site directions at the point of contact.

As pointed out in Sec. IV, the energy difference between the threshold for two-photon transition and for TPPAT is equal to $u\epsilon_{\vec{q}}/b$. u and b are equal to the absolute values of the gradients of $\epsilon_{12}(\vec{K})$ and $\epsilon_2(\vec{K})$, respectively, near the point of contact of the surfaces F_{12}, F_{23}, and F_2. Since in this case $\vec{q}$ is very small, $\epsilon_{\vec{q}}$ is, in most cases, known either from ir or Raman measurements. Thus, measurement of the transition-rate spectrum may yield the ratio u/b which can be directly compared to theoretical band-structure calculations.

The actual determination of the transition rate of electrons to band 3 is, of course, a lot more difficult than the measurement of the parametric beam. However, in cases where band 3 does not have points in common with band 2, it can be carried out in the following way:

Electrons which have been excited to band 3 will cascade to a local minimum in this band. From here they will make transition to the almost empty conduction band—band 2. Provided that radiative transitions are allowed by symmetry at this point, the transition will be predominantly radiative. The photon energy of the fluorescent light is equal to the energy gap between bands 2 and 3 at the local minimum energy point in band 3. Thus, measurement of the intensity of the fluorescent light at the appropriate wavelength as a function of $\hbar\omega$, will yield the desired spectrum.

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Application of the Method of Lattice Statics to Carbon Interstitials in α-Iron†

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The method of lattice statics has been applied to determine the strain-field displacements about single octahedral and tetrahedral carbon interstitials in α-iron as well as the strain-field interaction energies between pairs of octahedral interstitials. A comparison of the exact lattice-statics displacements to the corresponding results of an asymptotic lattice-statics calculation indicates that elasticity theory is not valid closer than $25a$ from the octahedral interstitial in either the [100] or [011] direction in the lattice, where a is half of a cubic unit-cell side. The lattice-statics displacements have also been compared to analogous results obtained from a direct-space calculation, and some differences between the two sets of results are apparent. Relaxation energies have been calculated for the two types of carbon interstitial, and the octahedral configuration is found to be the more stable of the two. Assuming the tetrahedral configuration to be the saddle point for interstitial migration, the migration energy is found to be 0.27 eV.

I. INTRODUCTION

Since the advent of the high-speed digital computer, it has become possible to perform theoretical calculations to determine the properties of crystal lattices containing point defects. In particular, given a reasonably reliable expression for the interatomic potential between the atoms of the lattice, one can obtain numerical results for the energy change, volume change, and atomic displacements associated with the creation or migration of vacancies or host-atom–type interstitials within the lattice.

The most common approach to this type of problem is to treat the defect as though it were surrounded by a small crystallite of host atoms, each of which is permitted to move as a discrete particle and allowed to interact by means of pairwise interatomic potentials. The remainder of the crystal is treated as an elastic continuum. The displacements of the discrete atoms surrounding the defect are found by minimizing the energy in the crystallite with the constraint that the displacements of the atoms on the boundary between the crystallite and the elastic continuum must be equal to the corresponding displacements predicted by elasticity theory. A number of workers have used this "semidiscrete" approach to investigate the properties of vacancies and interstitials in metallic lattices.[1–5]

In a number of recent papers Flocken and Hardy[6,7] and Flocken[8] have applied a different approach to this type of defect calculation. This technique, which is referred to as the method of lattice statics is based on Fourier transforming the direct-space equilibrium equations of the lattice to reciprocal space. The resulting set of equations are decoupled and can be solved for the Fourier amplitudes of the direct-space displacements by a straightforward matrix inversion. This procedure allows all of the atoms of the host lattice to relax as individual particles and therefore does not rely in any way on the theory of continuum elasticity. Rather, if one evaluates the equations of lattice statics in the long-wavelength limit, the equations for the discrete lattice are found to transform smoothly and naturally to the equations of elasticity theory. Hence, by comparing the displacements obtained from the exact theory with the corresponding results of the asymptotic theory, it is possible to determine the distance from the defect at which elasticity theory becomes valid.

In a recent series of calculations[6–8] the method of lattice statics has been applied to determine the properties of vacancies in the alkali metals and in α-iron, as well as the properties of interstitial Cu atoms in Cu. In each case a comparison of the results of the exact lattice-statics calculations to those of the asymptotic theory indicates that elasticity theory cannot justifiably be applied as close to the defect as it has been in previous semidiscrete calculations. The result poses a rather serious question as to the future usefulness of semidiscrete techniques in the study of point-defect problems.

The first application of Green's-function techniques (such as the method of lattice statics) to carbon interstitials in α-iron was the work of Krivoglaz and Tikhonova,[9] who determined the strain-field displacements in the vicinity of octahedral carbon interstitials in α-iron in order to investigate the diffuse scattering of x rays induced by such defects. Numerous other authors have applied such techniques to determine the formation energies,[10] interaction energies,[11] and most recently, the elastic free energy[12] of iron crystals containing carbon impurities. In all of these calculations the iron-iron and carbon-iron interactions are derived in terms of the elastic constants of the host lattice and of carbon-iron alloys.

An investigation of carbon interstitials in α-iron using a direct-space approach has been carried out by Johnson and Damask[13] and by Johnson, Dienes, and Damask[14] in which the host-host interaction was described by an explicit interatomic potential developed by Johnson.[5] The host-defect interaction was expressed in the form of a cubic equation whose parameters were obtained from experimental determinations of certain defect properties associated with carbon interstitials in α-iron.[14]

The purpose of the present paper is to perform a lattice-statics calculation for carbon interstitials in α-iron using the same potentials used by Johnson *et al.*[14] The results of the present calculation will therefore be directly comparable to those obtained by the direct-space approach.

