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Application of the Method of Lattice Statics to Interstitial Cu Atoms in Cu*

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We have calculated the lattice distortion produced by a body-centered interstitial Cu atom in a Cu host lattice. The calculations have been carried out consistently on the basis of discrete lattice theory, using the technique of lattice statics which is based on the Fourier transformation of the direct-space equilibrium equations. The force constants for the perfect lattice have been taken from measured phonon-dispersion curves, and we have used Huntington's Born-Mayer potential to describe the interaction between the interstitial atom and the atoms of the host lattice. The comparison of our results with those obtained by earlier workers, using semidiscrete matching techniques in which a continuum displacement solution is matched to the displacements of a few close neighbors of the defect, indicates that this latter technique is very unreliable. Similarly, the activation volumes estimated by semidiscrete techniques are also unreliable. We have also used the technique of lattice statics to calculate the strain-field interaction between two body-centered interstitial Cu atoms as a function of their separation. As in the case of the displacement fields, we have made these calculations for two different models which differ in the input elastic constants. For what we believe to be the most realistic of our models, we find a repulsive energy of 0.40 eV for two nearest-neighbor interstitials and a repulsive interaction of 0.0975 eV between two second-neighbor interstitials. For the same model, the calculated formation volume per interstitial is 1.12 atomic volumes.

I. INTRODUCTION

WHEN a point defect is introduced into an otherwise perfect crystal, the atoms become displaced from their equilibrium positions in the absence of the defect. For certain purposes, e.g., calculations of defect-induced electrical resistivity, an explicit knowledge of these displacements is necessary. They also determine that part of the defect formation energy which depends on the lattice relaxation. Furthermore, in the case of

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metals, where the total energy of the crystal contains a volume-dependent term, it is extremely important to be able to determine the volume change produced by a point defect, since the associated change in the volume-dependent part of the energy may make a large contribution to the total defect formation energy.

In the past, calculations of the atomic displacements about a point defect have almost all been made by using what may be described as a semidiscrete approach.[1] In this approach one divides the crystal into two regions: region I, consisting of the defect and a few close neighbors; and region II, which consists of the remainder of the crystal. The atoms in region I are then treated as discrete, while the remainder of the crystal is regarded as a continuum. Thus, while one carries out an explicit minimization of the total energy with respect to the displacements of the atoms in region I, it is nonetheless a constrained minimization since the atoms in region II are not permitted to relax independently, but are forced to adopt the continuum configuration. This "semidiscrete" approach is unsatisfactory in at least two respects: (1) For the approach to be realistic, region I has to be reasonably large, but as the size of the region increases, the equations governing the displacements increase rapidly both in number and complexity; and (2) as we shall show in detail later, it is extremely difficult to obtain any satisfactory matching of the unconstrained displacements in region I to the constrained displacements in region II. The effect of these limitations on the relaxation energies calculated by the semidiscrete method may not be too serious; however, the limitations on the calculated displacement field are very much more serious.[2]

In 1957, Kanzaki[3] presented an approach to the problem which eliminated the necessity for the continuum approximation and treated all the atoms in the lattice on a discrete basis. This approach, which we refer to as the method of lattice statics, enables us to calculate the actual displacements from normal coordinates which are essentially the Fourier inverses of the direct space displacements.

In order to determine these Fourier amplitudes, the lattice equilibrium equations are solved in reciprocal space and the results are back-transformed to direct space by summing over the allowed wave vectors within the first Brillouin zone. These wave vectors are determined by applying periodic boundary conditions across a supercell containing N primitive unit cells. By this approach, we are able to reduce the $3N\times3N$ array of linear equations, which determine the direct space displacements, to N 3×3 arrays, one for each Fourier amplitude, which are explicitly soluble. This is the crux of the method. In addition, it is also possible by this technique to evaluate the strain-field interaction between pairs of defects as a function of their separation.[4]

Recently, the first application of this technique to defects in metals has been made[4a], leading to a calculation of the displacement fields about single vacancies in Cu and Al and the interaction energy between pairs of such vacancies. In the present paper it is our intention to present analogous calculations for interstitial Cu atoms in a Cu host lattice. These calculations have been carried out on the assumption that an interstitial Cu atom occupies the body center of the face-centered unit cell. This assumption is probably invalid[1] since it is generally believed that the stable position is the ⟨100⟩ split or "dumb bell" interstitial, and it is our intention at a later stage to investigate this more complex configuration. However, we believe that the present results are meaningful since the body-centered interstitial is the simplest type of interstitial in a face-centered lattice, and it is logical to apply the new technique to the simplest defect first. Moreover, since there has been earlier theoretical work on this defect by a number of authors[5–7] who have applied the semidiscrete method, it is therefore possible to make direct comparison of their results and ours, and thus assess the value of the new technique.

In Sec. II we present a detailed derivation of the equations of lattice statics appropriate to the present problem as far as the calculation of the displacement field about the defect is concerned. In Sec. III this work is extended to cover the formal calculation of the interaction between pairs of defects. In Sec. IV, we present detailed calculations of the displacement field about a single interstitial and the analogous calculations of the interaction energies between pairs of interstitials. In Sec. V we give an over-all discussion of our present results and a comparison with the earlier results obtained by semidiscrete theory.

II. METHOD OF LATTICE STATICS

Let $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ be the basic vectors of an infinite lattice. This lattice can be built up from equivalent volumes, each containing N unit cells, with boundaries $L\mathbf{a}_1+L\mathbf{a}_2+L\mathbf{a}_3$, where $L^3=N$. At the center of each supercell we imagine a defect to be introduced. This automatically implies that the resultant displacements of the atoms will have the same periodicity as the supercells, and is thus equivalent to considering one defect at the center of an isolated supercell and imposing periodic boundary conditions across that supercell.

