omega_i), \quad (12)$$

then one has an isotropic Einstein trial state. For anisotropic crystals, it may be necessary to choose different frequencies for the zero-point motion along the three Cartesian axes, so that $\underline{\omega}_i$ is of the form

$$\underline{\omega}_i = \text{diag}(\omega_{i1}, \omega_{i2}, \omega_{i3}). \quad (13)$$

Regardless of crystal symmetry, it may be necessary, in the case of very strong lattice distortions, to allow some frequency matrices $\underline{\omega}$ to have principal axes in directions other than the Cartesian axes, and (11) is general enough to cover this case also.

The Fourier-transformed density corresponding to (11) is

$$f_i(\vec{k}) = \exp(-\frac{1}{2} \vec{k} \cdot \underline{\gamma}_i \cdot \vec{k}) \quad (14)$$

[see Eq. (7)]. Here,

$$\underline{\gamma}_i = (\hbar/2M_i) \underline{\omega}_i^{-1}, \quad (15)$$

and the trace of the matrix $\underline{\gamma}_i$ is the mean-square displacement of the i th particle about its average position \vec{x}_i . For much of the rest of this paper, $\underline{\gamma}$ will be used in place of $\underline{\omega}$ to specify the Einstein states.

III. GENERALIZED KANZAKI METHOD AT $T=0^\circ\text{K}$

In this section, a modified lattice “statics” is described which allows for changes in the zero-point motion as well as relaxation of particle positions. It is convenient to specify both the average position \vec{x}_j and mean-square Einstein amplitude matrix $\underline{\gamma}_j$ of the j th particle in terms of a single complex¹⁵ column vector \underline{X}_j , to be termed the “coordinate” of particle j . Symbolically,

$$\underline{X}_j = (\vec{x}_j, -\frac{1}{2} i \underline{\gamma}_j). \quad (16)$$

Thus, the first three components of \underline{X}_j are the Car-

tesian components of \vec{x}_j ,

$$X_{j\mu} = x_{j\mu} \quad (\mu = 1, 2, 3). \quad (17)$$

The remaining components of \underline{X}_j are chosen according to the degree of generality that has been built into the trial Einstein function. For example, if *isotropic* Einstein states are expected to give an adequate trial function then the mean-square amplitude matrix is specified by a single number γ_j , $\underline{\gamma}_j = \text{diag}(\gamma_j, \gamma_j, \gamma_j)$; thus, \underline{X}_j has dimension 4 with

$$X_{j4} = -\frac{1}{2} i \gamma_j. \quad (18)$$

On the other hand, for an anisotropic crystal one may need to have $\underline{\gamma}_j = \text{diag}(\gamma_{j1}, \gamma_{j2}, \gamma_{j3})$ in which case \underline{X}_j has dimension 6 with

$$X_{j4(5,6)} = -\frac{1}{2} i \gamma_{j1(2,3)}. \quad (19)$$

In the most general case, \underline{X}_j can be taken as a nine-component column with the last six components

$$\begin{aligned} X_{j4,5,6,7,8,9} = & -\frac{1}{2} i (\gamma_{j11}, \gamma_{j22}, \gamma_{j33}, \gamma_{j23} \\ & + \gamma_{j32}, \gamma_{j13} + \gamma_{j31}, \gamma_{j12} + \gamma_{j21}). \end{aligned} \quad (20)$$

The total energy can now be written

$$\begin{aligned} \langle \hat{H} \rangle = & E(\underline{X}_1, \dots, \underline{X}_N) \\ = & \sum_{i=1}^N \frac{\hbar^2}{8M_i} \text{Tr} \underline{\gamma}_i^{-1} + \frac{1}{2} \sum_{i \neq j}^N U(\underline{X}_i, \underline{X}_j), \end{aligned} \quad (21)$$

where the *smear*ed pair potential U can be found from (5) and (11) but is more compactly expressed in k space by using (8) with (14)

$$\begin{aligned} U(\underline{X}_i, \underline{X}_j) = & \frac{1}{(2\pi)^3} \int d^3k V(\vec{k}) \exp[-\frac{1}{2} \vec{k} \cdot (\underline{\gamma}_i + \underline{\gamma}_j) \cdot \vec{k} \\ & - i \vec{k} \cdot (\vec{x}_i - \vec{x}_j)] \\ = & \frac{1}{(2\pi)^3} \int d^3k V(\vec{k}) \exp[-i \underline{K} \cdot (\underline{X}_i - \underline{X}_j^*)]. \end{aligned} \quad (22)$$

Here a higher-dimensional wave number, symbolically

$$\underline{K} = (\vec{k}, \vec{k}\vec{k}) \quad (23)$$

has been introduced. To be specific, its components are

$$\underline{K} = (k_x, k_y, k_z, k^2)$$

or

$$\underline{K} = (k_x, k_y, k_z, k_x^2, k_y^2, k_z^2)$$

or

$$\underline{K} = (k_x, k_y, k_z, k_x^2, k_y^2, k_z^2, k_x k_y, k_y k_z, k_x k_z, k_x k_x, k_y k_y, k_z k_z), \quad (24)$$

in the three cases previously outlined in defining \underline{X} . (A caution: $\vec{k} = \vec{k}_1 + \vec{k}_2$ does not imply $\underline{K} = \underline{K}_1 + \underline{K}_2$).

The essence of the proposed method is that in an inhomogeneous situation one can *explicitly* minimize the energy (21) with respect to *all* the particle "coordinates" $\{X_i\}$, provided that the deviations from the perfect-crystal "coordinates" $X_i^0 = (\vec{R}_i, -\frac{1}{2}i\gamma_0)$ can be treated linearly *except* at a finite number of sites. These few nonlinear sites near the defect constitute the "core" (c) of the defect; the remaining sites will be termed the "bulk" sites. The calculation proceeds in several steps:

(a) The Einstein frequency $\omega_0 = \hbar\gamma_0^{-1}/2M$ is found which minimizes the energy for a perfect crystal.

(b) The core sites are assigned "coordinates" $\{X_i; i \in c\}$, which are later treated as explicit variational parameters. The energy cost of creating the core is computed with the bulk "coordinates" $\{X_i; i \notin c\}$ held at the perfect crystal values $\{X_i^0\}$.

(c) The bulk "coordinates" are given linear increments $X_i \rightarrow X_i^0 + \xi_i$, $i \in c$; the ξ_i are chosen to minimize the total energy subject to the given core "coordinates." This minimization is achieved explicitly in \vec{k} space by a generalization of the Green's-function method of lattice statics³: changes in the zero-point motion are computed self-consistently with static relaxation, by making the lattice Green's function a 4×4 (or 6×6 , or 9×9) matrix instead of a 3×3 one as in conventional lattice statics.^{2,3}

(d) The relaxed crystal energy is now known as a function of the core "coordinates." Finally, these core "coordinates" are chosen to give an overall minimum energy.

These four steps will now be discussed in detail.

