Application of the Method of Lattice Statics to Vacancies in α Iron

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The author has calculated the strain-field displacements produced by a single vacancy in α iron and has also calculated the strain-field interaction energies associated with pairs of such defects. These calculations were carried out using the method of lattice statics, which is based on the Fourier transformation of the direct-space force equations within a large "supercell" of the lattice. The author has also calculated the asymptotic displacements about a vacancy in α iron and compared these with the corresponding results obtained from the exact method of lattice statics. This comparison shows that elasticity theory cannot be assumed valid closer than the 14th neighbor to the defect along a $\langle 1\,1\,1 \rangle$ direction in α iron. Since the interatomic potential used consists of a set of splines extending out only to next-nearest neighbors, there is a strong implication that the long-range approach to the asymptotic limit is a feature of the open structure of the bcc lattice. Comparison has been made between these displacements and analogous results obtained by a semidiscrete method in which a spherical crystallite containing 530 atoms was treated on a discrete basis. Differences ranging from 5 to 11% are found between the results of the lattice statics calculation and those obtained from the semidiscrete approach. The interaction energy results show that the next-nearest-neighbor divacancy configuration is the most stable, and the nearest-neighbor pair is the next most stable configuration. The only other vacancy pair having a significant binding energy is that in which the vacancies are fourth-nearest neighbors.

I. INTRODUCTION

When defects are introduced in a crystal lattice, they give rise to a macroscopic volume change in the crystal, a change in electrical resistivity, and a diffuse x-ray scattering component superposed on the normal Bragg peaks of the lattice. In addition, the energy stored in the lattice, as the atoms of the host material relax in the presence of the defect, determines the energy necessary to form the defect and contributes to the activation energy of a defect and to the interaction energy between pairs of defects in the lattice.

In order to accurately determine the changes in physical characteristics induced by a defect and to understand the behavior of the defect itself, it is necessary to have an explicit knowledge of the atomic displacements in the imperfect crystal.

The most common methods of determining these strain-field displacements involve what might be called a "semidiscrete" approach. In this type of calculation the crystal is divided into two regions: Region I contains the defect and a certain number of host atoms which are allowed to interact by means of pairwise interatomic potentials; region II consists of the rest of the crystal and is treated as if it were an elastic continuum.

The displacements of the atoms in region I are found by minimizing the energy in that region with the constraint that the displacements of the atoms on the boundary between regions I and II must be equal to the displacements which would be predicted by elasticity theory.

Recently, a new approach to this type of problem, which we refer to as the method of lattice statics, has been applied to various types of point-defect problems. This technique is based on Fourier transforming the direct-space equilibrium equations to reciprocal space. This leads to a set of decoupled equations which can be solved for the Fourier amplitudes of the direct-space displacements by direct matrix inversion. The direct-space displacements can then be found by Fourier inversion.

Since the Fourier amplitudes are often a more convenient set of generalized coordinates with which to work than the real-space displacements, the calculation of quantities such as x-ray diffuse scattering intensities and strain-field interaction energies between pairs of defects can best be done completely in reciprocal space.

Unlike the semidiscrete methods, which are dependent upon elasticity theory being correctly applied at the boundaries between regions I and II, the method of lattice statics allows all of the atoms in the crystal to relax on an individual basis. Moreover, if the equations of lattice statics are evaluated in the limit of small wave vectors, one obtains an "asymptotic" form of the lattice statics equations which are exactly analogous to the equations of elasticity theory. Hence, by comparing the displacements obtained from the exact theory with the results of asymptotic calculations, one can determine the distance from the defect at which elasticity theory becomes valid.

In a number of recent papers,[1-4] Hardy and
Flocken have presented the results of lattice stat-
ics calculations for interstitial Cu atoms in Cu and
vacancies in Na, K, Cs, and Rb, using both the ex-
act and the asymptotic lattice statics equations.
The most crucial result of these investigations is
that in every semidiscrete treatment of these spe-
cific problems, elasticity theory was assumed to be
valid much closer to the defect than is actually the
case. This discrepancy was found to be most pro-
nounced in the relatively open "soft" lattices of the
alkali metals, in which the elastic regime was not
attained along the $\langle 111 \rangle$ direction until the 26th or
27th neighbor from the defect. The elastic limit
was reached nearer the defect in the case of the in-
terstitial Cu atom in Cu but was still well beyond
the region-I boundaries chosen for any semidis-
crete calculations.

