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We thus conclude that high-precision crystalline calculations are feasible with the PWG method of calculating energy bands.

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Volume Change Associated with Noncubic Defects in a Monatomic Lattice*

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(Received 3 May 1971)

The formalism of the method of lattice statics is applied to obtain an expression for the volume change associated with a noncubic point defect in a monatomic lattice, assuming that the defect exerts no shear stress. This expression is used to calculate the volume changes associated with the octahedral and tetrahedral carbon interstitials in α-iron.

One of the physically interesting changes in the properties of a crystal brought about by the introduction of a point defect into the lattice is the volume change, or dilatation induced by the relaxation of the atoms of the host crystal to new equilibrium conditions. Currently, the most common method of calculating the dilatation associated with a given defect is to treat a portion of the crystal as an elastic continuum and obtain the strength parameter of the defect by somehow matching the displacements of host atoms in a discrete "core" region near the defect to the displacements of the atoms along the boundary between the discrete region and continuum region of the crystal.

More recently, a completely atomistic approach has been applied to the problem of determining the properties of point defects[1-4] in crystals. This technique, known as the method of lattice statics, is unique in that the equations of elasticity theory can be obtained directly from the corresponding lattice-statics equations for points in the lattice far away from the defect. Hardy[5] has shown that this natural transition from lattice theory to elasticity theory can be used to obtain a consistent expression for the lattice-strength tensor G_{ij} which is used to represent the point defect as a singularity in the body force on the elastic medium:

$$-F_i = -\sum_j G_{ij} \frac{\partial}{\partial x_j} \delta(\vec{r}) , \tag{1}$$

where i and j are Cartesian-coordinate indices. In terms of the force $\vec{F}^l$ exerted by the defect on its lth neighboring atom and the position vector $\vec{R}^l$ of the lth atom in the perfect lattice, the strength tensor is

$$G_{ij} = \sum_l F_i^l R_j^l . \tag{2}$$

In the case of a cubic point defect, $G_{ij} = 0$ for $i \neq j$ and all of the diagonal elements, G_{ii} are equal to the same constant G. Hardy[5] has shown that for this case the dilatation Δv produced by the defect is

$$\Delta v = \frac{G}{K} = \sum_l \frac{F_i^l R_i^l}{K} , \tag{3}$$

where K is the bulk modulus of the host crystal.

The derivation given by Hardy can be extended

in a straightforward manner to the case of a point defect which does not exhibit cubic symmetry, assuming the defect does not induce shear stresses in the lattice. In this case the off-diagonal elements of the strength tensor $\vec{\vec{G}}$ vanish, but the diagonal elements are no longer identical. Hence, the lattice will not dilate uniformly along each of the $\langle 100 \rangle$ Cartesian axes, but will dilate by some amount δ_i along the ith axis, where i ranges from 1 through 3. The elastic energy density is then given by

$$w = \tfrac{1}{2}C_{11}(\delta_1^2 + \delta_2^2 + \delta_3^2) + C_{12}(\delta_1\delta_3 + \delta_1\delta_2 + \delta_2\delta_3) , \quad (4)$$

and the energy changes for the undilated lattice and the dilated lattice are, respectively,

$$\Delta U = \sum_l \Psi(|\vec{\mathbf{R}}^l + \vec{\xi}^l|) + \frac{1}{2}\sum_{l,i} F_i^l \xi_i^l \quad (5)$$

and

$$\Delta U' = \sum_l \Psi(|\bar{\vec{\mathbf{R}}}^l + \bar{\vec{\xi}}^l|) + \frac{1}{2}\sum_{l,i} \bar{F}_i^l \bar{\xi}_i^l + wNV_a . \quad (6)$$