Step (a): The perfect crystal

In the perfect crystal all sites have the same Einstein oscillator width γ_0 , and the particle coordinates are

$$X_j^0 = (\vec{R}_j, -\frac{1}{2}i\gamma_0). \quad (25)$$

Using (21), (22), and (25) and defining an equilibrium form U^0 of the smeared potential,

$$U^0(\vec{R}) = U(X_0, X_1), \quad (26)$$

with $X_0 = (\vec{O}, -\frac{1}{2}i\gamma_0)$ and $X_1 = (\vec{R}, -\frac{1}{2}i\gamma_0)$, one obtains the total energy per particle as a sum over direct lattice vectors \vec{R} ,

$$\begin{aligned} E^{(0)}(\gamma_0) &= \frac{E(X_1^0, \dots, X_N^0)}{N} \\ &= \frac{\hbar^2}{8M} \text{Tr}(\gamma_0^{-1}) + \frac{1}{2} \sum_{\vec{R} \neq 0} U^0(\vec{R}). \end{aligned} \quad (27)$$

With the aid of (9) this can also be expressed in reciprocal space

$$\begin{aligned} E^{(0)}(\gamma_0) &= \frac{\hbar^2}{8M} \text{Tr}(\gamma_0^{-1}) + \frac{1}{2} \left[\frac{N}{\Omega} \sum_{\vec{g}} S(\vec{g}) U^0(\vec{g}) \right. \\ &\quad \left. - (2\pi)^{-3} \int d^3k U^0(\vec{k}) \right]. \end{aligned} \quad (28)$$

Here $U^0(\vec{k})$ is the Fourier transform of the smeared equilibrium pair potential,

$$U^0(\vec{k}) = V(\vec{k}) \exp(-\vec{k} \cdot \gamma_0 \cdot \vec{k}). \quad (29)$$

This step of the calculation is completed by choosing γ_0 to minimize (27) or (28), whichever is more convenient.

Step (b): Formation of the core

The details of this step depend on the type of local defect being considered. In the case of vacancy or interstitial formation at constant²⁰ particle number N , a particle presumably has to be transferred to or from the surface. To begin with, this process will be considered without any relaxation of the coordinates X_i of the other $(N-1)$ particles. There appears to be some ambiguity concerning the energy involved in this process, and it has been the subject of some dispute.²¹ This controversy will not be entered into here, since it arises in any calculation involving vacancies or interstitials, and has nothing specifically to do with the new features of the model under consideration. For definiteness, the results of Caron¹⁰ for vacancy and interstitial formation without relaxation will be adopted; they have the advantage of being calculated in the framework of the Einstein model and so are compatible with the present work. The constant-volume method will be adopted. It is certainly more convenient in the case of metals, since the "volume-dependent forces" are not brought into play; at any rate, Caron¹⁰ has shown that the overall results at constant pressure must be the same. For reference, his result for vacancies will be quoted in the notation of the present work

$$\Delta E_{0(\text{vacancy})} = -\frac{1}{2} \sum_{\vec{R} \neq 0} \left(\frac{1}{3} \vec{R} \cdot \frac{\partial U^0(\vec{R})}{\partial \vec{R}} + U^0(\vec{R}) \right), \quad (30)$$

in the same notation as (27), where the two terms come from compression of the lattice at constant volume to create new sites, followed by removal of particles from those sites. This result can also be expressed in k space after an integration by parts

$$\begin{aligned} \Delta E_{0(\text{vacancy})} &= \frac{1}{6} \frac{N}{\Omega} \sum_{\vec{g}} S(\vec{g}) \vec{g} \cdot \frac{dU^0(\vec{g})}{d\vec{g}} \\ &\quad + \frac{1}{2(2\pi)^3} \int d^3k U^0(\vec{k}). \end{aligned} \quad (31)$$

The considerations given so far in this step were

special to vacancies and interstitials whose formation involved transfer of a particle to or from the surface. The second half of the present step involves a deformation of the core region ($\underline{X}_i^0 \rightarrow \underline{X}_i$,

$i \in c$); this applies equally to all kinds of local defects including for example mass defects and vacancy interstitial pairs²² as well as the above types considered. The core deformation costs an energy

$$\Delta E_{\text{core}} = \sum_{i \in c} \frac{\hbar^2}{8M_i} \text{Tr}(\underline{\gamma}_i^{-1} - \underline{\gamma}_0^{-1}) + \sum_{i \in c; j \in c} [U(\underline{X}_i, \underline{X}_j^0) - U(\underline{X}_i^0, \underline{X}_j^0)] + \frac{1}{2} \sum_{i \neq j \in c} [U(\underline{X}_i, \underline{X}_j) - U(\underline{X}_i^0, \underline{X}_j^0)], \quad (32)$$

with U given by (22). The second sum in (32) is an unrestricted sum on j over the direct lattice, with the core sites excluded. With the aid of (9), it can be reduced to a finite direct lattice sum, plus a reciprocal-lattice sum:

$$\begin{aligned} \sum_{i \in c; j \in c} [U(\underline{X}_i, \underline{X}_j^0) - U(\underline{X}_i^0, \underline{X}_j^0)] = & - \sum_{i \in c; j \in c^*} [U(\underline{X}_i, \underline{X}_j^0) - U(\underline{X}_i^0, \underline{X}_j^0)] \\ & + \frac{N}{\Omega} \sum_{i \in c} \sum_{\vec{g}} S(\vec{g}) V(\vec{g}) [\exp(-\frac{1}{2} \vec{g} \cdot (\underline{\gamma}_0 + \underline{\gamma}_i) \cdot \vec{g} - i\vec{g} \cdot \underline{x}_i) - \exp(-\vec{g} \cdot \underline{\gamma}_0 \cdot \vec{g} - i\vec{g} \cdot \vec{R}_i)]. \end{aligned} \quad (33)$$

(Here the perfect lattice sites in the core are denoted c^* .)

Step (c): Linear relaxation including zero-point motion

The major results of the present work are contained in this step. The bulk particles are now taken to undergo small "coordinate" changes

$$\underline{\xi}_i = \underline{X}_i - \underline{X}_i^0. \quad (34)$$

The first three components of $\underline{\xi}_i$ give the deviations of the average positions $\bar{\underline{x}}_i$ from the perfect lattice sites \vec{R}_i (i.e., they specify the conventional strain field) while the higher components $\{\xi_{i\mu}, \mu > 3\}$ measure the changes in the mean-square displacements $\underline{\gamma}_i$ around the average positions.

If the defect were not present, the energy required to produce the bulk distortions $\{\underline{\xi}_i, i \in c\}$ could be expanded to second order in the $\{\underline{\xi}_i\}$:

$$\Delta E_{\{\underline{\xi}_i\}}^{(\text{no defect})} = \frac{1}{2} \sum_{\mu, \nu=1}^4 \sum_{i, j \in c} D_{\mu\nu}(\vec{R}_i - \vec{R}_j) \times \xi_{i\mu} \xi_{j\nu} + O(\xi^3). \quad (35)$$

(Summation on μ and ν will henceforth be implicit for repeated indices.) In (35), D is the Taylor-series expansion coefficient

$$D_{\mu\nu}(\vec{R}_i - \vec{R}_j) = \left. \frac{\partial^2 E(\underline{X}_1, \dots, \underline{X}_N)}{\partial X_{i\mu} \partial X_{j\nu}} \right|_0. \quad (36)$$

The energy $E(\underline{X}_1, \dots, \underline{X}_N)$ is defined in (21) and the subscript 0 means that the \underline{X}_i are set to the perfect lattice values $\underline{X}_i^0 = (\vec{R}_i, -\frac{1}{2}i\underline{\gamma}_0)$ after differentiation. No linear term is present in (35) since

$$\left. \frac{\partial E(\underline{X}_1, \dots, \underline{X}_N)}{\partial X_{i\mu}} \right|_0 = 0. \quad (37)$$

For $\mu = 1, 2, 3$, (37) is just the statement that the perfect crystal is in equilibrium under the pair forces at the chosen volume or pressure; this is automatic for systems with inversion symmetry. For $\mu > 3$, (37) is not automatic but is satisfied because $\underline{\gamma}_0$ has been chosen in step (a) to guarantee precisely this stationarity of the energy.