The long-range asymptotic approach to the elas-
tic limit in the alkali metals could be ascribed ei-
ther to the rather "open" bcc structure of these
materials or to the relatively long-range interac-
tion potentials, extending out to fifth-nearest neigh-
bors, which were used in the lattice statics calcu-
lations. The present paper, which presents the
results of lattice statics calculations for vacancies
in α iron, is a continuation of the investigation con-
tained in Refs. 1–4. α iron has the same bcc
structure as the alkali metals, but its lattice is
considerably stiffer. A long-range approach to the
elastic limit in this material would therefore tend
to indicate that the open structure of the lattice
plays a more important role in producing the effect
than does the form of the interatomic potential. As
will be seen, this seems to be the case. Moreover,
if significant discrepancies are found to exist be-
tween the results of lattice statics calculations and
semidiscrete calculations in α iron, one would ex-
pect even more serious disagreements for other
metals having the bcc structure.

In Sec. II is presented a brief review of the lat-
tice statics approach and a description of the in-
teratomic potential used in the calculations. In
Sec. III is discussed the calculation of the strain-
field displacements and interaction energies asso-
ciated with vacancies in α iron. Section IV con-
tains a comparison of the exact lattice statics re-
sults with those obtained from calculations using
the asymptotic theory and with the corresponding
results of a semidiscrete calculation.[5] Section V
is a summary of the conclusions drawn from this
work.

II. THEORETICAL APPROACH

A detailed discussion of the method of lattice
statics has been given elsewhere[1,2] and will not be
repeated here. Instead, the author will give a

brief outline of the method along with a statement
of the equations used in the calculations.

In setting up the equations of lattice statics we
consider an infinite lattice divided into a number of
equivalent volumes called supercells, each con-
taining a defect at the center and a large number
N of host atoms. The boundaries of the supercells
are taken to be $L\vec{a}_1 + L\vec{a}_2 + L\vec{a}_3$, where $\vec{a}_1$, $\vec{a}_2$, and
$\vec{a}_3$ are the basic vectors of an infinite lattice. The
lattice can therefore be considered to be an infinite
"superlattice" of defects; by applying periodic
boundary conditions across the faces of a supercell
it becomes necessary to determine atomic displace-
ments only within a single supercell.

We assume further that the defect will interact
with the host atoms by means of a pairwise poten-
tial $\phi(r)$. We take the defect itself as the origin of
coordinates and denote the position of the lth host
atoms from the defect by the position vector $\vec{r}^l$
$+ \vec{\xi}^l$, where $\vec{r}^l$ is the position vector of the lth atom
in the perfect lattice and $\vec{\xi}^l$ is the displacement of
that atom in the presence of the defect.

In a cubic lattice it is convenient to establish a
set of Cartesian coordinates with the defect at the
origin and the axis taken along the $\langle 100 \rangle$ directions
in the crystal. The potential energy of the distort-
ed lattice can be written as

$$U = U_0 + \sum_l \phi\left(\left| \vec{r}^l + \vec{\xi}^l \right|\right) + \tfrac{1}{2} \sum_{ll',\alpha\beta} \xi_\alpha^l \Psi_{\alpha\beta}^{ll'} \xi_\beta^{l'}, \quad (1)$$

where α and β run 1–3 and refer to the three-com-
ponent axes of the Cartesian coordinates. U_0 is the
energy of the perfect undistorted lattice, and $\Psi_{\alpha\beta}^{ll'}$
is the $3N \times 3N$ force-constant matrix for the per-
fect lattice.

Minimizing U with respect to the set of displace-
ments gives a set of direct-space equilibrium equa-
tions which can be written as

$$F_\alpha^l = \sum_{l'} \sum_\beta \Psi_{\alpha\beta}^{ll'} \xi_\beta^{l'}, \quad (2)$$

where

$$F_\alpha^l = -\frac{\partial \Psi}{\partial \xi_\alpha^l}\left(\left| \vec{r}^l + \vec{\xi}^l \right|\right) \quad (3)$$

is the αth component of the direct-space force ex-
erted by the defect on the lth host atom.

The crucial step in the method of lattice statics
is the transformation to reciprocal space, which
is made at this point by introducing the normal co-
ordinates $\vec{Q}^{\vec{q}}$ in the equation

$$\xi^l = N^{-1} \sum_{\vec{q}} \vec{Q}^{\vec{q}} e^{i\vec{q} \cdot \vec{r}^l}, \quad (4)$$

where the sum is over the N allowed wave vectors
$\vec{q}$ in the first Brillouin zone of the superlattice.
Substituting Eq. (4) into Eq. (2), we obtain a set
of equilibrium equations in reciprocal space which

we express as

$$F_\alpha^{\vec{q}} = \sum_\beta V_{\alpha\beta}^{-\vec{q}} \, Q_\beta^{-\vec{q}} \ , \tag{5}$$

where we have made the definitions

$$F_\alpha^{\vec{q}} = \sum_l F_\alpha^l e^{-i\vec{q}\cdot\vec{r}^l} \ , \tag{6}$$

$$V_{\alpha\beta}^{-\vec{q}} \equiv \sum_{l'} \left(\frac{\partial^2 U}{\partial\xi_\alpha^l \, \partial\xi_\beta^{l'}} \right)_0 e^{i\vec{q}\cdot\vec{r}^{l'}} \ . \tag{7}$$

The subscript zero indicates that the force constants and their derivatives are evaluated at the undistorted lattice sites. It can be seen that the original set of direct-space equilibrium equations has been decoupled into a set of 3×3 independent matrix equations, one for each of the allowed wave vectors in the Fourier series. Once the Fourier amplitudes $\vec{Q}^{\vec{q}}$ have been found, the direct-space atomic displacements can be obtained by performing the back transformation indicated in Eq. (4).