Both the octahedral and tetrahedral orientations of the carbon interstitial will be treated, but since the octahedral configuration appears to be the stable one, the bulk of the calculations deal with that case.

The lattice-statics techniques applied in the present paper differ from those of Refs. 6–8 in another important respect in that the wave-vector sums involved in the Fourier transformations are accomplished by a Gaussian quadrature technique first applied by Boyer and Hardy,[15] rather than by use of a regular array of allowed wave vectors in reciprocal space. This technique results, not only in a significant savings in computer time, but also has the effect of removing the supercell boundaries to infinity so that one is treating a truly isolated defect. The results of the asymptotic lattice-statics calculation (in the long-wavelength limit) are therefore not influenced by "defects" in nearby supercells as in previous calculations.

Section II contains a brief discussion of the lattice-statics formalism used in the present calculations as well as a discussion of the interatomic potentials used. The details of the computer calculations, the strain-field displacements, and strain-field interaction energies obtained as a result of the present calculation will be discussed in Sec. III. In Sec. IV a comparison is made between the displacements obtained using exact lattice statics and those obtained from the asymptotic theory and also with the direct-space results of Johnson *et al.*[14] Section V is a summary of the conclusions drawn from this investigation.

II. THEORETICAL APPROACH

The lattice-statics technique has been described in detail elsewhere,[6] and the present discussion will be confined to a brief outline of the method and a statement of the equations used in the calculations.

In the lattice-statics approach, the host lattice—assumed to be infinite—is divided into a number of equivalent volumes called supercells, each of which contains a defect at the center surrounded by N host atoms. The supercell boundaries are taken to be

$L\vec{a}_1 + L\vec{a}_2 + L\vec{a}_3$ where $L^3 = N$ and $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ are the basic vectors of the host lattice. The crystal can therefore be considered to be a "superlattice" of defects having the same unit-cell structure as the host lattice. By applying periodic boundary conditions across opposite faces of the supercell, one can determine the displacement of any atom in the lattice simply by determining the displacements of each of the atoms in a single supercell.

The defect itself is considered to be at the origin of coordinates, and the position of the lth host atom from the defect is denoted by $\vec{r}^l + \vec{\xi}^l$ where $\vec{r}^l$ is the position vector of the lth atom in the perfect lattice and $\vec{\xi}^l$ is its displacement in the relaxed lattice. It is most convenient, in a cubic lattice, to use the $\langle 100\rangle$ directions in the crystal as the axes of a Cartesian coordinate system.

The method of lattice statics consists of transforming the direct-space equations of the form

$$F^l_\alpha = \sum_{l'} \sum_{\beta} (\Phi_I)^{ll'}_{\alpha\beta}\, \xi^{l'}_\beta \tag{1}$$

to a set of equivalent equations of the form

$$F^{\vec{q}}_\alpha = \textstyle\sum_\beta v^{-\vec{q}}_{\alpha\beta}\, Q^{\vec{q}}_\beta \tag{2}$$

by means of the Fourier transformation

$$\vec{\xi}^l = (1/N) \textstyle\sum_{\vec{q}} \vec{Q}^{\vec{q}} e^{i\vec{q}\cdot\vec{r}^l} . \tag{3}$$

In this set of equations, $\vec{F}^l$ is the force exerted by the defect on the lth atom in the lattice, $\Phi_I(r)$ is the host-host interaction potential, and $\vec{V}^{-\vec{q}}$ is essentially the dynamical matrix of the host lattice. The subscripts α and β refer to components along the Cartesian axes and range from 1 through 3. The $\vec{Q}^{\vec{q}}$ are the Fourier amplitudes of the direct-space displacements, and the sum in Eq. (3) is over the N allowed wave vectors in the first Brillouin zone of the superlattice.

The reciprocal-space equilibrium equations consist of a set of N 3×3 matrix equations, each of which is a function of the components of only one of the Fourier amplitudes $\vec{Q}^{\vec{q}}$. The Fourier amplitudes can therefore be found by a straightforward matrix inversion, and the direct-space displacements can be obtained by performing the back transformation indicated in Eq. (3).

It is often convenient to use the lattice-statics technique to calculate quantities other than the direct-space displacements in such a way that all computations are performed in reciprocal space. In particular, the equation for the strain-field interaction energy between pairs of defects given by

$$E = (1/N) \textstyle\sum_{\vec{q}} \vec{F}^{-\vec{q}} (\vec{V}^{-\vec{q}})^{-1} \vec{F}^{\vec{q}} \cos(\vec{q}\cdot\vec{R}) , \tag{4}$$

where $\vec{R}$ is the interdefect separation vector, will be used to determine the strain-field interaction between pairs of carbon interstitials in the octahedral configuration.