The zone Fourier transform of (36) is defined by the direct lattice sum

$$D_{\mu\nu}(\vec{q}) = \sum_{\vec{R}} D_{\mu\nu}(\vec{R}) e^{-i\vec{q} \cdot \vec{R}}, \quad (38)$$

with inversion formula

$$D_{\mu\nu}(\vec{R}) = \frac{1}{N} \sum_{\vec{q} \in Z} D_{\mu\nu}(\vec{q}) e^{i\vec{q} \cdot \vec{R}}, \quad (39)$$

where Z is the Brillouin zone. The matrix $D_{\mu\nu}(\vec{q})$ is a 4×4 (or 6×6 , or 9×9) generalization of the ordinary 3×3 dynamical matrix which appears in the classic theories of lattice statics and dynamics.^{3,5,6} The upper 3×3 block of D is just the ordinary dynamical matrix evaluated using the "smeared" particle interaction U^0 [Eq. (26) or (29)] in place of the pair potential V [Eq. (2) or (6)]. The remaining components of D (those with $\mu > 3$ or $\nu > 3$) have no counterpart in the classic theory: they express the response of the Einstein zero-point motion to disturbances in the crystal.²³

Explicit expressions for the generalized dynamical matrix can be obtained by application of the definition (36) and direct differentiation of the energy formula (21). For simplicity only the isotropic case will be written, so that \underline{D} is 4×4 and $\underline{\gamma}_0 = \text{diag}(\gamma_0, \gamma_0, \gamma_0)$. The result can be written in terms of direct lattice sums on the smeared potential U^0 of Eq. (26),

$$D_{\mu\nu}(\vec{q}) = \sum_{\vec{R} \neq 0} (1 - e^{-i\vec{q} \cdot \vec{R}}) \frac{\partial^2}{\partial R_\mu \partial R_\nu} U^0(\vec{R}) \quad (\mu, \nu \leq 3),$$

$$\begin{aligned} D_{\mu 4}(\vec{q}) &= D_{4\mu}(\vec{q}) \\ &= -2i \sum_{\vec{R} \neq 0} e^{-i\vec{q} \cdot \vec{R}} \frac{\partial^2}{\partial R_\mu \partial \gamma_0} U^0(\vec{R}) \quad (\mu \leq 3) \end{aligned} \quad (40)$$

and

$$D_{44}(\vec{q}) = 4 \sum_{\vec{R} \neq 0} (1 + e^{-i\vec{q} \cdot \vec{R}}) \frac{\partial^2}{\partial \gamma_0^2} U^0(\vec{R}) + \frac{3\hbar^2}{M\gamma_0^3}.$$

With the aid of Eq. (9), these results can also be written in k space, with μ, ν running from 1 to 3,

$$\begin{aligned} D_{\mu\nu}(\vec{q}) &= \frac{N}{\Omega} \sum_{\vec{g}} S(\vec{g}) [(\vec{g} + \vec{q})_\mu (\vec{g} + \vec{q})_\nu U^0(\vec{g} + \vec{q}) \\ &\quad - g_\mu g_\nu U^0(\vec{g})], \\ D_{\mu 4}(\vec{q}) &= D_{4\mu}(\vec{q}) = \frac{N}{\Omega} \sum_{\vec{g}} S(\vec{g}) (\vec{g} + \vec{q})^2 \\ &\quad \times (\vec{g} + \vec{q})_\mu U^0(\vec{g} + \vec{q}), \\ D_{44}(\vec{q}) &= \frac{3\hbar^2}{M\gamma_0^3} + \frac{N}{\Omega} \sum_{\vec{g}} S(\vec{g}) [|\vec{g} + \vec{q}|^4 U^0(\vec{g} + \vec{q}) + g^4 U^0(\vec{g})] \\ &\quad - 2(2\pi)^{-3} \int d^3k k^4 U^0(\vec{k}). \end{aligned} \quad (41)$$

The last expression exhibits $\underline{D}(\vec{q})$ as a real symmetric matrix.

Equation (35) was derived for small distortions in the bulk of an otherwise perfect crystal. In the presence of a defect core, these bulk distortions will cost an extra energy

$$- \sum_{i=1}^N F_\mu(\vec{R}_i) \xi_{i\mu}^* + O(\xi^2), \quad (42)$$

where the "generalized Kanzaki force" F_μ is given for $i \in c$ by

$$\begin{aligned} F_\mu(\vec{q}) &= \sum_{\vec{R}_i} F_\mu(\vec{R}_i) e^{-i\vec{q} \cdot \vec{R}_i} = \frac{N}{\Omega} \sum_{\vec{g}} iQ_\mu S(\vec{g}) V(\vec{g} + \vec{q}) \left[\sum_{j \in c^*} \exp(-i\vec{Q} \cdot \underline{X}_j') - \sum_{j \in c} \exp(-i\vec{Q} \cdot \underline{X}_j'') \right] \\ &\quad + \sum_{i \in c^*} \left(\sum_{j \in c} \frac{\partial U(\underline{X}_i^0, \underline{X}_j)}{\partial X_{i\mu}^0} - \sum_{j \in c^*} \frac{\partial U(\underline{X}_i^0, \underline{X}_j^0)}{\partial X_{i\mu}^0} \right) e^{-i\vec{q} \cdot \vec{R}_i}. \end{aligned} \quad (49)$$

[The four-columns $\underline{Q} = (\vec{g} + \vec{q}, (\vec{g} + \vec{q})^2)$, $\underline{X}_j' = (\vec{R}_j, -i\gamma_0)$, and $\underline{X}_j'' = (\vec{x}_j, -\frac{1}{2}i(\gamma_0 + \gamma_j))$ are introduced for brevity.]

It remains to find the bulk distortions $\{\xi_{ij}\}$, which are the solutions of (46). If it were not for the restriction $j \in c$ on the left-hand side, Eq. (46) would be solved trivially by Fourier transformation. Although the translational invariance is spoiled by this restriction, an exact k -space solution is still

$$\begin{aligned} F_\mu(\vec{R}_i) &= - \sum_{j \in c} \frac{\partial U(\underline{X}_j, \underline{X}_i)}{\partial X_{i\mu}^*} \Big|_{\underline{X}_i = \underline{X}_i^0} \\ &\quad + \sum_{j \in c^*} \frac{\partial U(\underline{X}_j^0, \underline{X}_i)}{\partial X_{i\mu}^*} \Big|_{\underline{X}_i = \underline{X}_i^0}, \end{aligned} \quad (43)$$

while

$$F_\mu(\vec{R}_i) = 0 \text{ for } i \in c^*. \quad (44)$$

(c^* again refers to the perfect lattice sites inside the core region: for a vacancy, c^* has one more site than c .) The neglect of terms higher than the first order in (42) is a standard approximation of lattice statics known as the "first Kanzaki approximation."² The total energy associated with the bulk distortions $\{\xi_i; i \in c\}$ is now

$$\frac{1}{2} \sum_{i, j \in c} D_{\mu\nu}(\vec{R}_i - \vec{R}_j) \xi_{i\mu} \xi_{j\nu}^* - \sum_{i \in c} F_\mu(\vec{R}_i) \xi_{i\mu}^*. \quad (45)$$

This is minimized when the $\{\xi_i\}$ satisfy

$$\sum_{j \in c} D_{\mu\nu}(\vec{R}_i - \vec{R}_j) \xi_{j\nu} = F_\mu(\vec{R}_i), \quad i \in c. \quad (46)$$

If the $\{\xi_i\}$ satisfy (46) then (45) can be simplified to give the minimum energy

$$\Delta E_{\text{bulk}} = -\frac{1}{2} \sum_i F_\mu(\vec{R}_i) \xi_{i\mu}^* = -\frac{1}{2} \sum_i F_\mu^*(\vec{R}_i) \xi_{i\mu}. \quad (47)$$

The restriction $i \in c$ has been dropped in the sum (47) since F_μ is defined in (44) to be zero for $i \in c^*$. This is very convenient since (47) can now be directly transcribed into k space as

$$\Delta E_{\text{bulk}} = -\frac{1}{2N} \sum_{\vec{q} \in Z} F_\mu(\vec{q}) \xi_\mu^*(\vec{q}). \quad (48)$$

The Fourier-transformed Kanzaki force is obtained from (43) and (44) with the help of (9) and (22);

possible at expense of solving a small matrix (of order $4n$, where n is the number of sites in the core). If the pair forces determining $\underline{D}(\vec{R})$ are very short-ranged the solution of (46) can be performed by the matrix partitioning method of Benedek and Ho.⁴ An alternative approach is given here, since the assumption of short-ranged forces is *not* being made.