One can, as well, apply the method of lattice statics to find quantities other than the direct-space displacements themselves. For example, the strain-field interaction energy between pairs of defects in the lattice can be shown[6] to be given by

$$E = -N^{-1}\sum_{\vec{q}} \vec{F}^{-\vec{q}} (\vec{V}^{-\vec{q}})^{-1}\vec{F}^{\vec{q}} \cos(\vec{q}\cdot\vec{R}) \ , \tag{8}$$

where $\vec{R}$ is the interdefect separation vector.

From Eqs. (5) and (8), it is apparent that all that is needed to perform a lattice statics calculation is the dynamical matrix $\vec{V}^{-\vec{q}}$ of the host lattice and the generalized force array $\vec{F}^{\vec{q}}$. In order to obtain the latter, one must perform the sum indicated in Eq. (6), in which the $\vec{F}^l$ are the defect-host forces evaluated at the relaxed positions of the host atoms in the imperfect lattice. If one knows the explicit form of the potential $\phi(r)$, the direct-space forces can be expressed as a function of the displacements $\vec{\xi}^l$ of those atoms which interact directly with the defect. One can then find the displacements $\vec{\xi}^l$ and forces $\vec{F}^l$ associated with those particular atoms by solving a set of equilibrium equations given by

$$\vec{\xi}^l = \sum_{l'} \rho^{ll'} F^{l'}(\xi) \ . \tag{9}$$

The matrix $\rho^{ll'}$ is called the response matrix of the crystal and gives the displacement of the lth atom from the defect when the defect-induced force on the l'th atom is 1 and all other defect-host forces are 0. The elements of the response matrix are themselves determined by a preliminary lattice statics calculation, letting each of the $\vec{F}^l$, in turn, be 1 and all other defect-host forces be 0.

In the limit as $\vec{q}\to0$, the equations of lattice statics take the form

$$\xi_\alpha^l = [G/(\pi a)^3]$$

$$\times \iiint \frac{q_1(Eq^4 + Fq_1^2q^2 + Hq_2^2q_3^2)\sin(\vec{q}\cdot\vec{r}^l)\,d^3q}{Dq^6 + Bq^2(q_1^2q_2^2 + q_2^2q_3^2 + q_3^2q_1^2) + Aq_1^2q_2^2q_3^2} \ , \tag{10}$$

where a is half of a cubic cell edge in the lattice and the constants E, F, H, D, B, and A are simple functions of the three independent elastic constants in a cubic crystal.[7] The constant G is called the strength parameter of the defect. In the lattice statics formalism, this constant can be shown for a cubic defect to be given by[7]

$$G = \sum_l F_\alpha^l \, r_\alpha^l \ , \tag{11}$$

where α is any *one* of the three Cartesian coordinates, but is not summed over. In addition, Hardy[7] has shown that the volume change induced by a defect in a crystal is given by

$$\Delta V = G/K \ , \tag{12}$$

where K is the bulk modulus of the crystal.

In the case of a vacancy, the direct-space forces can be determined without any explicit knowledge of the interatomic potential. However, for α iron, an explicit expression for the interatomic potential has been derived by Johnson[5] from the elastic constants and the threshold energy for radiation damage in the crystal. This potential is made up of three "splines" or sections of cubic equations joined in value and slope at two arbitrary boundary points. The potential and boundary points are shown in Table I. For convenience, we will refer to the ranges 1.9–2.4 Å as zone I, 2.4–3.0 Å as zone II, and 3.0–3.44 Å as zone III.

The first- and second-nearest-neighbor distances both fall within zone II and the potential in this region was obtained by integrating a parabolic curve for $\phi(r)$ chosen to match the elastic moduli of the perfect lattice. The potential for zone III was obtained from another parabolic curve which was matched in value and slope to the $\phi'(r)$ curve of zone II and which goes to 0 midway between the second- and third-nearest-neighbor positions. Once the potential $\phi(r)$ was determined for zone II, the potential for zone I was obtained by choosing a cubic equation which matched the potential of zone II in value and slope at 2.4 Å from the defect and which matched in value and slope a dynamical potential derived by Erginsoy *et al.*[8] from radiation damage considerations.