In the following discussion, it is assumed that a defect introduced into a crystal will interact with the host

[1] R. A. Johnson and E. Brown, Phys. Rev. **127**, 446 (1962).
[2] A. B. Lidiard, Natl. Bur. Std. Misc. Publ. **287**, 61 (1966).
[3] H. Kanzaki, J. Phys. Chem. Solids **2**, 24 (1957).
[4] J. R. Hardy and R. Bullough, Phil. Mag. **15**, 237 (1967).
[4a] See Ref. 9.
[5] A. Seeger and E. Mann, J. Phys. Chem. Solids **12**, 326 (1959).
[6] K. H. Bennemann and L. Tewordt, Z. Naturforsch. **15a**, 772 (1960).
[7] A. Seeger, E. Mann, and R. von Jan, J. Phys. Chem. Solids **23**, 639 (1962).

atoms by means of an effective pairwise potential, $\psi(r)$. We take the defect itself as the origin of coordinates and with respect to this origin, the position of the lth atom of the host lattice is represented by a vector $\mathbf{r}^l+\boldsymbol{\zeta}^l$ in which $\mathbf{r}^l$ is the position vector of the lth atom in the perfect lattice in the same coordinate system, and $\boldsymbol{\zeta}^l$ is the displacement of that atom due to the presence of the defect.

The potential energy of the distorted lattice can be written

$$U=U_0+\sum_l \psi(|\mathbf{r}^l+\boldsymbol{\zeta}^l|)+\tfrac{1}{2}\sum_{ll'}\sum_{\alpha\beta}\zeta_\alpha{}^l\phi_{\alpha\beta}{}^{ll'}\zeta_\beta{}^{l'}, \quad (1)$$

where α and β, which run from 1 through 3, refer to the Cartesian components of the atomic displacements along the three orthogonal $\langle 100\rangle$ directions of our cubic crystal, and U_0 is the energy of the undistorted perfect lattice. In this equation,

$$\phi_{\alpha\beta}{}^{ll'}=\left(\frac{\partial^2 U}{\partial\zeta_\alpha{}^l\partial\zeta_\beta{}^{l'}}\right)_0 \quad (2)$$

is the $3N\times 3N$ force-constant matrix for the perfect lattice (the subscript 0 indicates that the derivative is evaluated in the undistorted configuration).

The equilibrium configuration is determined by minimizing U with respect to the displacements,[8] which implies that

$$\partial U/\partial\zeta_\alpha{}^l=0, \quad (3)$$

which may be expressed as

$$F_\alpha{}^l=\sum_{l'}\sum_{\beta}\phi_{\alpha\beta}{}^{ll'}\zeta_\beta{}^{l'}, \quad (4)$$

where

$$F_\alpha{}^l=-\frac{\partial\psi(\downarrow\mathbf{r}^l+\boldsymbol{\zeta}^l\downarrow)}{\partial\zeta_\alpha{}^l}. \quad (5)$$

In order to perform the actual calculations, the displacements are expanded in terms of normal coordinates. Since we are considering a periodic superlattice of defects, the wave vectors $\mathbf{q}$ must satisfy periodic boundary conditions, and all such physically distinct $\mathbf{q}$ vectors will be contained within the first Brillouin zone. Thus we write

$$\boldsymbol{\zeta}^l=\frac{1}{N}\sum_{\mathbf{q}}\mathbf{Q}^{\mathbf{q}}\exp[i\mathbf{q}\cdot\mathbf{r}^l]. \quad (6)$$

Substituting from Eq. (6) into Eq. (4) we obtain for a wave vector $\mathbf{q}'$

$$F_\alpha{}^l=\frac{1}{N}\sum_{l'\beta}\sum_{\mathbf{q}}\phi_{\alpha\beta}{}^{ll'}Q_\beta{}^{\mathbf{q}'}\exp[i\mathbf{q}'\cdot\mathbf{r}^{l'}]. \quad (7)$$

We now multiply both sides by $\exp[-i\mathbf{q}\cdot\mathbf{r}^l]$ and sum over l; thus,

$$\sum_l F_\alpha{}^l\exp[-i\mathbf{q}\cdot\mathbf{r}^l]$$
$$=\frac{1}{N}\sum_{ll'}\sum_{\beta\mathbf{q}}\phi_{\alpha\beta}{}^{ll'}Q_\beta{}^{\mathbf{q}'}\exp[i\mathbf{q}'\cdot\mathbf{r}^{l'}]\exp[-i\mathbf{q}\cdot\mathbf{r}^l]$$
$$=\frac{1}{N}\sum_{ll'}\sum_{\beta\mathbf{q}}\phi_{\alpha\beta}{}^{ll'}Q_\beta{}^{\mathbf{q}'}\exp\{-i\mathbf{q}'\cdot[\mathbf{r}^l-\mathbf{r}^{l'}]\}\times\exp\{-i[\mathbf{q}-\mathbf{q}']\cdot\mathbf{r}^l\}. \quad (8)$$

Since the expression $\exp\{-i\mathbf{q}'\cdot[\mathbf{r}^l-\mathbf{r}^{l'}]\}$ depends only on the difference $l-l'$, we take l as the *zeroth* cell, hence

$$\sum_l F_\alpha{}^l\exp[-i\mathbf{q}\cdot\mathbf{r}^l]=\frac{1}{N}\sum_{l'}\sum_{\beta\mathbf{q}}\phi_{\alpha\beta}{}^{0l'}Q_\beta{}^{\mathbf{q}'}\exp[i\mathbf{q}'\cdot\mathbf{r}^{l'}]\times\sum_l\exp\{-i[\mathbf{q}-\mathbf{q}']\cdot\mathbf{r}^l\}. \quad (9)$$