The solution proceeds by first augmenting (46)

with a set of equations on the core sites

$$\sum_{j \in c} D_{\mu\nu}(\vec{R}_i - \vec{R}_j) \xi_{j\nu} = f_\mu(\vec{R}_i), \quad i \in c^*, \quad (50)$$

where f_μ is to be determined. Equations (46) and (50) can next be combined to give a single equation on the entire perfect lattice

$$\sum_{\text{all } j} D_{\mu\nu}(\vec{R}_i - \vec{R}_j) \Xi_{j\nu} = \mathfrak{F}_\mu(\vec{R}_i) \quad (\text{all } i), \quad (51)$$

where

$$\Xi_{j\nu} = \begin{cases} 0, & j \in c^*, \\ \xi_{j\nu}, & j \in c \end{cases}$$

and

$$\mathfrak{F}_\mu(\vec{R}_i) = \begin{cases} f_\mu(\vec{R}_i), & i \in c^*, \\ F_\mu(\vec{R}_i), & i \in c. \end{cases} \quad (52)$$

Since (51) has a translationally invariant kernel and is valid on all sites, its solution (with periodic boundary conditions) is trivial in k space;

$$\Xi_\mu(\vec{k}) = D_{\mu\nu}^{-1}(\vec{k}) \mathfrak{F}_\nu(\vec{k}) \quad (\vec{k} \neq 0), \quad (53)$$

where D^{-1} means the 4×4 reciprocal matrix. If one defines the *generalized lattice Green's function* G by

$$G_{\mu\nu}(\vec{R}) = \frac{1}{N} \sum_{\vec{k} \in Z} D_{\mu\nu}^{-1}(\vec{k}) e^{i\vec{k} \cdot \vec{R}}, \quad (54)$$

then (53) becomes, in real space,

$$\Xi_\mu(\vec{R}_i) = \sum_{\text{all } j} G_{\mu\nu}(\vec{R}_i - \vec{R}_j) \mathfrak{F}_\nu(\vec{R}_j). \quad (55)$$

This is more conveniently represented in a $4N \times 4N$ matrix notation as

$$\begin{pmatrix} 0 \\ \underline{\xi} \end{pmatrix} = \underline{G} \begin{pmatrix} \underline{f}_1 \\ \underline{F}_2 \end{pmatrix} = \begin{pmatrix} \underline{g}_{11} & \underline{g}_{12} \\ \underline{g}_{21} & \underline{g}_{22} \end{pmatrix} \begin{pmatrix} \underline{f}_1 \\ \underline{F}_2 \end{pmatrix}, \quad (56)$$

where the matrices have been partitioned so that, for example, \underline{g}_{11} is a $4n \times 4n$ submatrix; it is the restriction of G to the core sites, $i \in c^*$. Expansion of the matrix product in (56) gives two equations, the first of which, namely

$$0 = \underline{g}_{11} \underline{f}_1 + \underline{g}_{12} \underline{F}_2,$$

gives the unknown "force" \underline{f}_1 ,

$$\underline{f}_1 = -\underline{g}_{11}^{-1} \underline{g}_{12} \underline{F}_2.$$

The second part of (56) now gives the desired solution

$$\underline{\xi} = \underline{g}_{21} \underline{f}_1 + \underline{g}_{22} \underline{F}_2 = (-\underline{g}_{21} \underline{g}_{11}^{-1} \underline{g}_{12} + \underline{g}_{22}) \underline{F}_2. \quad (57)$$

The energy associated with the linear relaxation of all the "bulk" particles is now found by putting

(57) into (47):

$$\Delta E_{\text{bulk}} = -\frac{1}{2} \underline{F}_2^* (\underline{g}_{22} - \underline{g}_{21} \underline{g}_{11}^{-1} \underline{g}_{12}) \underline{F}_2. \quad (58)$$

Noting from (44) that $F_\mu(\vec{R}_i)$ vanishes for $i \in c^*$ [and that the Fourier transform $F_\mu(\vec{k})$, Eq. (49), is computed with this in mind] one can extend (58) to a full matrix equation on the whole space

$$\Delta E_{\text{bulk}} = -\frac{1}{2} \underline{F}^* (\underline{G} - \underline{G} \underline{g}^{-1} \underline{G}) \underline{F}, \quad (59)$$

where

$$\underline{g} = \begin{pmatrix} \underline{g}_{11} & 0 \\ 0 & 0 \end{pmatrix}$$

and

$$\underline{F} = \begin{pmatrix} 0 \\ \underline{F}_2 \end{pmatrix}.$$

This can be transcribed into k space as

$$\Delta E_{\text{bulk}} = -\frac{1}{2} \left(\frac{1}{N} \sum_{\vec{k} \in Z} F_\mu^*(\vec{k}) D_{\mu\nu}^{-1}(\vec{k}) F_\nu(\vec{k}) - \sum_{i \in c^*} f_\mu^0(\vec{R}_i) \underline{\xi}_\mu^0(\vec{R}_i) \right), \quad (60)$$

where

$$\xi_\mu^0(\vec{R}_i) = \frac{1}{N} \sum_{\vec{k} \in Z} e^{-i\vec{k} \cdot \vec{R}_i} D_{\mu\nu}^{-1}(\vec{k}) F_\nu(\vec{k}),$$

and f^0 is the solution of a small equation

$$\sum_{j \in c^*} G_{\mu\nu}(\vec{R}_i - \vec{R}_j) f_\nu^0(\vec{R}_j) = \xi_\mu^0(\vec{R}_i) \quad \text{for } i \in c^*. \quad (61)$$

Equations (59) or (60) completely solve the problem of minimizing the bulk distortion energy (45). To evaluate (59) or (60), one need only compute the generalized dynamical matrix $D[k]$ from (40) or (41), the Green's function $G(\vec{R})$ from (54), and the Kanzaki force F_μ from (43) or (49). Then the problem reduces to solution of the small matrix equation (61), equivalent to finding \underline{g}^{-1} . In practice, this solution is often dramatically simplified by point symmetry at the defect site.

The solution (60) becomes especially simple in the case of *completely linear* vacancy relaxation. Here the strongly distorted core c is a null set, so that $\Delta E_{\text{core}} = 0$, while (in the case of a vacancy) c^* consists of the single site from which a particle is missing. This site can be taken as the origin. It is evident from symmetry that the on-site generalized Green's function $G_{4\nu}(\vec{0})$ is zero when $\nu = 1, 2, 3$; this can be verified formally by inspection of (54) and (41). Further, the first three components of the distortion vector $\xi^0(\vec{0})$ also vanish because of point symmetry at the defect site. Hence, from (61), $f_\mu^0(\vec{0}) = 0$ except for $\mu = 4$. Specifically,

$$f_{\mu}^0(\vec{O}) = \begin{cases} \xi_4^0(\vec{O})/G_{44}(\vec{O}), & \mu = 4, \\ 0, & \mu = 1, 2, 3. \end{cases} \quad (62)$$

The expression for the Kanzaki force F_{μ} can also be simplified when there is no strongly distorted core. Equations (43) and (49) become

$$F_{\mu}(\vec{R}_i) = \begin{cases} \left. \frac{\partial U(X_0^0, X_i)}{\partial X_{i\mu}^0} \right|_{X_i = \vec{X}_i^0}, & \vec{R}_i \neq \vec{O}, \\ 0, & \vec{R}_i = \vec{O} \end{cases} \quad (63)$$

and

$$F_{\mu}(\vec{q}) = \frac{N}{\Omega} \sum_{\vec{g}} iQ_{\mu} S(\vec{g}) U^0(\vec{g} + \vec{q}) - \frac{i\delta_{\mu 4}}{(2\pi)^3} \int d^3k k^2 U^0(\vec{k}), \quad (64)$$

with Q_{μ} defined as in (49).