In attempting to use the Johnson potential of Ref. 5 in the lattice statics calculations presented in this paper, certain difficulties were encountered which made it necessary to modify the potential slightly. In the lattice statics approach, the second derivatives $\phi''(r)$ of the interatomic potential appear as force constants in the dynamical matrix $\vec{V}^{-\vec{q}}$. Since the potentials of zones II and III were obtained by integrating curves for $\phi(r)$, which were

TABLE I. Interatomic potentials in α iron.

Zone	Range (Å)	Potential (eV)
A. Potential of Ref. 5		
I	1.9–2.4	$-2.195\,976\,(r-3.097\,910)^3 + 2.704\,060r - 7.436\,448$
II	2.4–3.0	$-0.639\,230\,(r-3.115\,829)^3 + 0.477\,871r - 1.581\,570$
III	3.0–3.44	$-1.115\,035\,(r-3.066\,403)^3 + 0.466\,892r - 1.547\,967$
B. Modified potential		
I	$1.35 - r_b$	$-11.608\,415\,(r-2.396\,716)^3 - 0.571\,601r + 1.170\,619$

matched in value and slope at the boundary between these two zones, $\phi''(r)$ is continuous at this bound-ary. However, the potential curve for zone I was not obtained from such an integration, $\phi(r)$ and $\phi'(r)$ were made continuous at the boundary between zones I and II, but $\phi''(r)$ was not. Indeed, the value of $\phi''(r)$ obtained by evaluating the zone-I poten-tial at $r = 2.4$ Å is more than three times as large as $\phi''(r)$ obtained at the same point using the poten-tial of zone II.

There is no inherent difficulty in this discrepancy as long as the nearest neighbor to the defect re-mains outside of zone I after relaxing to its new equilibrium position. This is the case for the semidiscrete calculation but not for the lattice stat-ics treatment. The abrupt "stiffening" of the force constants at the zone-I boundary makes the prob-lem virtually insoluble using the potential of Ref. 5 as given.

In modifying the Johnson potential, the equations for $\phi(r)$ for zones II and III were not changed. The arbitrary boundary point at 2.4 Å between zones I and II was discarded, and the new boundary point was designated r_b and became a variable of the cal-culation. In order to determine r_b and the four constants in the potential equation for zone I, five simultaneous boundary equations were needed. Three of these were provided by the conditions that $\phi(r)$, $\phi'(r)$, and $\phi''(r)$ be continuous across the boundary between zones I and II. The remaining two equations were provided by matching the zone-I potential and its slope to the Erginsoy[8] potential at a suitable point near the defect.

The Erginsoy potential has the form

$$\phi(r) = 8573.\,0e^{-6.547r} \text{ eV}$$

in the range $0.7\,a$–$1.9\,a$, where r is in units of a, which is half of a cubic cell edge. It is the form of the potential in this range which determines the threshold energy of radiation damage in the crys-tal. After considering several points within this range, a reasonable match to the Erginsoy poten-tial and the Johnson[5] potential was obtained by matching the former at $1.35\,a$ from the defect. The boundary r_b between zones I and II was then

found to be at 2.3548 Å from the defect. The modi-fied zone-I potential is shown in part B of Table I.

A comparison of the modified Johnson potential to the Erginsoy potential in the range 1.3–2.0 Å is shown in Fig. 1; a comparison of the modified potential to the Johnson potential of Ref. 5 and the Erginsoy potential in the range 2.0–3.0 Å is shown in Fig. 2.

III. NUMERICAL CALCULATIONS OF DISPLACEMENTS AND INTERACTION ENERGIES

We have used the modified Johnson potential $\phi(r)$ described in Sec. II to evaluate the displace-ments of host atoms about a single vacancy in α iron and to obtain the strain-field interaction ener-gy between pairs of such defects. The defect-host interaction potential for these calculations was tak-
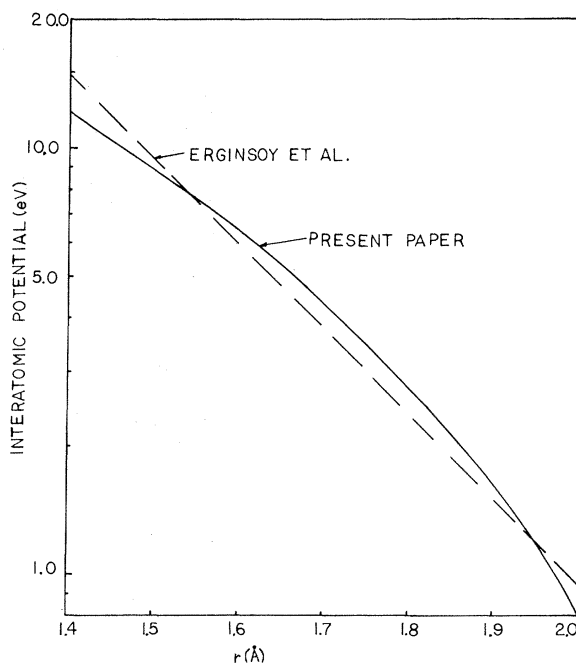