The sum $\sum_l\exp\{-i[\mathbf{q}-\mathbf{q}']\cdot\mathbf{r}^l\}$ must vanish unless $\mathbf{q}-\mathbf{q}'$ is a reciprocal lattice vector, in which case each term in the sum is unity; thus, since $\mathbf{q}$ and $\mathbf{q}'$ both lie within the first Brillouin zone, $\mathbf{q}=\mathbf{q}'$ and (9) becomes

$$\sum_l F_\alpha{}^l\exp[-i\mathbf{q}\cdot\mathbf{r}^l]=\sum_{l'\beta}\sum_{\mathbf{q}}Q_\beta{}^{\mathbf{q}}\phi_{\alpha\beta}{}^{0l'}\exp[i\mathbf{q}\cdot\mathbf{r}^{l'}]. \quad (10)$$

We now define

$$F_\alpha{}^{\mathbf{q}}\equiv\sum_l F_\alpha{}^l\exp[-i\mathbf{q}\cdot\mathbf{r}^l], \quad (11)$$

and

$$V_{\alpha\beta}{}^{-\mathbf{q}}\equiv\sum_{l'}\phi_{\alpha\beta}{}^{0l'}\exp[i\mathbf{q}\cdot\mathbf{r}^{l'}]; \quad (12)$$

then Eq. (10) can be written

$$F_\alpha{}^{\mathbf{q}}=\sum_\beta V_{\alpha\beta}{}^{-\mathbf{q}}Q_\beta{}^{-\mathbf{q}}, \quad (13)$$

or, in matrix form,

$$\mathbf{F}^{\mathbf{q}}=\mathbf{V}^{-\mathbf{q}}\mathbf{Q}^{\mathbf{q}};$$

thus,

$$\mathbf{Q}^{\mathbf{q}}=(\mathbf{V}^{-\mathbf{q}})^{-1}\mathbf{F}^{\mathbf{q}}. \quad (14)$$

Once we have used Eqs. (11) and (12) to find the Fourier transforms of the direct space forces and the dynamical matrix, the normal coordinates may be found from Eq. (14) and the direct-space displacements are then given by Eq. (6). Thus, the displacement of any given atom may be obtained without any need to relax the whole lattice explicitly.

In practice it is necessary to solve Eq. (14) numerically and also to perform the Fourier inversion numer-

[8] This minimization, we would like to emphasize, is carried out at *constant volume*. Subsequently one calculates the macroscopic volume change due to the defect according to the prescription given in Ref. 12; the fact that the effective pairwise interaction between atoms in the perfect lattice is not in equilibrium because the presence of a volume-dependent term in the total energy in no way affects the validity of the present *constant volume* minimization. Subsequently, when the lattice is allowed to dilate uniformly, there will be a slight change in the displacements we calculate, but this will be of order $1/N$.

ically. Since we cannot deal with an infinitely dense sample of $\mathbf{q}$ vectors, we are compelled to deal with finite regular samples. Physically this is equivalent to solving the problem for an infinite superlattice in which the number of atoms in each supercell is exactly equal to our total number of sample wave vectors. However, it is possible to obtain sample densities sufficiently high to enable us to determine the displacements of the first 22 neighbors of the defect in an infinite crystal (the criterion of this fact is that the calculated displacements become independent of the sample density).

In the case of a vacancy[4,9] the appropriate direct-space forces can be determined without any explicit knowledge of the interatomic potential. But in the present paper we wish to consider the case of an interstitial Cu atom in a Cu lattice. For this problem it is necessary that we have some knowledge of the interatomic potential between the interstitial atom and those of the host lattice.

We therefore use, for this interaction, Huntington's[10] Born-Mayer potential which has been used extensively by other authors,[1,5–7]

$$\psi(r)=\lambda \exp[-\nu(r-r_0)/r_0], \tag{15}$$

with λ and ν constants characteristic of the metal which one is considering (for Cu, $\lambda=0.053$ eV and $\nu=13.9$), r the interatomic separation, and r_0 the perfect lattice nearest-neighbor distance ($r_0=\sqrt{2}a$, where $2a$ is the cubic unit cell side). However, in the calculation of the dynamical matrix, we follow the procedure given by Bullough and Hardy[9] and derive the elements of this matrix directly from measured phonon dispersion curves. In this derivation it is implicit that the lattice energy of the perfect crystal may be regarded a sum over pairwise potentials (of which we neglect all but the first- and second-neighbor components) and a volume-dependent term. The components of this pairwise potential contain contributions which are additional to the closed-shell Born-Mayer potential, and these components should also in principle contribute to the interaction between the interstitial atom and the atoms of the host lattice. However, there is at present no way of determining them, and it seems reasonable to assume that the dominant contribution to this interaction comes from the rapidly varying Born-Mayer potential. Moreover, this assumption is consistent with that made by other workers, and we would therefore expect our results to be at least as good as theirs and probably significantly better in that we are using, for the remainder of the crystal, the correct interatomic force constants, whereas they assumed the Born-Mayer form for all interactions.

We are considering an interstitial atom at the body center of a cubic cell of side $2a$. Since the Born-Mayer potential falls off rapidly, we consider it adequate to assume that the defect exerts an appreciable force only on its first neighbors, the magnitude of which we denote by F_1. It can then be shown that the components of $\mathbf{F}^{\mathbf{q}}$ are

$$\begin{aligned} F_1{}^{\mathbf{q}}&=-2iF_1 \sin q_1 a,\\ F_2{}^{\mathbf{q}}&=-2iF_1 \sin q_2 a,\\ F_3{}^{\mathbf{q}}&=-2iF_1 \sin q_3 a. \end{aligned} \tag{16}$$

The dynamical matrix for a face-centered cubic lattice with central first- and second-neighbor interactions has elements

$$\begin{aligned} V_{11}{}^{-\mathbf{q}}=&2A_1+4B_1+A_2+2B_2-(A_1+B_1)\\ &\times\cos q_1 a(\cos q_2 a+\cos q_3 a)-A_2\cos 2q_1 a\\ &-2B_1\cos q_2 a\cos q_3 a\\ &-B_2(\cos 2q_2 a+\cos 2q_3 a) \end{aligned} \tag{17}$$

and

$$V_{12}{}^{-\mathbf{q}}=(A_1-B_1)\sin q_1 a \sin q_2 a. \tag{18}$$

The remaining elements can be obtained from Eqs. (17) and (18) by cyclic permutation of the indices of the components of $\mathbf{q}$. A_i and B_i are, respectively, the axial and tangential force constants between ith neighbors.