Now, noting that the operation $(1/N) \sum_{\vec{k} \in Z}$ is just the Brillouin-zone average $\langle \rangle_{\text{BZ}}$, we reduce (60) to the form

$$\Delta E_{\text{bulk}} = -\frac{1}{2} \left(\langle F_{\mu}^*(\vec{k}) \xi_{\mu}^0(\vec{k}) \rangle_{\text{BZ}} - \frac{\langle \xi_4^0(\vec{k}) \rangle_{\text{BZ}}^2}{\langle (D^{-1})_{44}(\vec{k}) \rangle_{\text{BZ}}} \right), \quad (65)$$

with

$$\xi^0(\vec{k}) = D^{-1}(\vec{k}) F(\vec{k}). \quad (66)$$

Equation (65) is now the total distortion energy including changes in vibrational energy. Only the undistorted formation energy (30) or (31) need be added to obtain the total vacancy formation energy in this fully linear approximation.

It is also worth noting that in the absence of any relaxation of the Einstein frequencies one would have the usual 3×3 lattice statics formalism. The result for the linear distortion energy would then be

$$\Delta E_{\text{bulk}}^{(3)} = -\frac{1}{2} \langle F_{\alpha}(\vec{k}) (D^{(3)})_{\alpha\beta}(\vec{k}) F_{\beta}(\vec{k}) \rangle_{\text{BZ}}, \quad (67)$$

where α and β are summed from 1 to 3 and $D^{(3)}$ is the usual 3×3 dynamical matrix evaluated with the smeared pair potential U^0 . [$D^{(3)}$ is the upper 3×3 block of the 4×4 dynamical matrix D defined in (40) or (41).]

Step (d): Final minimization

The total energy required to form the defect with a core configuration $\{\vec{X}_i; i \in c\}$ is

$$\Delta E(\{\vec{X}_i; i \in c\}) = \Delta E_0 + \Delta E_{\text{core}} + \Delta E_{\text{bulk}}, \quad (68)$$

where the individual terms are given by (30) and (31) (for the case of a vacancy²⁴), (32)–(33), and (59)–(60). If ΔE_{bulk} is a substantial fraction of the formation energy (which it can be even though the bulk distortions ξ_i were treated linearly) then it

will be necessary to treat ΔE_{core} and ΔE_{bulk} together when searching for the optimal core “coordinates” $\{\vec{X}_i; i \in c\}$. On the other hand, if ΔE_{bulk} is formally regarded as a small quantity then only ΔE_{core} need be varied explicitly, and ΔE_{bulk} can be evaluated afterwards using the core coordinates \vec{X}_i so determined; changes caused by varying the two together are formally of second order. Whether or not the full procedure is necessary can only be decided in specific cases, according to the accuracy required.

In either case, the appropriately computed minimum of (68) is the final answer for the defect formation energy at $T=0$ °K within the Einstein-Kanzaki model.

IV. EXTENSION TO FINITE TEMPERATURE

If the migration of defects between lattice sites is ignored, the generalization of Sec. III to $T \neq 0$ °K is straightforward. The procedure is essentially to minimize the free energy F over an Einstein trial state. This imprecise notion can be formalized by using the Gibbs-Bogoliubov inequality²⁵

$$F \leq F_{\text{trial}} = F^0 + \langle \hat{H} - \hat{H}_0 \rangle_0. \quad (69)$$

Here \hat{H} is the actual Hamiltonian [i.e., (2)], \hat{H}_0 is an exactly soluble trial Hamiltonian, and $\langle \rangle_0$ is an exact quantum thermal average over \hat{H}_0 . In (69), F^0 is the exact free energy for H_0 .

The trial Hamiltonian appropriate to an Einstein picture is

$$\hat{H}_0(\hat{r}_1, \dots, \hat{r}_N) = \sum_{i=1}^N \frac{1}{2} M_i (\hat{r}_i - \vec{x}_i) \cdot \underline{\omega}_i^2 \cdot (\hat{r}_i - \vec{x}_i) + \sum_{i=1}^N \frac{\hat{p}_i^2}{2M_i} = \hat{V}_0 + \hat{T}. \quad (70)$$

Here, as in Sec. III, the variational parameters $\{\vec{x}_i\}$ and $\underline{\omega}_i$ are average particle positions and Einstein frequency matrices. The idea is to choose these parameters to minimize F_{trial} .

Since the kinetic energy term is common to \hat{H} and \hat{H}_0 , (69) can be rewritten

$$F \leq F_{\text{trial}} = F^0 - \langle \hat{V}_0 \rangle_0 + \langle \hat{V} \rangle_0 \quad (71)$$

The terms of (71) can be evaluated explicitly by using standard harmonic-oscillator results.²⁶ As before it is convenient to define a “coordinate” $\underline{\chi}_i = (\vec{x}_i, -\frac{1}{2} i \underline{\gamma}_i)$ where the mean-square excursion matrix $\underline{\gamma}$ is now evaluated at finite temperature:

$$\underline{\gamma}_i = \langle (\hat{r}_i - \vec{x}_i)(\hat{r}_i - \vec{x}_i) \rangle_T = \frac{\hbar}{2M_i} \underline{\omega}_i^{-1} \coth\left(\frac{\hbar}{2k_B T} \underline{\omega}_i\right). \quad (72)$$

The trial free energy is

$$F_{\text{trial}}(\underline{X}_1, \dots, \underline{X}_N) = \sum_{i=1}^N \text{Tr} \left\{ k_B T \ln \left[2 \sinh \left(\frac{\hbar}{2k_B T} \underline{\omega}_i \right) \right] - \frac{1}{4} \hbar \underline{\omega}_i \coth \left(\frac{\hbar}{2k_B T} \underline{\omega}_i \right) \right\} + \frac{1}{2} \sum_{i \neq j}^N U(\underline{X}_i, \underline{X}_j), \quad (73)$$

with $U(\underline{X}_i, \underline{X}_j)$ defined, in terms of the $\{\underline{y}_i\}$ and $\{\underline{x}_i\}$, by (22). Equation (73) is typical of the way in which the theory generalizes to finite temperature. The potential energy terms U depend only on the probability distribution of an Einstein particle, and hence have the same dependence on mean-square displacement \underline{y} as the corresponding $T=0$ °K terms. [Note, however that \underline{y} is now related to the frequency $\underline{\omega}$ by (72)]. On the other hand, the kinetic energy terms *do* change when one goes to finite temperature, as summarized in Table I. The quantity t appearing in the last column of the table is the "kinetic" energy (free energy minus potential energy) of an Einstein oscillator, and is given by

$$t(\underline{\omega}) = k_B T \text{Tr} \left[\ln(2 \sinh \underline{y}) - \frac{\hbar}{2} \underline{y} \coth \underline{y} \right], \quad (74)$$

with

$$\underline{y} = (\hbar/2k_B T) \underline{\omega}. \quad (75)$$

V. EXAMPLE: VACANCY IN METALLIC HYDROGEN

As an example of the method developed in Secs. I-IV, the free energy of vacancy formation in fcc metallic hydrogen will now be calculated. The problem is of interest because of the possible role of localized defects in the decay of metastable metallic hydrogen. This system may exhibit high-temperature superconductivity²⁷ (or other forms or electronic or nuclear order) and also has astrophysical significance.²⁸

Although pressures in excess of a megabar are

apparently required to form the metal,²⁹ it has been conjectured that it may be metastable relative to the molecular phase when the pressure is decreased to more easily maintained values, perhaps on the order of tens of kilobars or less. Surface decay of the metal³⁰ can probably be controlled by a suitable coating, and in the absence of unstable phonon modes down to moderate pressures³¹ it appears that the principal decay modes will involve some kind of crystal defect. A likely decay mode is the formation of hydrogen atoms or molecules inside voids or aggregates of vacancies. The prototype of this configuration is the monovacancy, which will be studied here. If this can be understood properly, one can hope to proceed to more complicated defects. A very low or negative vacancy formation energy would be suggestive of an instability; it will be shown here that no such instability towards monovacancies occurs in low-temperature fcc metallic hydrogen.