FIG. 1. Comparison of the interatomic potential of Ref. 8 with that used in the present paper for the range 1.4–2.0 Å.
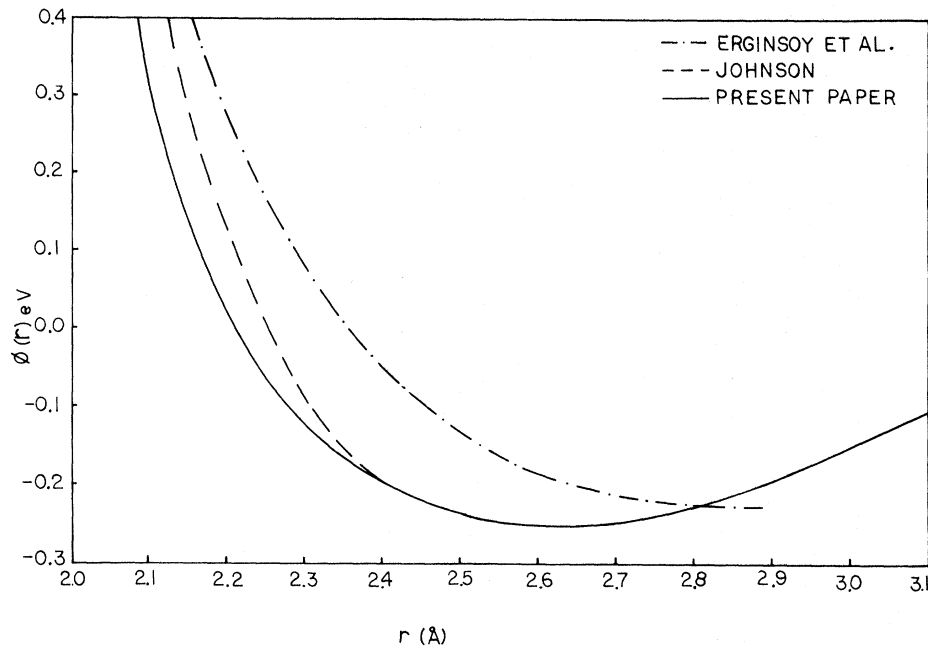
FIG. 2. Comparison of the interatomic potential of Refs. 5 and 8 with that used in the present paper for the range 2.0–3.1 Å. The potential of Ref. 5 is identical to the present potential beyond 2.4 Å.

en as $-\phi(r)$, the negative of the host-host interaction. Atomic displacements were obtained using both the exact lattice statics theory and the asymptotic theory. According to elasticity theory, the displacements in any given direction should fall off inversely as the square of the distance from the defect, so that for any crystallographic direction in the lattice, $|\vec{\xi}| r^2$ should be a constant and should be equal to the value obtained from the asymptotic theory for this quantity.

Table II shows the displacements of the 40-nearest neighbors to the defect and the interaction energies for pairs of defects for which one defect is at $(0, 0, 0)$ and the other at $(L_1 a, L_2 a, L_3 a)$ in the lattice. In addition, the value of $|\vec{\xi}| r^2$ is shown for each displacement. The supercell used in these calculations contained $N = 64\,000$ host atoms.

It is quite apparent that values of $|\vec{\xi}| r^2$ along the more prominent directions in the crystal, such as the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, do not settle down to a constant elastic limit within a range of $8\,a$ from the defect. Therefore, in order to determine the distance from the defect at which the elastic limit is reached, it was necessary to perform a more extensive calculation using a supercell containing $512\,000$ host atoms. Because of the large amounts of computer time involved in such a calculation, displacements were obtained only for atoms lying along the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions in the lattice.

Figure 3 shows $|\vec{\xi}| r^2$ plotted against r for the $\langle 100 \rangle$ direction. Figure 4 shows $|\vec{\xi}| r^2$ as a function of $\sqrt{2}\, r$ in the $\langle 110 \rangle$ direction, and Fig. 5

shows $|\vec{\xi}| r^2$ as a function of $\sqrt{3}\, r$ along the $\langle 111 \rangle$ direction. In each figure the elastic limit is indicated by a horizontal line.

The strength of the defect G and the dilatation ΔV, given by Eq. (11) and Eq. (12), respectively, have been computed and are shown in Table III. We have also calculated the relaxation energy, which is defined as the difference between the energy of the imperfect crystal before and after the atoms are allowed to relax to their equilibrium positions. It has been shown elsewhere[2] that the relaxation energy can be expressed as

$$E_R = \tfrac{1}{2} \sum_{\alpha,l} \xi_\alpha^l F_\alpha^l \Big|_0 \, ,$$

provided one retains only terms up to second order in ξ. The subscript 0 indicates that the forces are to be evaluated in the unrelaxed positions. The relaxation energy is also given in Table III.