Since the forces in Eq. (5) are those evaluated at the *relaxed* positions of the atoms, and in the present problem it is likely that the first-neighbor relaxations will be significant, we must use the value of F_1 in our equations, evaluated at the relaxed positions. Thus, from Eq. (15),

$$F_1=-\left[\frac{\partial\psi(r)}{\partial r}\right]_{r=a+\xi^1},$$

where ζ^1 is the nearest-neighbor displacement. Then

$$F_1=(-\nu\lambda/r_0)\exp[-\nu(a+\zeta^1-r_0)/r_0].$$

If we let $\gamma_l=|\zeta_l|/2a$ and use the fact that $r_0=\sqrt{2}a$, we have

$$\begin{aligned} F_1&=\frac{-\nu\lambda}{\sqrt{2}a}\exp[-\nu(1+2\gamma_1-\sqrt{2})/\sqrt{2}]\\ &=\frac{-\nu\lambda}{\sqrt{2}a}\exp(0.293\nu)\exp(-2^{1/2}\nu\gamma_1). \end{aligned}$$

Let

$$K_1=\frac{\nu\lambda}{\sqrt{2}a}\exp(0.293\nu),$$

and

$$\eta=\sqrt{2}\nu.$$

Then

$$F_1=-K_1\exp(-\eta\gamma_1). \tag{19}$$

Substituting Eq. (19) into Eqs. (16) we find that the generalized force $\mathbf{F}^{\mathbf{q}}$ can be written

$$F_\alpha{}^{\mathbf{q}}=C_\alpha{}^1\exp(-\eta\gamma_1), \tag{20}$$

where

$$C_\alpha{}^1=2iK_1\sin q_\alpha a. \tag{21}$$

[9] R. Bullough and J. R. Hardy, Phil. Mag. **17**, 833 (1968).
[10] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

Thus, Eqs. (14) can be written

$$Q_\alpha{}^q=\sum_\beta (V^{-q}{}_{\alpha\beta})^{-1}F_\beta{}^q=\exp(-\eta\gamma_1)\sum_\beta (V^{-q}{}_{\alpha\beta})^{-1}C_\beta{}^1.$$

Define

$$g_\alpha{}^1\equiv\sum_\beta (V^{-q})_{\alpha\beta}{}^{-1}C_\beta{}^1.$$

Then

$$Q_\alpha{}^q=g_\alpha{}^1\exp(-\eta\gamma_1). \tag{22}$$

To find the direct-space displacements, we use the expression

$$\zeta_\alpha{}^l=\frac{i}{N}\sum_q Q_\alpha{}^q\sin(\mathbf{q}\cdot\mathbf{r}^l), \tag{23}$$

which follows from Eq. (6) when we use the fact that $\mathbf{Q}^q=(\mathbf{Q}^{-q})^*$. Thus from Eqs. (22) and (23) we have

$$\zeta_\alpha{}^l=\frac{i}{N}\sum_q g_\alpha{}^1\exp(-\eta\gamma_1)\sin(\mathbf{q}\cdot\mathbf{r}^l)$$
$$=\frac{i}{N}\exp(-\eta\gamma_1)[\sum_q g_\alpha{}^1\sin(\mathbf{q}\cdot\mathbf{r}^l)]. \tag{24}$$

If we let $\gamma_\alpha{}^l=\zeta_\alpha{}^l/2a$, we have

$$\gamma_\alpha{}^l=\rho_\alpha{}^l\exp(-\eta\gamma_1), \tag{25}$$

in which

$$\rho_\alpha{}^l=\frac{i}{2Na}\sum_q g_\alpha{}^1\sin(\mathbf{q}\cdot\mathbf{r}^l).$$

In general,

$$\gamma_l=[(\gamma_1{}^l)^2+(\gamma_2{}^l)^2+(\gamma_3{}^l)^2]^{1/2},$$

but for first neighbors, $\gamma_2{}^1=\gamma_3{}^1=0$. Hence $\gamma_1=\gamma_1{}^1$ and Eq. (25) may be written

$$\gamma_1=\rho_1{}^1\exp(-\eta\gamma_1). \tag{26}$$

This transcendental equation can be solved for γ_1 by iteration. Since we then know γ_1, we find the associated forces in the relaxed configuration from Eqs. (2) and (21).

III. STRAIN-FIELD INTERACTION BETWEEN TWO INTERSTITIALS

The general expression for the interaction energy between two defects has been given by Hardy and Bullough[4] as

$$E=-\frac{1}{N}\sum_q \mathbf{F}^{-q}(\mathbf{V}^{-q})^{-1}\mathbf{F}^q\cos(\mathbf{q}\cdot\mathbf{R}), \tag{27}$$

in which the summation is again taken over the N distinct $\mathbf{q}$ vectors in the first Brillouin zone (BZ) and $\mathbf{R}$ is the vector separating the defects. This expression is correct to first order in the displacement field of the first defect at the position of the second defect and vice versa, and all that is necessary to apply it to the calculation of the interaction between two interstitials is the substitution of the appropriate expressions for $\mathbf{F}^q$ and $\mathbf{V}^{-q}$. For small interdefect spacings, the energy E has to be evaluated by numerical integration, but for large values of $|\mathbf{R}|$, the asymptotic form of E may be evaluated analytically, when the host lattice is elastically isotropic. This is possible because the integral over $\mathbf{q}$ is dominated by the contribution from small values of $\mathbf{q}$ when $|\mathbf{R}|$ is large. Thus one can expand the integrand, exclusive of the $\cos(\mathbf{q}\cdot\mathbf{R})$ term, as a power series in $\mathbf{q}$ and retain only the lowest-order terms. Thus we find