Here $\vec{\mathbf{R}}^l$ is the position vector of the lth atom in the perfect lattice, $\vec{\xi}^l$ is the displacement of the lth atom from its perfect lattice position, and $\Psi(|\vec{\mathbf{r}}|)$ is the interaction between the defect and a host atom a distance r away from the defect. N is the number of atoms per unit volume, v_a. A bar over any quantity means that it is to be evaluated for the dilated lattice and, in particular,

$$\bar{\vec{\mathbf{R}}}^l = [R_1^l(1+\delta_1),\ R_2^l(1+\delta_2),\ R_3^l(1+\delta_3)] . \quad (7)$$

We assume that the same force-constant matrix $\phi_{ij}^{ll'}$ is valid for both the dilated and undilated lattice, i.e., $\bar{\xi}_i^l = \phi_{ij}^{ll'} \bar{F}_j^{l'}$ and $\xi_i^l = \phi_{ij}^{ll'} F_j^{l'}$. Letting

$$\bar{F}_i^l = F_i^l + \Delta F_i^l$$

and

$$\bar{\xi}_i^l = \xi_i^l + \Delta\xi_i^l ,$$

one can expand $\Psi(|\bar{\vec{\mathbf{R}}}^l + \bar{\vec{\xi}}^l|)$ in a Taylor's series about δ_i and ξ_i^l, and then we have

$$\Delta U' - \Delta U = -\sum_{l,i} F_i^l R_i^l \delta_i - \frac{1}{2}\sum_{l,i} F_i^l \Delta\xi_i^l + \frac{1}{2}\sum_{l,i} \Delta F_i^l \xi_i^l + NV_a w . \quad (8)$$

Using the fact that $\Delta\xi_i^l = \phi_{ij}^{ll'} F_j^{l'}$, this becomes

$$\Delta U' - \Delta U = -\sum_{l,i} F_i^l R_i^l \delta_i + NV_a w - \frac{1}{2}\sum_{l,i} (F_i^l \phi_{ij}^{ll'} F_j^{l'}) - \Delta F_i^l \phi_{ij}^{ll'} F_j^{l'} . \quad (9)$$

Since $\phi_{ij}^{ll'}$ is a symmetric matrix, the last term in Eq. (9) vanishes and

$$\Delta U^1 - \Delta U = -\sum_{l,i} F_i^l R_i^l \delta_i + NV_a w . \quad (10)$$

The δ_i are now determined by minimizing this energy change with respect to δ_i, which gives a set of three equations of the form

$$\sum_l F_i^l R_i^l = \tfrac{1}{2}NV_a[2C_{11}\delta_i + 2C_{12}(\delta_j + \delta_k)] , \quad (11)$$

where i, j, and k may take on values from 1 through 3, but $i \neq j \neq k$. Adding these together, one obtains

$$\sum_{l,i} F_i^l R_i^l = \tfrac{1}{2}NV_a(2C_{11}\delta_\tau + 4C_{12}\delta_\tau) , \quad (12)$$

where $\delta_\tau = \delta_i + \delta_2 + \delta_3$. To first order, the dilatation ΔV is given by $\Delta V \simeq NV_a\delta_\tau$. Hence, Eq. (12) becomes

$$\sum_{l,i} F_i^l R_i^l = (C_{11} + 2C_{12})\Delta V , \quad (13)$$

and using the definition of the bulk modulus $K = \frac{1}{3}(C_{11} + 2C_{12})$, one obtains, finally,