The zero-temperature vacancy formation energy in fcc metallic hydrogen has already been estimated by Caron,¹⁰ who used an Einstein model for the proton zero-point motion. As noted above he permitted relaxation of the positions of a few protons near the vacancy, but took as negligible any changes in the zero-point motion during defect formation. However, Straus and Ashcroft³¹ recently showed that the proton zero-point motion is crucial in determining the structure of a perfect crystal of metallic hydrogen. One might therefore suspect that changes in the zero-point motion, not necessarily localized near the defect, would be important in the vacancy formation process.

The motivation for the present calculation, then is twofold: (a) one would like to know if there are any slight but poorly localized changes in zero-point motion which might significantly affect the free energy of formation, both at zero temperature and above; and (b) such a calculation will demonstrate that the present Einstein-Kanzaki method

TABLE I. Modifications for $T \neq 0$ °K. [See Eqs. (74) and (75) for definitions of $t(\underline{\omega})$ and y .] All equations in Sec. III remain unchanged when one goes to finite temperature, except those listed here.

$T=0$ quantity	$T \neq 0$ quantity	$T=0$ kinetic term	$T \neq 0$ kinetic term
E , Eq. (21)	F_{trial}	$\frac{\hbar^2}{8M_i} \text{Tr} \underline{\gamma}_i^{-1}$	$t(\underline{\omega}_i)$
$E^{(0)}$, Eqs. (27), (28)	$F^{(0)}$	$\frac{\hbar^2}{8M} \text{Tr} \underline{\gamma}_0^{-1}$	$t(\underline{\omega}_0)$
ΔE_{core} , Eq. (32)	ΔF_{core}	$\frac{\hbar^2}{8M_i} \text{Tr} (\underline{\gamma}_i^{-1} - \underline{\gamma}_0^{-1})$	$t(\underline{\omega}_i) - t(\underline{\omega}_0)$
$D_{44}[\underline{q}]$, Eqs. (40), (41)	$D_{44}[\underline{q}]$	$\frac{3\hbar^2}{M\gamma_0^3}$	$24\hbar^{-1} M^2 \omega_0^3 \left(\coth y_0 + \frac{y_0}{\sinh y_0} \right)^{-1}$

can be carried out in practice for a complicated long-ranged oscillatory pair potential.

The model used for metallic hydrogen was an fcc lattice of vibrating protons³¹ interacting via an electronically screened pair potential, given in k space by

$$V(\vec{k}) = \begin{cases} 4\pi e^2/k^2 \epsilon(k/2k_F), & \vec{k} \neq \vec{0}, \\ 0, & \vec{k} = \vec{0}. \end{cases} \quad (76)$$

Here ϵ is the linear dielectric function of the electron gas, and the vanishing of the screened potential for $\vec{k} = \vec{0}$ reflects the overall charge neutrality of the system. A screened pair-potential model of this kind neglects two phenomena:

(i) Even in the linear screening regime the energy depends on the total volume (i.e., there are "volume-dependent forces"). Here the formation energy at *constant volume* will be considered, so that this effect does not enter into the calculation.

(ii) Nonlinear distortions in the electron gas, caused by the protons, will give rise to *many-proton* forces as well as pair forces. While the present formalism can in fact be generalized to cover many-particle potentials,¹⁷ the proton motion can be expected to wash out such three-body and higher effective forces to a large degree. (This phenomenon is discussed by Straus³¹ in connection with the perfect metallic hydrogen crystal.) Here only pair potentials were considered, as was the case in Caron's¹⁰ work.

The linear electron-gas dielectric function was taken to be the Hubbard³² version, as modified by Geldart and Vosko³³ so as to satisfy the compressibility sum rule. Thus

$$\epsilon(x) = 1 + \Lambda(x)g(x)\alpha r_s / \pi x^2, \quad (77)$$

$$g(x) = \frac{1}{2} + \frac{1}{4x} (1-x^2) \ln \left| \frac{1+x}{1-x} \right|, \quad (78)$$

$$\Lambda(x) = \left(1 - \frac{g(x)}{r_K + (2\pi/\alpha r_s)x^2} \right)^{-1}. \quad (79)$$

Here r_s is the usual Wigner-Seitz radius measured in Bohr radii, and $\alpha = (4/9\pi)^{1/3}$. In (79), $r_K = K/(K - K_0)$ is determined by the ratio of the true electron gas compressibility K to the compressibility K_0 of the noninteracting electron gas. The value of r_K was taken as that obtained by differentiating the Vashishta-Singwi electron-gas energy formula.^{34,35} Thus,

$$r_K^{-1} = 1 - \frac{K_0}{K} = \frac{\alpha}{\pi r_s} \left(1 + \frac{0.0335}{2} \pi \alpha r_s + \frac{0.02\pi\alpha r_s^2}{3} \frac{0.1 + 2r_s}{(0.1 + r_s)^3} \right). \quad (80)$$

The above form of the dielectric function has the

advantage of being analytic while yielding a good "compressibility limit"³⁵ as $k \rightarrow 0$. It is important to treat ϵ accurately near $k = 2k_F$, since the behavior there is responsible for the long-ranged Friedel oscillations of the real-space screened potential. However, for values $k/2k_F \gtrsim 1.5$, which are safely away from the $2k_F$ singularity, it is convenient to know the large-wave-number asymptotic expansion of (76)–(79),

$$\begin{aligned} \epsilon^{-1}(x) \underset{x \rightarrow \infty}{\sim} & 1 - \frac{\alpha r_s}{3\pi} x^{-4} - \frac{\alpha r_s}{15\pi} x^{-6} \\ & - \left[\frac{\alpha r_s}{35\pi} - \frac{1}{18} \left(\frac{\alpha r_s}{2} \right)^2 \right] x^{-8} \\ & - \left[\frac{\alpha r_s}{63\pi} - \frac{1}{45} \left(\frac{\alpha r_s}{\pi} \right)^2 \right. \\ & \left. - \frac{r_K}{36} \left(\frac{\alpha r_s}{\pi} \right)^3 \right] x^{-10} + O(x^{-12}). \end{aligned} \quad (81)$$

Since the interest here is principally in any slight but long-ranged disturbance to the proton motion, the completely linear relaxation is sufficient. There is thus no strongly perturbed "core," and the set of sites c^* is just the vacant site at the origin. The free energy ΔF of vacancy formation was found by working through Sec. III step by step, using the electronically screened and motionally smeared proton-proton potential

$$U^0(\vec{k}) = \begin{cases} 4\pi e^2 e^{-\gamma \alpha k^2} / k^2 \epsilon(k/2k_F), & \vec{k} \neq \vec{0}, \\ 0, & \vec{k} = \vec{0} \end{cases} \quad (82)$$

The necessary steps are now listed for reference, together with some relevant details of numerical methods.