$$E=-\frac{1}{N}\sum_q\{[\mathbf{F}_1{}^{-q}(\mathbf{V}_2{}^{-q})^{-1}\mathbf{F}_1{}^q+2\mathbf{F}_1{}^{-q}(\mathbf{V}_2{}^{-q})^{-1}\mathbf{F}_3{}^q$$
$$-\mathbf{F}_1{}^q(\mathbf{V}_2{}^{-q})^{-2}\mathbf{V}_4{}^{-q}\mathbf{F}_1{}^q]\cos(\mathbf{q}\cdot\mathbf{R})\} \tag{28}$$

to the fourth order in $\mathbf{q}$. The subscripts denote the order of $\mathbf{q}$ in the subscripted quantities. The expression is general, but to evaluate the integral explicitly, we need to assume elastic isotropy. Thus, for the first term we find

$$E^{(0)}=-\frac{(F_1)^2}{\pi C_{11}}\int\int\int_{1\text{st BZ}} d\mathbf{q}\cos(\mathbf{q}\cdot\mathbf{R}).$$

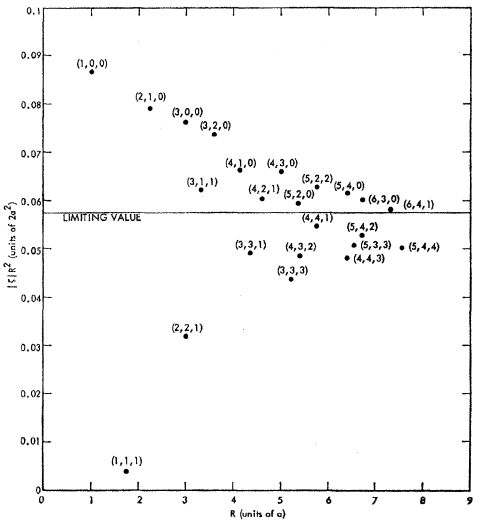
By performing the integration in spherical coordinates with $\mathbf{R}$ taken along the pole, it can easily be shown that $E^{(0)}\propto -2\pi^2\nabla^2(1/|\mathbf{R}|)$ which vanishes identically. After a considerable amount of algebraic manipulation (see Ref. 4) we find that the remaining terms of Eq. (28) give

$$E=\frac{1}{288\pi}\Big[-\frac{8154M+4536P}{|\mathbf{R}|^5}+\frac{(31\,815P-7560M)}{|\mathbf{R}|^9}$$
$$\times(X_1{}^4+X_2{}^4+X_3{}^4)-\frac{25\,515}{|\mathbf{R}|^{11}}(X_1{}^6+X_2{}^6+X_3{}^6)\Big], \tag{29}$$

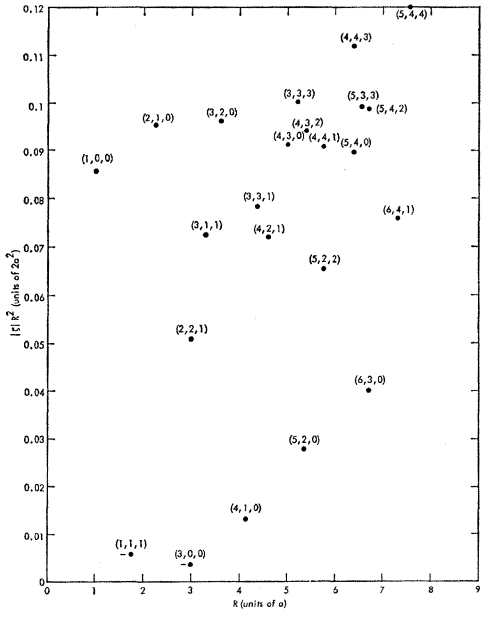
in which

$$M=\frac{F_1{}^2a^4(C_{11}-C_{44})}{C_{11}{}^2},$$
$$P=-\frac{4}{3}\frac{a^4}{C_{11}}F_1{}^2-\frac{a^3F_1{}^2}{C_{11}{}^2}\Big(\frac{C_{11}}{4}a+\frac{3}{16}M\omega_t{}^2-\frac{19}{12}aC_{44}\Big), \tag{30}$$

in which C_{11} and C_{44} are the elastic constants of the host material, M is the mass of a host atom, and $\omega_t{}^2$ is the frequency of the transverse acoustic (TA) mode at the (100) zone-face center. The manner in which these quantities enter into the computations will be explained in Sec. V. The energy given by Eq. (29) varies as $|\mathbf{R}|^{-5}$ and its angular average is zero (cf. the vacancy results of Hardy and Bullough[4]).



(a)



(b)

FIG. 1. (a) Variation of the displacement ζ of the neighbors of an interstitial Cu atom in Cu, using Voigt-averaged elastic constants and considering first-neighbor defect-lattice interactions. (b) Variation of displacement ζ of the neighbors of an interstitial Cu atom in Cu, using observed elastic constants and considering first-neighbor defect-lattice interactions. Inward displacements are indicated by a negative sign attached to the appropriate $|\zeta|R^2$ point.

IV. NUMERICAL CALCULATIONS OF THE DISPLACEMENTS AND INTERACTION ENERGIES

In this section we shall present numerical results of our calculations for interstitial Cu atoms in Cu. We have used two different models. In both cases we have assumed that the interstitial exerts forces only on its first neighbors. However, in the case of model I, the force constants of the host lattice have been derived from the measured elastic constants together with the TA frequency at the (100) zone-face center. In model II we have instead used Voigt-averaged elastic constants which satisfy the isotropy condition.

TABLE I. Elastic constants in 10^{12} dyn/cm^2.