The modification of the Johnson potential and certain preliminary lattice statics calculations were carried out on the NCR 315 at the University of Nebraska at Omaha. The remainder of the calculations were done on the IBM 360/65 at the University of Nebraska, Lincoln campus.

IV. DISCUSSION

One of the most interesting features of our calculations is that we can compare the displacement results obtained from exact lattice statics to the corresponding results of the asymptotic theory and thereby determine the distance from the defect at which elasticity theory becomes valid. It is ap-

TABLE II. Displacement and interaction energy results for α iron.

Neighbor (L_1, L_2, L_3)	Interaction energy in eV between $(0, 0, 0)$ and (L_1, L_2, L_3) vacancies	Displacement components of neighbors around a vacancy (units of $2a$)			$\lvert\xi\rvert(L_1^2+L_2^2+L_3^2)$ + indicates outward relaxation − indicates inward relaxation
		ξ_1	ξ_2	ξ_3	
111	0.090 43	−0.016 10	−0.016 10	−0.016 10	−0.083 68
200	−0.027 61	0.026 99	0.0	0.0	+0.1080
220	0.041 08	−0.003 205	−0.003 205	0.0	−0.036 26
222	0.027 15	−0.005 565	−0.005 565	−0.005 565	−0.1157
311	−0.045 56	0.001 588	0.001 504	0.001 504	+0.029 20
331	0.014 67	−0.001 209	−0.001 209	−0.000 2403	−0.032 81
333	0.009 068	−0.002 035	−0.002 035	−0.002 035	−0.095 15
400	0.040 67	0.003 019	0.0	0.0	+0.048 30
420	−0.006 081	0.000 0870	−0.000 0366	0.0	+0.001 889
422	−0.011 50	−0.000 0957	0.000 0653	0.000 0653	−0.003 192
440	0.003 084	−0.000 5688	−0.000 5688	0.0	−0.025 74
442	0.003 801	−0.000 5911	−0.000 5911	−0.000 1999	−0.030 94
444	0.003 268	−0.000 8189	−0.000 8189	−0.000 8189	−0.068 09
511	−0.000 237	0.000 5997	0.000 2902	0.000 2902	+0.019 62
531	−0.000 955	−0.000 1528	−0.000 1189	−0.000 0282	−0.006 849
533	−0.003 013	−0.000 2922	−0.000 1871	−0.000 1871	−0.016 95
551	0.001 190	−0.000 3154	−0.000 3154	−0.000 0451	−0.022 86
553	0.001 060	−0.000 3380	−0.000 3380	−0.000 1667	−0.029 87
555	0.001 160	−0.000 3814	−0.000 3814	−0.000 3814	−0.049 54
600	0.003 887	0.000 4428	0.0	0.0	+0.015 94
620	−0.000 712	0.000 1677	0.000 0798	0.0	+0.007 431
622	−0.000 756	0.000 1150	0.000 0873	0.000 0873	+0.007 425
640	−0.000 258	−0.000 1462	−0.000 1236	0.0	−0.009 956
642	−0.000 190	−0.000 1674	−0.000 1344	−0.000 0528	−0.012 38
644	−0.000 721	−0.000 2397	−0.000 1783	−0.000 1783	−0.023 68
660	0.000 472	−0.000 1924	−0.000 1924	0.0	−0.019 59
662	0.000 453	−0.000 1959	−0.000 1959	−0.000 0524	−0.021 43
664	0.000 334	−0.000 2071	−0.000 2071	−0.000 1266	−0.028 08
666	0.000 427	−0.000 2019	−0.000 2019	−0.000 2019	−0.037 76
711	0.000 350	0.000 1594	0.000 0494	0.000 0494	+0.008 875
731	−0.000 343	0.000 0184	0.000 0098	0.000 0046	+0.001 259
733	−0.000 465 5	−0.000 0317	−0.000 0105	−0.000 0105	−0.002 349
751	−0.000 038 28	−0.000 1246	−0.000 1062	−0.000 0162	−0.012 34
753	−0.000 031 39	−0.000 1396	−0.000 1164	−0.000 0606	−0.015 90
755	−0.000 137 0	−0.000 1694	−0.000 1333	−0.000 1333	−0.025 10
771	0.000 212 7	−0.000 1282	−0.000 1282	−0.000 0155	−0.018 01
773	0.000 184 6	−0.000 1312	−0.000 1312	−0.000 0504	−0.020 57
775	0.000 126 0	−0.000 1353	−0.000 1353	−0.000 0939	−0.026 21
777	0.000 166 2	−0.000 1211	−0.000 1211	−0.000 1211	−0.030 83
800	0.000 376 8	0.000 1003	0.0	0.0	+0.006 42

parent, from consideration of the values of $\lvert\vec{\xi}\rvert\,r^2$ given in Table II for various directions in the lattice, that the elastic regime is not attained within a radius of 8 a from the defect.