(a) The perfect crystal free energy $F^{(0)}(\gamma_0)$ was found from Eq. (28), modified as in Table I when $T \neq 0$ °K. γ_0 was chosen to minimize $F^{(0)}$.

(b) The free energy $\Delta F_{0,\text{vac}}$ required to form the vacancy without any lattice distortion was found from Eq. (31): The "core distortion" energy ΔF_{core} is, of course, zero.

(c) The total free energy of linear distortion ΔF_{bulk} , including relaxation of lattice vibrations, was found from (65). For comparison, the corresponding result $\Delta F_{\text{bulk}}^{(3)}$ without relaxation of lattice vibrations was found from (67). The Brillouin-zone averages specified in (65) and (67) were performed using the ten-term "special point" prescription given for fcc lattices by Chadi and Cohen.³⁶ The quantities needed in these zone averages were the generalized dynamical matrix $D(\vec{k})$ [found from Eqs. (41) with a $T \neq 0$ °K modification as in Table I for D_{44}] and the Kanzaki force vector $\underline{F}(\vec{k})$ [found from Eq. (64)].

(d) The total free energy of formation was found as

$$\Delta F = \Delta F_{0,\text{vac}} + \Delta F_{\text{bulk}}, \quad (83)$$

there being no need for a separate variation of nonlinear core parameters in this purely linear distortion calculation.

Steps (a), (b), and (c) involved numerical evaluation of reciprocal lattice sums of the form

$$\sum_{\vec{g} \neq 0} |\vec{g} + \vec{q}|^{-n} \epsilon^{-1} \left(\frac{|\vec{g} + \vec{q}|}{2k_F} \right) e^{-\gamma_0 (\vec{g} + \vec{q})^2} \quad (84)$$

and integrals of the form

$$\int d^3k k^{-n} \epsilon^{-1} \left(\frac{k}{2k_F} \right) e^{-\gamma_0 k^2}, \quad (85)$$

where n is a small positive integer. Since $\epsilon^{-1} \sim 1$ and $\gamma_0 > 0$, (84) and (85) are formally convergent at large wave number. However, the value of γ_0 is small enough that convergence was too slow for direct numerical evaluation in practice. This difficulty was circumvented by using the five-term asymptotic expansion (81) for $k/2k_F > \lambda$, where $\lambda \sim 1.5$. (The final results were independent of λ over a considerable range, of course.) The advantage of this is that one now has finite sums and integrals, plus infinite sums and integrals of the form

$$\sum_{\vec{g}} |\vec{g} + \vec{g}|^{-p} e^{-\gamma_0 (\vec{g} + \vec{g})^2}, \quad (86)$$

$$\int d^3k k^{-p} e^{-\gamma_0 k^2}$$

for several positive values of p . The integrals can be reduced to known special functions and combined with terms which arise when the sums are converted using modified Ewald methods. (See the work of Cohen and Keffer³⁷ for details of the Ewald methods). The outcome is that one has a number of fairly complicated but rapidly convergent sums. The results of the calculations are shown in Tables II and III and in Fig. 1.

TABLE II. Calculated vacancy formation energy, ΔE (rydbergs), in metallic hydrogen at $T=0^\circ\text{K}$ and constant volume $\Omega = \frac{4}{3} \pi N (r_s a_0)^3$. The quantities listed are, from left to right, the Wigner-Seitz radius r_s , the rms proton excursion in units of the nearest-neighbor separation, the energy $\Delta E_{0,\text{vac}}$ required to form a vacancy without any lattice relaxation, the linear lattice relaxation energy $\Delta E_{\text{bulk}}^{(3)}$ *ignoring* changes in Einstein frequencies, the linear lattice relaxation energy ΔE_{bulk} *including* changes in the Einstein frequencies, the total vacancy formation energy ΔE in the linear approximation. All energies are in rydbergs.

r_s	$(3\gamma_0)^{1/2}/d_{\text{nn}}$	$\Delta E_{0,\text{vac}}$	$\Delta E_{\text{bulk}}^{(3)}$	ΔE_{bulk}	ΔE
0.6	0.13 ₇	+0.57 ₁	-0.27 ₃	-0.27 ₅	+0.29 ₆
0.7	0.13 ₆	+0.42 ₆	-0.19 ₉	-0.20 ₀	+0.22 ₆
0.8	0.13 ₅	+0.32 ₄	-0.14 ₉	-0.15 ₀	+0.17 ₄
0.9	0.13 ₅	+0.25 ₀	-0.11 ₄	-0.11 ₅	+0.13 ₅
1.0	0.13 ₅	+0.19 ₅	-0.08 ₈	-0.09 ₀	+0.10 ₅
1.1	0.13 ₆	+0.15 ₃	-0.07 ₀	-0.07 ₁	+0.08 ₂
1.2	0.13 ₇	+0.12 ₀	-0.05 ₆	-0.05 ₇	+0.06 ₂
1.3	0.14 ₀	+0.09 ₄	-0.04 ₅	-0.04 ₆	+0.04 ₈
1.4	0.14 ₂	+0.07 ₃	-0.03 ₇	-0.03 ₈	+0.03 ₅
1.5	0.14 ₅	+0.05 ₇	-0.03 ₁	-0.03 ₂	+0.02 ₅

Table II shows that the vacancy formation energy is *not* significantly altered by relaxation of the proton motion at $T=0^\circ\text{K}$ in the range of densities $1.0 \leq r_s \leq 1.5$ relevant to metastable metallic hydrogen. This is seen by comparing columns 4 and 5 of Table II, which give the relaxation energy, first without, then with relaxation of zero-point motion ($\Delta E_{\text{bulk}}^{(3)}$ and ΔE_{bulk}).

Figure I shows that, in the same range of densities, the present results do not differ appreciably from Caron's¹⁰ values. This is actually a valuable check on both calculations, since Caron used a real-space method in which only a few neighbors were relaxed nonlinearly, while the present results came from a linear k -space method which

TABLE III. Temperature dependence of free energy of vacancy formation, ΔF (rydbergs), in fcc metallic hydrogen at $r_s=1.36$. The quantities listed are, from left to right, the temperature $T^\circ\text{K}$, the rms proton excursions as a fraction of nearest-neighbor distance, the free energy $\Delta F_{0,\text{vac}}$ required to form the vacancy without lattice relaxation, the linear lattice relaxation energy $\Delta F_{\text{bulk}}^{(3)}$ *ignoring* changes in proton motion, the linear lattice relaxation energy ΔF_{bulk} *including* changes in proton motion, the total free energy ΔF required to form a vacancy, the concentration $\exp(-\Delta F/k_B T)$ of vacancies in an independent random vacancy model.