In applying the lattice-statics formalism to impurities in α-iron, the direct interaction between pairs of iron atoms was represented by the interatomic potential developed by Johnson.[5] This potential is composed of smoothly joined sections of three cubic equations in such a way that the potential vanishes midway between the second- and third-nearest-neighbor positions and provides a good match to the radiation-damage potential of Erginsoy *et al.*[16] at short interaction ranges. The entire potential is given by

$$\begin{aligned}
\Phi_I(r) &= 2.195\,976\,(r - 3.097\,910)^3 + 2.704\,060r - 7.436\,448 \text{ eV} \\
&\qquad \text{for } 1.9\text{ Å} < r < 2.40\text{ Å} , \\
\Phi_I(r) &= -0.639\,230\,(r - 3.115\,829)^3 + 0.477\,871r - 1.581\,570 \text{ eV} \\
&\qquad \text{for } 2.40 < r < 3.00\text{ Å} , \\
\Phi_I(r) &= -1.115\,035(r - 3.066\,403)^3 + 0.466\,892r - 1.547\,967 \text{ eV} \\
&\qquad \text{for } 3.00 < r < 3.44\text{ Å} .
\end{aligned} \tag{5}$$

Since both the first- and second-nearest-neighbor positions in the perfect lattice lie in range $2.40 < r < 3.00$ Å, the force constants used in the dynamical matrix, $V^{\vec{q}}_{\alpha\beta}$ can be obtained from the middle section of the α-iron potential, and the other two sections play no part in the calculation.

The carbon-iron interaction potential was developed by Johnson *et al.*[14] and is given by

$$\Phi_C(r) = -3.365(2.236 - r)^3 + 0.886r - 2.156 \text{ eV} , \tag{6}$$

where r is in Angstroms. The parameters of this cubic equation were determined by matching to experimental values for the migration energy and the activation volume of carbon impurities in α-iron and to the binding energy between a carbon atom and a vacancy in α-iron.

A carbon interstitial in α-iron, which has a bcc symmetry, can assume two possible configurations: an octahedral or "*O*" configuration at the face center of a body-centered cube, and a tetrahedral or "*T*" configuration in which the carbon defect is translated $\frac{1}{2}a$ in a $\langle 100\rangle$ direction from the octahedral site, where a is half of a cubic unit-cell side in the α-iron lattice. These two configurations are shown in Figs. 1(a) and 1(b), respectively. Evidence seems fairly conclusive[14] that the *T* configuration is the saddle-point configuration for the defect migration. For this reason, more extensive calculations have been done for the *O* configuration than for the *T* configuration.

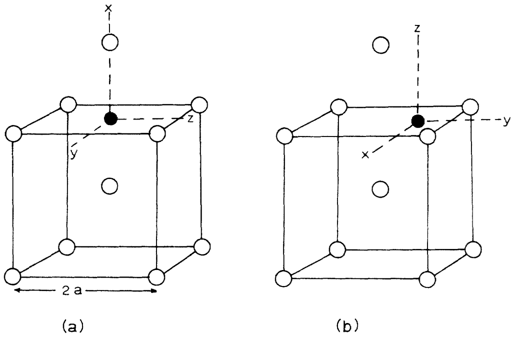

FIG. 1. Two carbon interstitial configurations in α-iron showing the Cartesian coordinate systems adopted for the numerical calculations. (a) shows the octahedral configuration in the unrelaxed lattice, and (b) shows the tetrahedral configuration in the unrelaxed lattice.

In the octahedral configuration the carbon interstitial reacts with two atoms at a distance a in the unrelaxed lattice and with four iron atoms at a distance $2a$ away. The form of the force array, $\vec{F}^{\vec{q}}$, for an octahedral interstitial defect in a bcc lattice is given in Eq. (16) of Ref. (9) and will not be repeated here, although all of the equations involved in the present work were derived separately in the formalism presented above. Hence, $\vec{F}^{\vec{q}}$ is expressed in terms of direct-space forces F_1 and F_2 exerted by the defect on its nearest and next-nearest neighbors rather than in terms of elastic parameters.

The initial phase of the calculation involves obtaining numerical values of F_1 and F_2 by simultaneously solving the set of equations of the form

$$\xi^l_\alpha = F_1 C^l_{\mathrm{I}\alpha} + F_2 C^l_{\mathrm{II}\alpha} \tag{7}$$

for $l = 1$ and 2 and obtaining a second set by differentiating Eq. (6) with respect to ξ:

$$\begin{aligned} F_1 &= 10.095(0.806 - \xi^1)^2 - 0.886 \text{ eV/Å} , \\ F_2 &= 10.095(0.214 - \xi^2)^2 - 0.886 \text{ eV/Å} . \end{aligned} \tag{8}$$

The constants $C^l_{\mathrm{I}\alpha}$ and $C^l_{\mathrm{II}\alpha}$ can be thought of as elements of a "response" matrix and are obtained by a process described in some of our previous calculations.[6,7]

Once F_1 and F_2 are obtained from Eqs. (7) and (8) by numerical methods, the force array $\vec{F}^{\vec{q}}$ for the defect is defined, and Eq. (2) can be used to find the exact Fourier amplitudes $\vec{Q}^{\vec{q}}$ for the imperfect lattice. Equations (3) and (4) can then be used to find the direct-space displacement for any atom in the lattice and the strain-field interaction energy for any desired pair of defects.