Elastic constant	Measured values,[a] anisotropic	Voigt-averaged values[b]
C_{11}	1.70	2.112
C_{12}	1.23	1.024
C_{44}	0.75	0.544

[a] Used for model I.
[b] Used for model II. Note: The isotropy condition $C_{11}-C_{12}=2C_{44}$ holds for these constants.

The manner in which the force F_1 is evaluated has been described in Sec. II. In evaluating the A_i's and B_i's we follow the procedure of Hardy and Bullough.[4] Thus we obtain

$$\begin{aligned} 2aC_{11}&=A_1+B_1+2A_2\,,\\ 2aC_{44}&=\tfrac{1}{2}(A_1+3B_1)+2B_2\,,\\ 2aC_{12}&=\tfrac{1}{2}(A_1-5B_1)-2B_2\,. \end{aligned} \tag{31}$$

To provide the fourth equation necessary to define all four unknowns, we also use

$$M\omega_t^2=2A_1+6B_1\,. \tag{32}$$

The appropriate values of the elastic constants are shown in Table I. As a check on the adequacy of the resultant A_i and B_i values, we have calculated the values of three other zone-boundary phonon frequencies, and these are compared with the measured values[11] in Table II. It can be seen that the agreement between theory and experiment is reasonable for both sets of elastic constants. Three values of N were used in the displacement and interaction energy calculations: 1000, 8000, and 64 000.

The results for $N=1000$ are not sufficiently accurate to be of interest, and even the sample of 8000 $\mathbf{q}$ vectors gives accurate results only out to a distance of about 5a from the defect. Hence, the results quoted in the following tables are those for $N=64\,000$. At a later stage we hope to refine our sampling technique to improve the accuracy by a factor of 2 or 3 for more distant neighbors and the largest interdefect spacings.

TABLE II. Comparison of experimental and theoretical values of $M\omega^2$ (10^4 dyn/cm).

Zone center; mode	Theoretical (model I)	Theoretical (model II)	Experimental
(100) TA	10.6999	10.6999	10.6999
(100) LA	24.995	22.020	21.7503
(111) TA	4.29	5.892	4.7087
(111) LA	25.736	22.837	22.297

[11] S. K. Sinha, Phys. Rev. 143, 422 (1966).

TABLE III. Displacements due to an interstitial defect in Cu—model I. Displacements are in units of $2a$; $|\zeta|R^2$ is in units of $2a^3$; $a=1.805$ Å.

Neighbor	ζ_1	ζ_2	ζ_3	$\lvert\zeta\rvert R^2$
100	0.08560	0.0	0.0	0.08560
111	−0.001137	−0.001137	−0.001137	−0.005909
210	0.01413	0.01274	0.0	0.09513
221	0.003038	0.003038	0.003651	0.05074
300	−0.0003915	0.0	0.0	−0.003524
311	0.004917	0.003074	0.003074	0.07219
320	0.004925	0.005527	0.0	0.09623
331	0.002627	0.002627	0.001796	0.07840
333	0.002153	0.002153	0.002153	0.1007
410	0.0002448	0.0007412	0.0	0.01327
421	0.002410	0.002157	0.001124	0.07191
430	0.002430	0.002724	0.0	0.09125
432	0.002119	0.001929	0.001521	0.09407
441	0.001855	0.001855	0.0008170	0.09067
443	0.001658	0.001658	0.001409	0.1121
520	0.0005321	0.0007948	0.0	0.02774
522	0.001370	0.001006	0.001006	0.06519
533	0.001526	0.001224	0.001224	0.09921
540	0.001492	0.001598	0.0	0.08965
542	0.001469	0.001398	0.0008483	0.09891
544	0.001313	0.001171	0.001171	0.1204
630	0.0005626	0.0006896	0.0	0.04005
641	0.0009838	0.001003	0.0002790	0.07590

The computations were all carried out on an IBM 360/50 computer. Table III gives the results for model I and Table IV gives those for model II. For an elastically isotropic crystal, one expects the displacements at large distances from a single defect to be radial and to fall off inversely as R^2 (where R is the distance from the defect).

It can be shown,[12] by comparison of the equations of lattice statics with those of elasticity theory, that the

TABLE IV. Displacements in Cu due to an interstitial defect—model II. Displacement are in units of $2a$; $|\zeta|R^2$ is in units of $2a^3$; $a=1.805$ Å

Neighbor	ζ_1	ζ_2	ζ_3	$\lvert\zeta\rvert R^2$
100	0.08657	0.0	0.0	0.08657
111	0.0006885	0.0006885	0.0006885	0.003578
210	0.01330	0.008543	0.0	0.07905
221	0.002238	0.002238	0.001596	0.03190
300	0.008469	0.0	0.0	0.07622
311	0.005009	0.001866	0.001866	0.06228
320	0.004535	0.003397	0.0	0.07366
331	0.001720	0.001720	0.0007204	0.04819
333	0.0009389	0.0009389	0.0009389	0.04391
410	0.003763	0.001032	0.0	0.06634
421	0.002469	0.001323	0.0006630	0.06045
430	0.002070	0.001649	0.0	0.06618
432	0.001225	0.0009357	0.0006518	0.04854
441	0.001153	0.001153	0.0003370	0.05497
443	0.0007302	0.0007302	0.0005585	0.04814
520	0.001995	0.0008423	0.0	0.06280
522	0.001498	0.0006243	0.0006243	0.05737
533	0.0008919	0.0005502	0.0005502	0.05090
540	0.001162	0.0009576	0.0	0.06175
542	0.0008650	0.0007012	0.0003673	0.05276
544	0.0005773	0.0004681	0.0004681	0.05007
630	0.001194	0.0006172	0.0	0.06047
641	0.0008996	0.0006146	0.0001593	0.05836

[12] J. R. Hardy, Lawrence Radiation Laboratory, Livermore, Report No. UCRL-70834 (unpublished).