$T^\circ\text{K}$	$(3\gamma_0)^{1/2}/d_{\text{nn}}$	$\Delta F_{0,\text{vac}}$	$\Delta F_{\text{bulk}}^{(3)}$	ΔF_{bulk}	ΔF	$e^{-\Delta F/k_B T}$
0	0.14 ₁	+0.080 ₉	-0.040 ₃	-0.041 ₃	+0.038 ₆	0
1 000	0.15 ₅	+0.084 ₈	-0.039 ₂	-0.041 ₂	+0.043 ₆	0.001 ₀
2 000	0.18 ₅	+0.094 ₄	-0.037 ₈	-0.040 ₃	+0.054 ₁	0.01 ₄
3 000	0.20 ₁	+0.103 ₈	-0.037 ₅	-0.040 ₅	+0.063 ₃	0.03 ₆
4 000	0.22 ₈	+0.112 ₁	-0.037 ₈	-0.041 ₃	+0.070 ₈	0.06 ₁
5 000	0.24 ₅	+0.120 ₀	-0.038 ₅	-0.042 ₅	+0.077 ₅	0.08 ₈
10 000	0.30 ₉	+0.154 ₀	-0.045 ₁	-0.051 ₆	+0.102 ₄	0.19 ₉

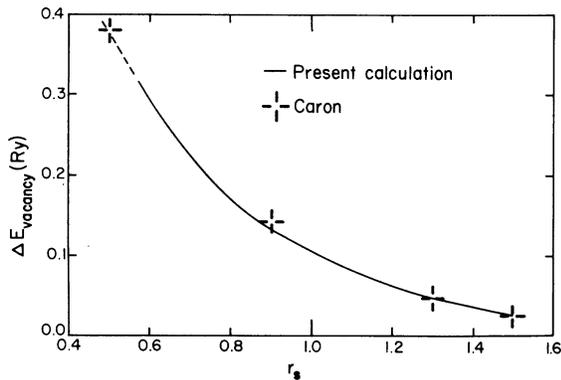


FIG. 1. Vacancy formation energy ΔE in fcc metallic hydrogen at $T=0^\circ\text{K}$. Present calculation is compared with the results of Caron, obtained from Table VI and Figs. 12 of Ref. 10.

included static and dynamic relaxation of every proton in the crystal.

Table III shows the effect of raising the temperature. The quantities given are now Helmholtz free energies ΔF for the formation of an isolated vacancy, ignoring the entropy of vacancy location. In the model of randomly placed noninteracting vacancies, the equilibrium vacancy concentration is then

$$C(T) = \exp[-\Delta F(T)/k_B T], \quad (87)$$

which is tabulated in the last column of Table III. Two trends are noticeable in Table III.

(i) The free energy of formation *increases* with temperature, so that the concentration of vacancies does not rise as fast as exponentially when the temperature increases. For example, if the crystal still exists at 5000°K , the present model gives a concentration $C(T)=9\%$ of vacancies, whereas the usual model involving the $T=0^\circ\text{K}$, formation energy $\Delta F(0)$ would give

$$C_0(T) = \exp[-\Delta F(0)/k_B T] \approx 29\%$$

of vacancies, a very substantial difference.

(ii) With increased temperature the dynamic relaxation becomes more important, so that at 5000°K the dynamic relaxation energy is 10% of the total relaxation energy.

Actually it is likely that the crystal has melted by 5000°K . In addition to the 9% vacancy concentration shown in column 7 of Table III, the notion of melting by a few thousand degrees is also supported by column 2 which gives the Lindemann³⁸ ratio r_L . (This is the ratio of rms particle excursion to nearest-neighbor distance: in classical crystals r_L is about $\frac{1}{7}$ at melting.) In hydrogen at $r_s = 1.36$, r_L is already³¹ $\frac{1}{7}$ at $T=0^\circ\text{K}$, and doubles by 5000°K . It should be borne in mind, however,

that in computer experiments on quantum crystals with soft-cored pair potentials, Chester³⁹ *et al.* found values of r_L significantly above $\frac{1}{7}$ at melting.

VI. FURTHER POSSIBILITIES

Existence of the "generalized lattice statics" approach suggests that an even simpler theory might be available; the $\vec{q} \rightarrow 0$ limit of the present work should yield a "jiggling elastic continuum" model, related to the present microscopic approach in the same way that the usual elastic continuum model is related to the conventional^{2,3} lattice statics. This is currently under investigation.

An effect which was not directly considered in Sec. I–IV (and is missing also from Refs. 9–13) is the migration of point defects. This will be important in classical crystals near melting,⁷ and may occur in quantum crystals with small enough mass to permit significant tunneling.^{15,16} In the classical case, a crude way to remedy the omission is simply to assume that the total defect free energy (at low defect concentration $C = n/N$) is

$$F/N = C\Delta F + TS/N, \quad (88)$$

where $S \sim k \ln^N C_n$ is the configurational entropy associated with the possible sites occupied by n defects, and ΔF is the free energy of defect formation as calculated in Sec. III–IV. Minimization of (88) leads to the equilibrium defect concentration $C(T)$ given in Eq. (87), and tabulated for metallic hydrogen in Table III. A more complete approach would be to use a lattice gas picture of the defect crystal.⁷ Here ΔF will play the role of a temperature-dependent chemical potential for defects and in this context one could also use the generalized lattice statics to calculate an effective interaction between defects,⁵ as mediated by their static *and* dynamic strain fields.

In the case of quantal defect tunneling, the relaxation described in the present work can significantly lower the tunneling probability or even cause self-trapping.⁴⁰ To describe this case one can invoke a tight-binding Hubbard model for defect motion, in which the hopping matrix element t is to be computed from an overlap integral between two of the Einstein states (as used in this paper), one with the defect on a neighboring site relative to the other. The formation energy ΔF computed above will then play the role of a site occupation energy ϵ_i .

Thus, the present model may be useful even near melting or for highly quantal crystals, in the sense that it provides an explicit method of computing the input parameters to more sophisticated theories.

VII. CONCLUSIONS

It has been shown in detail how to use the Einstein model to calculate formation energies of crystalline defects, including relaxation of zero-point and thermal lattice motions as well as the usual static lattice deformation. Relaxation of every site in the crystal was explicitly calculated by a generalization of the Kanzaki method; static and dynamic contributions appeared self-consistently in the same 4×4 matrix formalism.

The method is substantially easier to carry out in full than the self-consistent phonon approaches,^{12,13} which require specific use of localized phonon modes as well as a separate minimization for static relaxation. On the other hand, the method is more complete than previous Ein-

stein theories of defects^{10,11} in which only a few particles are usually relaxed.

Application to metallic hydrogen shows that the method is a practical means of calculating static and dynamic relaxation in the case of complicated long-ranged pair forces. For hydrogen in the density range $0.6 \leq r_s \leq 1.5$, it was possible to show that dynamical relaxation does *not* upset the stability of the system to vacancy formation as might perhaps have been supposed.

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¹A "localized" defect means that a point or small cluster is the focus of the defect, rather than a line or plane of sites. Of course, even a "localized" defect has a long-ranged disturbing influence which is in fact the main concern here.

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¹⁸There is no need to restrict $\phi_i(\mathbf{x})$ to be a Gaussian, in general, and indeed for highly nonclassical crystals one may gain an advantage over the usual self-

consistent phonon scheme (Ref. 14) by allowing more freedom in the $\{\phi_i\}$ within an Einstein scheme. This point has been taken up by D. Rosenwald [*Phys. Rev.* **154**, 160 (1967)] who concluded, however, that in comparing the approximations involved the neglect of correlation is far more difficult to justify than the restriction of the trial functions to Gaussian form.

¹⁹There is no deep significance to the fact that some elements of \underline{X} are imaginary. It turns out to be convenient in \mathbf{k} space, giving rise to *real* 4×4 lattice Green's functions.

²⁰In the case of vacancy or interstitial formation in metals it is highly advantageous to treat the process at constant particle number N , because overall removal or addition of an ion entails removal or addition of a conduction electron also: this is most inconvenient when one is treating the conduction sea as merely a screening agent for the ions.

²¹See conference proceedings *Interatomic Potentials and Simulation of Lattice Defects*, edited by P. C. Gehlen, J. R. Beeler, and R. I. Jaffee (Plenum, New York, 1972); discussion of this point is on p. 456 and elsewhere.

²²In the case of a vacancy-interstitial pair, one of the displacements $|\mathbf{x}_i - \mathbf{R}_i|$ is on the order of a lattice spacing or more.

²³Terms like D_{41} couple static and dynamic relaxation.

²⁴ ΔE_0 is zero for mass defects or vacancy-interstitial pairs.

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