The calculation of the strain-field displacements and interaction energies for the tetrahedral configuration proceeds in the same manner as outlined above, except that the tetrahedral interstitial interacts directly with only its first-nearest neighbors. The form of the force array for the tetrahedral configuration is given by Eq. (4) of Ref. 10. The force T exerted by the defect on its nearest neighbor is again found by simultaneous solution of an equation involving the elements of a response matrix and another obtained by differentiation of Eq. (6) with respect to displacement $\vec{\xi}$. However, in order to avoid assuming that the nearest neighbors relax radially (which effectively was assumed for the octahedral configuration), it is necessary to solve for the x and y components of displacement $\vec{\xi}$ and obtain the magnitude of the separation vector r from the equation

$$r = [(r_{0x} + \xi_x)^2 + (r_{0y} + \xi_y)^2]^{1/2} , \tag{9}$$

where r_0 is the position vector of the nearest-neighbor atom in the perfect lattice. Once T is determined, the force array $\vec{F}^{\vec{q}}$ associated with the defect can be specified exactly and the Fourier amplitudes and direct-space quantities can be found.

The derivation of the equations used in obtaining values of the strain-field displacements in the asymptotic limit as $\vec{q} \to 0$ has been discussed in detail in a previous paper[17] for cubic defects and double-force defects. In the present work, asymptotic displacements were calculated for the octahedral carbon interstitial, which does not exhibit either of these symmetries exactly, hence, a more general set of equations than those derived in Ref. 17 must be obtained. From Ref. 9 it can be seen that the first-order approximation of $\vec{F}^{\vec{q}}$ for the octahedral interstitial in the limit as $\vec{q} \to 0$ has the form

$$\vec{F}^{\vec{q}\to 0} = \begin{pmatrix} C_1 k_1 \\ C_2 k_2 \\ C_3 k_3 \end{pmatrix} , \tag{10}$$

where $C_1 = -2iF_1$, $C_2 = C_3 = -2\sqrt{2}\, iF_2$, and $k_\alpha = q_\alpha a$. Using the approach outlined in Ref. 17, one arrives at an expression for $\vec{Q}^{\vec{q}\to 0}$ of the form

$$\begin{aligned} Q^{q\to 0}_\alpha = [\, & C_\alpha k_\alpha (Ek^4 + Fk_\alpha k^2 + Hk_\beta{}^2 k_\gamma{}^2) \\ & + C_\beta k_\alpha (Mk^2 k_\beta{}^2 + Nk_\beta{}^2 k_\gamma{}^2) \\ & + C_\gamma k_\alpha (Mk^2 k_\gamma{}^2 + Nk_\beta{}^2 k_\gamma{}^2)]/P(\vec{k}) , \end{aligned} \tag{11}$$

where α, β, and γ again range from 1 through 3, but $\alpha \neq \beta \neq \gamma$. We have

$$P(\vec{k}) = Dk^6 + Bk^2(k_\alpha{}^2 k_\beta{}^2 + k_\beta{}^2 k_\gamma{}^2 + k_\gamma{}^2 k_\alpha{}^2) + Ak_\alpha{}^2 k_\beta{}^2 k_\gamma{}^2 , \tag{12}$$

and the constants A, B, D, E, F, H, M, and N are the functions of the three independent elastic constants of the host lattice given by Eq. (10) and Eq. (20) of Ref. 17. The asymptotic direct-space dis-

TABLE I. Displacement results for octahedral carbon interstitials in α-iron.

Neighbor (L_1, L_2, L_3)	Displacement components of neighbors around an interstitial (units of $2a$) ξ_1	ξ_2	ξ_3	$\lvert\vec\xi\rvert r^2$ + indicates outward relaxation − indicates inward relaxation
1, 0, 0	0.099192	0.0	0.0	+0.099192
0, 1, 1	0.0	−0.020847	−0.020847	−0.058964
1, 2, 0	0.007096	−0.005233	0.0	+0.044086
2, 1, 1	0.018127	0.007699	0.007699	+0.126874
1, 2, 2	−0.002184	−0.005766	−0.005766	−0.075974
3, 0, 0	0.016945	0.0	0.0	+0.152500
0, 3, 1	0.0	−0.005918	−0.003696	−0.069771
3, 2, 0	0.008143	0.002481	0.0	+0.110663
2, 3, 1	0.002808	−0.000964	0.000253	−0.041736
1, 4, 0	0.000946	−0.002749	0.0	−0.049426
3, 2, 2	0.006444	0.003092	0.003092	+0.132393
4, 1, 1	0.007394	0.001862	0.001862	+0.141281
0, 3, 3	0.0	−0.003146	−0.003146	−0.080086
1, 4, 2	−0.000393	−0.002747	−0.001978	−0.071561
2, 3, 3	−0.000616	−0.001955	−0.001955	−0.062270
5, 0, 0	0.005297	0.0	0.0	+0.132428
3, 4, 0	0.002050	−0.000295	0.0	+0.051782
0, 5, 1	0.0	−0.002218	−0.000940	−0.062648
4, 3, 1	0.004021	0.001496	0.000684	+0.112957
3, 4, 2	0.001424	−0.000219	0.000254	+0.042438
5, 2, 0	0.004406	0.001333	0.0	+0.133493
2, 5, 1	0.000585	−0.001341	−0.000258	−0.044550

placements are found by evaluating the expression

$$\xi^l = [iv/(2\pi)^3] \iiint_{\mathrm{FBZ}} \vec{Q}^{\vec{q}-0} \sin(\vec{q}\cdot\vec{r}^{\,l})\, d\vec{q}\ , \tag{13}$$

where v is the volume of a unit cell in the iron lattice and FBZ stands for the first Brillouin zone. The actual evaluation of Eq. (13) is accomplished by a complicated numerical integration procedure, also discussed in Ref. 17.