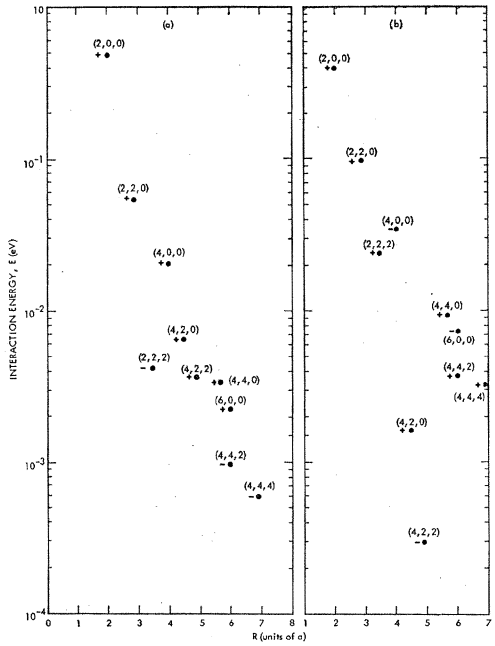


FIG. 2. Interaction energy between two body-centered interstitials as a function of their separation R. (a) Using Voigt-averaged elastic constants (model II); (b) using observed elastic constants (model I). (The signs of the interactions are indicated at each point.)

elastic strength of the defect G is given by

$$G=-\sum_l r_\alpha{}^l \frac{\partial\psi(|\mathbf{r}^l+\zeta^l|)}{\partial\zeta_\alpha{}^l}=\sum_l r_\alpha{}^l F_\alpha{}^l. \qquad (33)$$

For our present case, Eq. (33) gives

$$G=2aF_1.$$

For an isotropic lattice, it can be shown that $G=4\pi C_{11}\times|\zeta|R^2$; thus

$$|\zeta|R^2=F_1/2\pi C_{11}a \quad \text{(in units of } 2a^3).$$

Hence, for model II, we find that

$$|\zeta|R^2=0.0576\ (2a^3).$$

In Figs. 1(a) and 1(b) we have plotted the calculated values of $|\zeta|R^2$ for models II and I, respectively, as a function of $|\mathbf{R}|$ for the first 23 neighbors taking the values of $|\zeta|R^2$ from Tables III and IV. In the case of model II, the horizontal line shows the asymptotic value.

The interaction energies for the ten closest-neighbor defect pairs have also been calculated from Eq. (27) and are plotted in Figs. 2(a) and 2(b). The asymptotic values for the same pairs in an isotropic lattice have been found from Eq. (29). The results of all of these calculations are presented in Table V.

TABLE V. Interaction energies (eV).

Neighbor	Model II [Eq. (27)]	Model II [Eq. (29)]	Model I [Eq. (27)]
200	0.4933	0.329	0.4004
220	0.05509	0.0205	0.09751
222	−0.004192	−0.0363	0.02414
400	0.02027	0.0102	−0.03468
420	0.006506	0.0034	0.001639
422	−0.003662	−0.0021	−0.0002973
440	0.003377	0.006	0.009381
442	−0.0009754	−0.0012	0.003737
444	−0.0005963	−0.00113	0.003284
600	0.002214	0.0013	−0.007348

V. DISCUSSION

A. Lattice Distortion

Figure 1(a) bears out the conclusion of Hardy[13] and of Hardy and Bullough[4] that elasticity theory cannot be trusted to give accurate displacements close to a lattice defect. The values of $|\zeta|R^2$ for model II approach the required asymptotic form at large distances rather well [e.g., for the (6,4,1) neighbor $|\zeta|R^2=0.0584$ which is close to the required asymptotic value of 0.0576]. The one discrepancy appears to be in the value for the most distant neighbor (5,4,4) which is significantly below the required asymptotic value, but this deviation arises from the inadequacy of our **q**-vector sample density for computing the displacements of such distant neighbors for which, in any case, we can see that continuum theory is valid. Furthermore, increasing N from 8000 to 64 000 was found to change the displacements very little for neighbors closer than (3,3,3). Thus we can be sure of the displacement values for neighbors closer than $\sim 5a$ to the defect, and can trust the displacement values on out to (6,4,1) to one or two significant figures.

Consequently, we are now in a position to test the validity of the approximate displacement fields used by other authors. The most recent attempts to calculate displacements due to an interstitial Cu atom in Cu have been those of Seeger and Mann,[5] Bennemann and Tewordt,[6] and Seeger *et al.*[7] In all cases, a semidiscrete method of calculation has been used (cf. Sec. I). The details of the computations vary from paper to paper, but in all cases displacement results are given for a model in which the interaction is confined to act only between nearest-neighbor atoms and is assumed to be given by a Born-Mayer potential identical to the one used in the present paper; thus direct comparison can be made between our results and those of the references cited. This is done in Table VI.

The results of Refs. 6 and 7 have been computed for an anisotropic host medium, while those of Ref. 5 have been derived for an isotropic host medium. In Ref. 5 only the first four neighbor shells were treated on a discrete basis, while in Ref. 7 only the first three shells were treated as discrete. The results of the present work show quite clearly that these last two matching procedures are inadequate, since our calculated displacement fields do not begin to approach the asymptotic values until well beyond the fifth-neighbor shell. In the case of Ref. 6 it is rather more difficult to make a direct comparison, but it would appear that these authors also make the approximation of assuming the results of elasticity theory (in this case anisotropic) to be valid too close to the defect. Certainly there are very marked discrepancies between our results and those quoted in all three references, and it appears from the foregoing discussion that the validity of the matching techniques used by these authors is extremely dubious. However, it is probable that the most significant cause of these discrepancies is the failure of any of these workers to use the correct interatomic force constants for the host lattice. In all three cases the Born-Mayer contribution alone was considered, and this leads to A_i and B_i values significantly different from those derived from the measured phonon dispersion curves.[11]

However, the most important discrepancy between our results and those of Refs. 5–7 is the difference in the predicted dilatations associated with a single interstitial. We calculate this dilatation using the relationship due originally to Eshelby,

$$\Delta V = G/K, \tag{34}$$

where K is the bulk modulus. Eshelby derived this result for an elastic continuum, but it can be shown[12] that it is a general result which can be derived rigorously from lattice theory, which also provides the precise prescription given previously [Eq. (33)] for calculating the strength parameter G from interatomic force constants.