$$\Delta V = \sum_{l,i} \frac{F_i^l R_i^l}{3K} . \quad (14)$$

Lattice-statics calculations have recently been carried out to determine the atomic relaxations about tetrahedral and octahedral carbon interstitials in α-iron.[6] The strength tensors for these defects contain no off-diagonal elements, so that Eq. (14) should be applicable. It should be noted at this point that recent disacommodation experiments by Wuttig and Keiser[7] indicate that in ferroelectric materials, the magnetic energy strongly affects the activation volume of defects. However, the interatomic potentials used in the lattice-statics calculations were derived on a strictly mechanical basis and the remainder of this treatment will be carried out on the same assumption. Using the numerical values for $\vec{\mathbf{F}}^l$ and $\vec{\xi}^l$ obtained in Ref. 6, one obtains a volume change of 0.26 atomic volumes for the tetrahedral case but only 0.14 atomic volumes for the octahedral case. Direct-space calculations using the same interatomic potentials have been done by Johnson *et al.*,[8] and a volume change of 0.28 atomic values was found for both cases. Assuming the tetrahedral configuration to be the saddle-point configuration for defect migration, Johnson *et al*,[8] obtained an activation volume of 0.0 atomic volumes, whereas the present calculations indicate an activation volume of 0.12 atomic volumes. Since the parameters of the carbon-iron interaction were obtained by Johnson *et al.*[8] in such a way as to match the experimentally determined condition that the activation volume be zero, it is natural that this result should be reproduced in

their direct-space calculations.

The method of calculating the formation volumes in the direct-space approach differs from that outlined in the present paper, so that one cannot, in this case, construe the differences in the activation-volume results as being due to the shortcomings of the direct-space technique pointed out earlier.[3,4] However, Hardy[5] has pointed out that current elasticity-theory methods of obtaining the volume changes induced by a defect are generally unreliable. The discrepancies in the activation volume found here, along with the corresponding differences in migration energies found in Ref. 6, cast a certain amount of doubt on the parameters of the carbon-iron interaction developed in Ref. 8 by direct-space technique.

*Work supported by the Senate Research Committee of the University of Nebraska at Omaha, Omaha, Neb.

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Lattice Thermal Conductivity of Solids

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Reformulation of the lattice thermal conductivity of solids has been given, using the fact that the three-phonon umklapp processes can be divided into different classes depending on the reciprocal-lattice vectors of the crystal concerned, and that they tend towards displaced distribution functions characteristic of their own. The expression obtained differs from that of Callaway by terms which are expected to be of minor importance in real systems.

I. INTRODUCTION

In the past, most of the calculations of the lattice thermal conductivity of crystals have been made by using the Boltzmann transport equation for phonons.[1-3] In its linearized form, this equation can be written as

$$\vec{v}\cdot\vec{\nabla}T\,\frac{dN}{dT}=\left(\frac{\partial N}{\partial t}\right)_{\text{scatt}}, \tag{1}$$

where $N=N(\vec{q}j)$ is the phonon occupation number corresponding to state $\vec{q}j$ in the crystal under study and $\vec{v}=\vec{v}(\vec{q}j)$ is the phonon group velocity, $\vec{q}$ and j being the phonon wave vector in the reduced-zone scheme and the polarization index, respectively. The term $\vec{\nabla}T$ is the steady-state thermal gradient.

To calculate the lattice thermal conductivity, one has to solve Eq. (1) for N. Usually, it is assumed that N differs only slightly from the corresponding Planck distribution N^0, characteristic of the temperature of the system. This assumption can be taken to be valid at least for vanishingly small thermal gradient. One can therefore replace N by N^0 on the left-hand side of Eq. (1), obtaining

$$\frac{dN}{dT}=\frac{x}{T}\,\frac{e^x}{(e^x-1)^2}, \tag{2}$$

where $x=\omega\hbar/kT$, $\omega=\omega(\vec{q}j)$ being the phonon frequency and k being the Boltzmann constant.

The term $(\partial N/\partial t)_{\text{scatt}}$ on the right-hand side of Eq. (1) describes the rate of increase of N as a result of the various scattering processes taking place in the crystal. If the scattering events do not interfere, then it is possible to write this term equal to the sum of the individual contributions $(\partial N/\partial t)_i$ of the different types of scattering processes, where i specifies the type of process. (By interference we mean that there exists no scattering event which belongs to two different types of scattering processes.) Since $(\partial N/\partial t)_i$ has a very complicated form even for highly simplified systems, the relaxation-time approach is often used. The relaxation time gives a statistical description of how the scattering processes of a given type tend to modify the phonon occupation number. Formally, the relaxation time τ_i is defined by