III. NUMERICAL CALCULATIONS AND RESULTS

The method of lattice statics has been applied to determine the strain-field displacements for 22 nonequivalent neighboring iron atoms in the vicinity of an octahedral carbon interstitial and for 20 such neighbors near a tetrahedral carbon interstitial. The results of these calculations are shown in Tables I and II, respectively. Equation (4) was used to evaluate the strain-field interaction energies between 20 nonequivalent pairs of octahedral carbon interstitials in α-iron and the results of this calculation appear in Table III.

The approach to the numerical computations in the present investigation differs from that of previous lattice-statics calculations[6-8] in two important respects: First, in previous calculations in which the defect had cubic symmetry, it was possible to shorten considerably the computer calculations by making use of the fact that the Cartesian components of the Fourier amplitudes $\vec{Q}^{\vec{q}}$ exhibited the same symmetry as the components of the wave vector $\vec{q}$ itself. Hence, a cyclic permutation of the components of $\vec{q}$ resulted in an identical permutation of the $\vec{Q}^{\vec{q}}$ components. In the calculations presented here this was no longer true. The elements of $\vec{V}^{\vec{q}}$ and $\vec{F}^{\vec{q}}$ had to be permuted separately whenever the q_α were permuted; $\vec{Q}^{\vec{q}}$ was then obtained from the equation

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

However, since the host lattice had cubic symmetry, it was still possible to generate all of the allowed wave vectors $\vec{q}$ in the FBZ of the supercell from the wave vectors contained in $\frac{1}{48}$th of the FBZ.

A second modification to the lattice-statics approach used here involves the manner in which the wave-vector sums in Eqs. (3) and (4) were performed. In previous calculations these sums were evaluated using a regular array of allowed wave vectors within the FBZ of the supercell. The larger the size of the supercell, the more nearly the defect can be considered as being "isolated," and in practice it is generally necessary to consider

TABLE II. Displacement results for tetrahedral carbon interstitials in α-iron.

Neighbor (L_1, L_2, L_3)	Displacement components of neighbors around an interstitial (units of $2a$) ξ_1	ξ_2	ξ_3	$\lvert\vec{\xi}\rvert r^2$ + indicates outward relaxation − indicates inward relaxation
1, $\frac{1}{2}$, 0	0.049356	0.015774	0.0	+0.064769
0, $\frac{3}{2}$, 1	0.0	−0.011910	−0.004437	−0.041308
1, $\frac{1}{2}$, 2	0.006289	0.002658	0.004533	+0.043029
1, $\frac{5}{2}$, 0	0.002234	−0.002320	0.0	+0.023350
2, $\frac{3}{2}$, 1	0.009948	0.006101	0.006443	+0.096646
3, $\frac{1}{2}$, 0	0.005978	0.000348	0.0	+0.055390
0, $\frac{3}{2}$, 3	−0.000796	−0.001037	0.000848	−0.015067
1, $\frac{5}{2}$, 2	0.0	−0.002058	−0.000704	−0.026822
3, $\frac{1}{2}$, 2	0.003580	0.000046	0.002608	+0.058696
0, $\frac{7}{2}$, 1	0.0	−0.003087	−0.000861	−0.042467
2, $\frac{3}{2}$, 3	0.002712	0.001636	0.002512	+0.061647
3, $\frac{5}{2}$, 0	0.003673	0.001643	0.0	+0.061367
1, $\frac{1}{2}$, 4	0.001217	0.000536	0.001894	+0.039926
2, $\frac{5}{2}$, 1	0.001107	−0.000378	0.000565	+0.022407
3, $\frac{5}{2}$, 2	0.003659	0.002404	0.002765	+0.099678
4, $\frac{3}{2}$, 1	0.002868	0.000939	0.001189	+0.062435
1, $\frac{5}{2}$, 4	0.000086	−0.000173	0.000589	+0.014412
2, $\frac{7}{2}$, 3	−0.000049	−0.000369	0.000229	+0.011034
5, $\frac{1}{2}$, 0	0.001441	0.000006	0.0	+0.036392
4, $\frac{3}{2}$, 3	0.002038	0.000553	0.001616	+0.072451

supercells containing at least 64 000 atoms in order to obtain reliable displacements for atoms within a radius of ~$5a$ from the defect. Supercells containing 512 000 atoms have been used in investigating the asymptotic properties of the direct-space displacements, but the increase of computer time with increasing supercell size makes it prohibitive to use larger supercells.

Recently, Boyer and Hardy[15] have used a new approach in evaluating wave-vector sums, which is equivalent to extending the supercell walls to infinity and transforming the wave-vector sum to an integral

$$\frac{1}{N}\sum_{\vec{q}} \to \frac{v}{(2\pi)^3}\iiint_{\text{FBZ}} d\vec{q}\,, \tag{15}$$

where v is atomic volume. As Boyer points out, this integral can be more easily evaluated as an integral over the cube C, which inscribes the more complicated FBZ since

$$\iiint_{\text{FBZ}} f(\vec{q})\,d\vec{q} = \tfrac{1}{2}\iiint_{C} f(q)\,d^3q\,. \tag{16}$$

Hence, Eq. (4) becomes

$$\vec{\xi}^{\,l} = \frac{1}{2}\,\frac{va}{2(\pi)^3}\iiint_{-\pi/a}^{\pi/a} \vec{Q}^{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}^{\,l}}\,d\vec{q}\,. \tag{17}$$

The numerical evaluation of the integral in this expression was performed by a Gaussian quadrature technique, which is discussed in detail by Boyer.[15] Briefly, the Gaussian quadrature method is equivalent to representing the integral in Eq. (17) as a polynomial function in the variables $p_\alpha = q_\alpha a/\pi$. Such an integral can be evaluated numerically by a summation of the form

$$\vec{\xi}^{\,l} = \frac{v}{16}\sum_{i,j,k=0}^{m-1} Q_\alpha^{\vec{p}}\sin(\vec{p}\cdot\vec{r}^{\,l})A_i(p_i)A_j(p_j)A_k(p_k)\,, \tag{18}$$

where the p_i, p_j, and p_k are the roots of the Legendre polynomial of order m and the A_i, A_j, and

TABLE III. Strain-field interaction energies for octahedral carbon interstitials in α-iron.