In order to examine $\lvert\vec{\xi}\rvert\,r^2$ for more distant neighbors, exact lattice statics calculations were done for the $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ directions using a supercell containing 512 000 host atoms, and these results are shown graphically in Figs. 3–5. The asymptotic values of $\lvert\vec{\xi}\rvert\,r^2$ for each of these directions are shown in each figure by a horizontal line.

From Fig. 3, which shows the variation of $\lvert\vec{\xi}\rvert\,r^2$ as a function of r along $\langle 100\rangle$, it appears that the asymptotic limit is not attained until one is about 18 a from the defect. It is possible that elasticity theory is actually valid somewhat nearer the defect since the $(18, 0, 0)$ neighbor is relatively close to the zone boundary at $(20, 0, 0)$. Hence, the neighboring defect at $(40, 0, 0)$ undoubtedly contributes something to the displacement of the $(18, 0, 0)$ atom. On the other hand, the value of $\lvert\vec{\xi}\rvert\,r^2$ for the $(8, 0, 0)$ neighbor obtained using a supercell of 64 000 atoms only varies in the third significant figure from the corresponding value obtained using a supercell of 512 000 atoms.
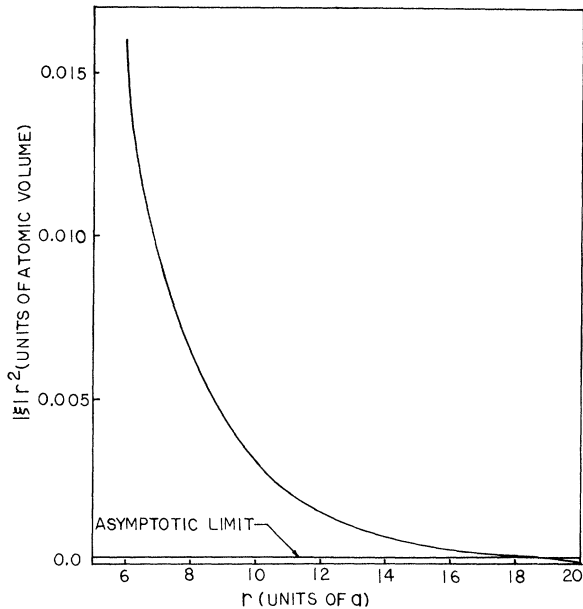
FIG. 3. $|\xi|r^2$ calculated from exact lattice statics, as a function of distance r from the defect along $\langle 1\ 0\ 0 \rangle$ in α iron. A sample of 512 000 wave vectors was used. The horizontal line shows the elastic limit predicted by the asymptotic theory (0. 002 02 at. vol.).

Hence, this value is quite reliable and is definitely not close to the asymptotic limit. Based on previous calculations, we feel that the displacements for neighbors out to (14, 0, 0) will not change appreciably when larger supercell sizes

are used and elasticity theory is therefore not expected to be valid closer than 14 a from the defect in this direction.

In Fig. 4 we show $|\vec{\xi}|\ r^2$ as a function of $\sqrt{2}\ r$ along the $\langle 110 \rangle$ direction. It is difficult in this case to assess the effect of the surrounding defects; such influences apparently become effective rather close to the defect. There is certainly no tendency for the $|\vec{\xi}|\ r^2$ curve to level off at the asymptotic limit, which intersects the curve at the (14, 14, 0) site. The tendency is for values of $|\vec{\xi}|\ r^2$ to drop slightly as larger supercell sizes are utilized, so that the curve extending from (10, 10, 0) out to at least (16, 16, 0) should probably lie entirely below the asymptotic limit. If this is the case, one would not expect the crystal to behave as an elastic continuum closer than about 19. 8 a from the defect.

In Fig. 5, which shows $|\vec{\xi}|\ r^2$ versus $\sqrt{3}\ r$ along $\langle 111 \rangle$, the approach to the elastic limit is better defined than along either of the two directions considered previously. There is a definite tendency for the curve to settle down to the elastic limit at about (13, 13, 13). Interference from neighboring defects becomes noticeable just beyond that point, but it seems fairly certain that the asymptotic limit is not attained much closer to the defect than the 12th nearest neighbor in the $\langle 111 \rangle$ direction.