TABLE VI. Comparison of our displacements with those given by other authors (in units of 2a).

	Ref. 5 (isotropic)			Ref. 6 (anisotropic)			Ref. 7 (anisotropic)			Present (isotropic)			Present (anisotropic)		
Neighbor	ζ_1	ζ_2	ζ_3	ζ_1	ζ_2	ζ_3	ζ_1	ζ_2	ζ_3	ζ_1	ζ_2	ζ_3	ζ_1	ζ_2	ζ_3
100	0.109	0	0	0.122		0	0.11	0	0	0.0866	0.0	0.0	0.0856	0.0	0
111	0.0065	0.0065	0.0065	−0.0085	−0.0025	0	0.005	0.005	0.005	0.0007	0.0007	0.0007	−0.0011	−0.0011	−0.0011
210[a]	0.016	0.016	0	0.0025	0.0027	0	0.015	0.015	0	0.0133	0.0085	0.0	0.0141	0.0127	0
300	0.008	0	0	...	...	...	...	...	...	0.00847	0.0	0.0	−0.00039	0.0	0
320	...	...	...	0.0095	0.009	0	...	...	...	0.00453	0.0034	0	0.00493	0.0055	0

[a] Displacements taken in the ⟨110⟩ direction (radially from the nearest-neighbor sites).

[13] J. R. Hardy, J. Phys. Chem. Solids **15**, 39 (1960).

Thus, using Eq. (33) and substituting the value of F_1 for each model we can immediately calculate the appropriate value of G. Then using Eq. (34) with the appropriate value of K, we arrive at the values of ΔV for each model presented in Table VII, in which the analogous values from Refs. 5–7 have also been quoted. Comparing these results with our value for model II we see that there is a discrepancy of the order of 30%. However, in the case of model I our value falls between those quoted in Refs. 6 and 7.

If one uses the first-neighbor displacements given by these other authors in the expression for F_1 and then computes the elastic strengths according to Eq. (33), the values so obtained are little more than half the value which we obtain for the corresponding model II. Since the dilatations they compute are $\sim$30% greater than ours, this must mean that the asymptotic elastic displacement fields which these authors use are almost twice as great as the true value which would be predicted by Eq. (33) using their first-neighbor displacements.

Therefore, for all these reasons, it would seem to us that the various semidiscrete approximations used by these authors and, for that matter, the technique in general cannot be used as a means of deriving information about the displacement field produced by a point defect. How far this affects derived quantities (e.g., formation energy) is not obvious, but since the formation energy contains a volume-dependent term, it would appear to be essential to have a precise method for calculating the formation volume before a reliable calculation of the formation energy can be made, and our present approach offers a much more reliable way of doing this.

B. Interaction Energy

Certainly the most significant result of the present investigation into the strain-field interaction energy between two interstitials is the magnitude of this interaction for the (2,0,0) defect pair. In the case of model I, which is physically the most realistic of our models, we obtain a repulsive interaction energy of 0.40 eV. Additional calculations done in the course of the present investigation indicate that this energy is sensitive to the range of the assumed defect lattice interaction potential, and can in fact become negative if significant second-neighbor forces ($\sim$50% of the first-neighbor forces) are present. Another interesting result is that for model I the interaction energy between the (4,0,0) defect pair is attractive, having a magnitude of 0.035 eV.

It should be remembered that the linearization procedure used in deriving Eq. (27) is only strictly applicable for widely separated defects, and higher-order effects are probably significant for close pairs. At a later stage we intend to investigate the importance of these, but we believe our present results to be a good approximation. Certainly the strain-field interaction is many times greater than the Born-Mayer interaction between the members of the (2,0,0) interstitial pair. Thus, a precise knowledge of the lattice configuration about the di-interstitial is essential for the computation of its binding energy. As regards the validity of our results for more widely separated pairs, we believe them to be adequate as far as the (4,4,2) neighbor for model II.

TABLE VII. Dilatations due to an interstitial defect (units of 1 atomic volume).

	Model I	Model II
Present work	1.12	1.10
Ref. 5	...	1.39
Ref. 6	1.22	1.37
Ref. 7	1.09	...

Unfortunately, we have not been able to obtain a satisfactory match between the values calculated from Eq. (27) and those calculated from the asymptotic form for model II. We hope to remedy this deficiency in later work by using a more refined wave vector sampling technique. However, it can be clearly seen from Table V that any attempt to use the asymptotic form for close neighbors of the defect leads to interaction energies which differ markedly from the exact numerical values.

VI. CONCLUSIONS

We have applied the method of lattice statics to the calculation of the lattice distortion produced by a body-centered interstitial Cu atom in a Cu host lattice, and by the same method we have also calculated the strain-field interaction between various pairs of such interstitials. Our results show quite clearly that earlier calculations[5–7] based on semidiscrete models of the crystal give a very inadequate representation of its true displacement field. Similarly, they are also unreliable as a means of predicting the macroscopic volume change produced by an interstitial.

Our present results are limited in accuracy by the validity of the interatomic potentials we have assumed, and it is probable that the use of more refined potential will change our numerical results. However, this does not affect the validity of the technique we have used which provides a logical and straightforward method of obtaining the exact displacement field consistent with any assumed potential. Similarly, the results we have derived for the defect pair interaction energies are subject to a subsequent modification. In this case, the modifications will arise both from changes in the model force constants and also from the inclusion of higher-order terms (e.g., the "induced interaction"[14]) which are probably significant for interstitial close pairs.

[14] J. R. Hardy and R. Bullough, Phil. Mag. **16**, 405 (1967).