Neighbor (L_1, L_2, L_3)	Interaction energy (eV) between interstitials at (0, 0, 0) and (L_1, L_2, L_3)
(1, 1, 0)	0.000281
(1, 1, 1)	−0.113536
(2, 0, 0)	0.438958
(0, 2, 0)	−0.075626
(1, 2, 1)	0.000051
(2, 2, 0)	−0.005368
(0, 2, 2)	0.022726
(2, 2, 2)	−0.045519
(3, 1, 0)	−0.000216
(1, 3, 0)	−0.000002
(3, 2, 1)	−0.000028
(1, 2, 3)	−0.000008
(3, 3, 0)	0.000032
(3, 3, 2)	0.000039
(4, 0, 0)	0.062078
(0, 4, 0)	−0.010336
(1, 4, 1)	0.000035
(4, 2, 0)	0.019869
(2, 4, 0)	−0.005914
(4, 2, 2)	0.013211

A_k are weight factors. The roots and weight factors for various orders of Legendre polynomials ranging from $m = 2$ to $m = 96$ have been tabulated in Ref. 18.

The displacement results obtained from the Gaussian quadrature technique do not exhibit the supercell effect since there are no surrounding defects in the lattice. However, the accuracy of numerical results improves with the order m of the polynomial representation of the integrand in Eq. (17). The summations which must be performed in the Gaussian quadrature approach converge much more rapidly than the corresponding wave-vector sums evaluated using a regular array of wave vectors associated with a finite supercell. Hence, it is generally necessary to use only a polynomial of order $m = 20$ to obtain direct-space displacements comparable to those obtained using a supercell containing 64 000 host atoms. The results presented in Tables I–III were obtained using a polynomial representation of order 20. Polynomials of order 40 were used to investigate the asymptotic behavior of atoms surrounding an ocathedral carbon defect along the [100] direction in the lattice.

The exact lattice-statics calculations were performed on the IBM 360/65 at the University of Nebraska at Lincoln, and smaller supporting programs were performed on the NCR 315 at the Univerisity of Nebraska at Omaha.

In addition to the atomic displacements and interaction energies, it is of interest to calculate the relaxation energy E_R associated with a defect.

The relaxation energy, defined as the difference between the energy of the imperfect crystal before and after relaxation, can be expressed, to a second-order approximation, as

$$E_R = \frac{1}{2} \sum_{\alpha, l} \xi^l_\alpha F^l_\alpha \Big|_0 , \tag{19}$$

where the superscript zero indicates that the forces are to be evaluated in the unrelaxed positions. The relaxation energies for the tetrahedral and octahedral configurations are shown in Table IV.

IV. DISCUSSION

In applying the method of lattice statics to determine the properties of interstitial carbon atoms in α-iron we have purposely adopted the host-host and defect-host interactions used by Johnson *et al.*[14] in order that the atomic displacements obtained by the method of lattice statics would be directly comparable to those obtained from a semidiscrete approach. A comparison between the atomic-displacement results of Ref. 14 and the corresponding lattice-statics values for 14 iron atoms near an octahedral carbon interstitial and 10 iron atoms in the vicinity of a tetrahedral interstitial is given in Table V. The semidiscrete results were obtained by considering the 530 host atoms to move as individual particles and treating the remainder of the crystal as an isotropic elastic continuum. It is apparent that the semidiscrete displacements in the octahedral case are consistantly higher than the corresponding lattice-statics results. While there is no definite trend in the tetrahedral case for one set of displacements to be higher or lower than the other, there are certainly noticeable discrepancies between the two sets of results. Also, except for atoms which lie along the high symmetry axes of the crystal, there is no tendency for the Cartesian components of displacement from one set of results to be proportional to the corresponding components in the other set.

It is difficult to make an analytic comparison of the lattice-statics technique to the semidiscrete approach since the defects considered in this case do not exhibit cubic symmetry. In the case of the octahedral interstitial, for example, the defect essentially exerts a direct force only along the [100] direction in the lattice, and the corresponding

TABLE IV. Relaxation energies for carbon interstitials in α-iron.

Symmetry	Relaxation energy (eV) Present work
Octahedral	−1.68
Tetrahedral	−0.94

TABLE V. Comparison of the atomic displacements obtained in the present calculations to those of Ref. 14 (units of a).

Octahedral carbon interstitial

	ξ_1		ξ_2		ξ_3	
Neighbor (L_1, L_2, L_3)	Ref. 14	Present calc	Ref. 14	Present calc	Ref. 14	Present calc
1, 0, 0	0.225	0.198	0.0	0.0	0.0	0.0
0, 1, 1	0.0	0.0	−0.042	−0.042	−0.042	−0.042
1, 0, 2	0.017	0.014	0.0	0.0	−0.014	−0.011
2, 1, 1	0.045	0.036	0.025	0.015	0.025	0.015
3, 0, 0	0.046	0.034	0.0	0.0	0.0	0.0
1, 2, 2	−0.004	−0.004	−0.01	−0.012	−0.01	−0.012
0, 1, 3	0.0	0.0	−0.008	−0.007	−0.012	−0.012
3, 0, 2	0.018	0.016	0.0	0.0	0.007	0.005
2, 1, 3	0.005	0.006	0.001	0.0005	0.0	−0.002
1, 0, 4	0.002	0.002	0.0	0.0	−0.005	−0.005
3, 2, 2	0.015	0.013	0.01	0.006	0.01	0.006
4, 1, 1	0.016	0.015	0.006	0.016	0.006	0.016
0, 3, 3	0.0	0.0	−0.005	−0.006	−0.005	−0.006
1, 2, 4	−0.001	−0.0008	−0.003	−0.004	−0.004	−0.005

Tetrahedral carbon interstitial

	ξ_1		ξ_2		ξ_3	
Neighbor (L_1, L_2, L_3)	Ref. 14	Present calc	Ref. 14	Present calc	Ref. 14	Present calc
0, $\frac{1}{2}$, 1	0.0	0.0	0.029	0.032	0.116	0.099
1, $\frac{3}{2}$, 0	−0.017	−0.008	−0.041	−0.024	0.0	0.0
2, $\frac{1}{2}$, 1	0.011	0.009	0.006	0.005	0.015	0.012
0, $\frac{5}{2}$, 1	0.0	0.0	−0.008	−0.005	0.004	0.004
1, $\frac{3}{2}$, 2	0.015	0.013	0.013	0.012	0.023	0.020
0, $\frac{1}{2}$, 3	0.0	0.0	0.0	0.0007	0.018	0.012
3, $\frac{3}{2}$, 0	0.001	0.002	−0.003	−0.002	0.0	0.0
2, $\frac{5}{2}$, 1	−0.004	−0.001	−0.007	−0.004	−0.004	−0.002
1, $\frac{7}{2}$, 0	−0.003	−0.002	−0.008	−0.006	0.0	0.0
2, $\frac{1}{2}$, 3	0.006	0.005	0.0	0.0	0.008	0.007

contraction of the lattice in the vicinity of the (011) plane is primarily due to the host-host interaction. It would seem that assuming a portion of the crystal to act as an isotropic medium might have a rather strong influence on the nature of the displacement results obtained in this case.

In general, as we have pointed out before[8,17] there appear to be two possible sources of discrepancy between the results obtained from a semidiscrete calculation. The first is that the lattice-statics results are exact only within the harmonic approximation, i.e., in the expansion of the lattice energy only terms out to the second order in the expansion are retained. It should be stressed, however, that the defect-host interaction has been used exactly throughout the present calculation and only the host-host interaction has been treated in the harmonic approximation. The largest relative displacement between any two host atoms in the vicinity of an octahedral carbon interstitial occurs between the atoms at (1, 0, 0) and (3, 0, 0) and amounts to approximately 8% of the perfect-lattice separation between the two. The direct interaction energy between these two atoms calculated using the exact potential Φ_I varies from that obtained from the harmonic expansion of Φ_I by only a few tenths of a percent. It does not seem, therefore, that anharmonic effects should contribute greatly to the discrepancies noted between the lattice-statics and semidiscrete results.

A second source of discrepancy arises from the approximation made in semidiscrete calculations that elasticity theory is valid beyond some arbitarily chosen distance from the defect. If this "cutting radius" is too small, the effect will be equivalent to imposing a nonphysical constraint on the motion of the atoms in the discrete region.

Since the equations of lattice statics in the limit as $\vec{q} \to 0$ are identical to those of elasticity theory, it is possible to determine the distance from the defect at which elasticity theory becomes valid by comparing the results of the exact lattice-statics calculation for atoms far from the defect to the corresponding results obtained from the asymptotic lattice statics.

In an elastic continuum the value of $|\vec{\xi}|r^2$ will be a constant for any given direction in the medium. Hence, the values of $|\vec{\xi}|r^2$ obtained from exact lattice statics for atoms along a given crystallographic direction will approach a constant limit as one considers atoms sufficiently far away from the defect. Exact lattice-statics results have been obtained for $|\vec{\xi}|r^2$ for atoms lying along the [100] and [011] directions relative to an octahedral carbon interstitial oriented as shown in Fig. 1(a). Atoms as far away as (37, 0, 0) were considered in the first case and as far as (0, 37, 37) in the second. The Gaussian quadrature technique was used to evaluate the lattice-statics equations, using a polynomial of $m = 40$ to represent the integral in Eq. (17). A plot of $|\vec{\xi}|r^2$ as a function of r along the [100] direction is shown in Fig. 2. It is apparent that the asymptotic limit is not attained within the distance shown on the plot. It is quite obvious that the elastic regime has not been approached at a distance of $8a$ from the defect, which is the cutting radius assumed by Johnson *et al.*[14]

Figure 3 shows the variation of $|\vec{\xi}|r^2$ as a function of $\sqrt{2}r$ along the [011] direction in the lattice. The $|\vec{\xi}|r^2$ curve crosses the asymptotic limit in this case at a distance of about $40a$ from the defect, and one can only assume that it oscillates about the limit before settling down at some greater distance from the defect. In any case, it is again apparent that elasticity theory is certainly not valid within a radius of $8a$ from the defect.

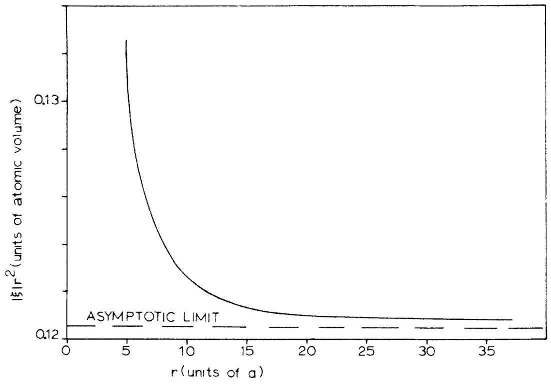

FIG. 2. $|\vec{\xi}|r^2$ calculated from exact lattice statics as a function of distance from the octahedral interstitial along the [100] direction in α-iron. The dotted line shows the elastic limit predicted by elasticity theory (0.1205 atomic volume).

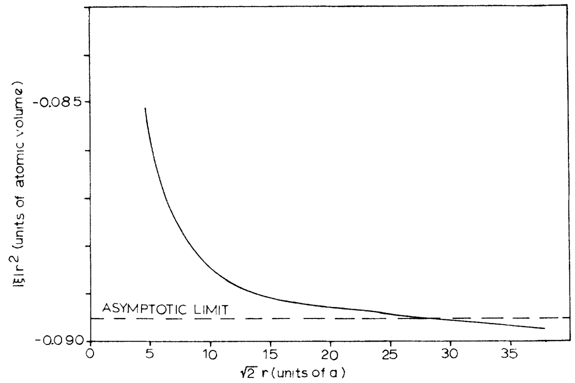

FIG. 3. $|\vec{\xi}|r^2$ calculated from exact lattice statics as a function of $\sqrt{2}r$ from the octahedral defect along the [011] direction in α-iron. The dotted line show the elastic limit predicted by elasticity theory (−0.089 53 atomic volume).

Johnson *et al.*[14] calculated the strain-field interaction energies between pairs of octahedral carbon atoms and found binding energies of 0.13, 0.11, and 0.108 eV for the [111], [020], and [210] interstitial pairs. These values compare favorably with the values shown in Table III for the [111] and [020] orientations. The interaction energy for the [210] case was not calculated. Binding energies greater than 0.01 eV were also found for the [222] and [040] interstitial pairs. As one would expect, the [200] and [400] interstitial pairs show large repulsive interaction energies. The values shown in Table III represent only the strain-field interaction energies; since the direct carbon-carbon interaction has not been specified, the total interaction energy between these carbon interstitials can not be found.

Although no relaxation energies as such are quoted in Ref. 10, if one assumes that the tetrahedral configuration is the saddle point for the migration of carbon interstitials, the lattice-statics results yield a value of 0.27 eV for the migration energy. This is considerably different from the experimental value of 0.86 eV used by Johnson *et al.*[14] in determining the parameters of the carbon-iron interaction. The migration energy depends upon the relaxation energies of the tetrahedral and octahedral configurations as well as the energy required for direct defect-host bond formation in the unrelaxed lattice. The latter quantity is the same in both the direct-space and lattice-statics calculations. The relaxation energies, on the other hand, are calculated in different ways in the two approaches. Equation (19) for the relaxation energy is admittedly an approximation, but has been checked against the work of others[7] and found to give reasonably good numerical results. It is interesting to note that if one used the displacements of Ref. 14 in Eq. (19) of this paper, one obtains a migration energy of 0.36 eV, rather than 0.86 eV as claimed in Ref. 14. However, if one neglects the energy due to direct bonds and merely takes the difference between the *relaxation* energies using the direct-space displacements, one obtains a value of 0.83 eV, which is in very good agreement with the experimental value of *migration* energy.

V. SUMMARY

The method of lattice statics has been extended to treat point defects which do not exhibit cubic symmetry. The resulting equations have been applied to determine the strain-field displacements about isolated octahedral and tetrahedral interstitials in α-iron as well as strain-field interaction energies between pairs of octahedral carbon interstitials. The strain-field displacements have been utilized to calculate the relaxation energies associated with the tetrahedral interstitial.

The atomic displacements obtained by means of exact lattice statics were compared to the corresponding results obtained from a semidiscrete calculation[14] using identical interatomic potentials. While the over-all agreement between the two sets of results is rather good, discrepancies do exist due to certain approximations made in the two different approaches. A comparison of the exact lattice-statics results with those of the asymptotic theory indicates that the discrepancies which do exist arise primarily from the choice of cutting radius used in the semidiscrete calculations.

The discrepancies observed in the present case are not as large as those found in earlier investigations,[6-8] and the lattice-statics results agree quite well with the direct-space results for experimentally observable quantities such as the strain-field interaction energies and the migration energy. In addition, the qualitative results of the lattice-statics calculation agree quite well with those presented in Ref. 14. It is apparent, for example, that the octahedral carbon interstitial is much more stable than the tetrahedral interstitial, and the directions in which various atoms relax in the vicinity of the defect are the same in both cases. It is only the actual numerical results which differ somewhat as a result of the approximations used in the two approaches. However, the lattice-statics results are exact within the limits of the harmonic approximation which, in the present case, appears to be valid. The successful application of lattice-statics theory to noncubic defects should provide the groundwork for the extension of this very powerful technique to multiple defects and the calculation of atomic relaxations near crystal surfaces.

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