Another important aspect of these calculations is that the present results can be compared directly to those obtained by Johnson[5] using a semidiscrete approach. Displacement results obtained
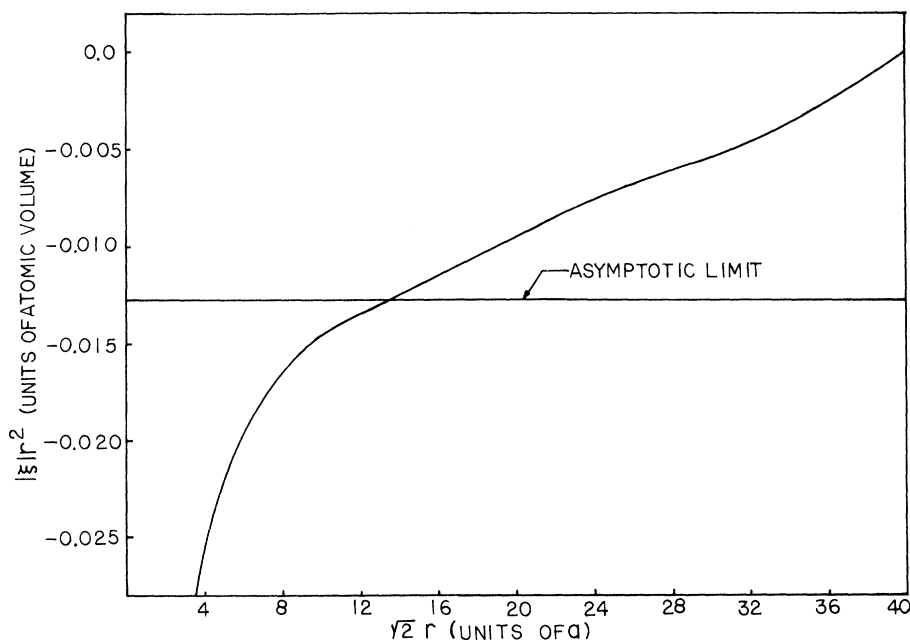

FIG. 4. $|\xi|r^2$ calculated from exact lattice statics, as a function of distance $\sqrt{2}\ r$ from the defect along $\langle 1\ 1\ 0 \rangle$ in α iron. A sample of 512 000 wave vectors was used. The horizontal line shows the elastic limit predicted by the asymptotic theory (− 0. 0127 at. vol.).

FIG. 5. $|\xi|r^2$ calculated from exact lattice statics as a function of distance $\sqrt{3}\,r$ from the defect along $\langle 1\,1\,1\rangle$ in α iron. A sample of 512 000 wave vectors was used. The horizontal line shows the elastic limit predicted by the asymptotic theory $(-0.017\,85$ at. vol.).
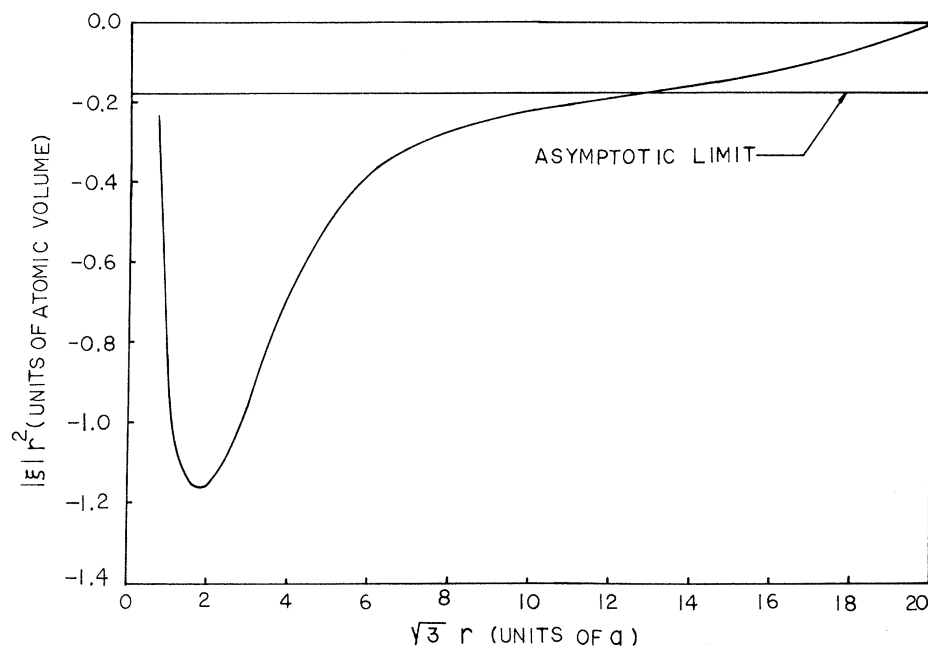
from exact lattice statics as well as the equivalent results from Johnson's[9] calculations are shown in Table IV for six host atoms close to the defect. With the exception of the displacement of the (4, 0, 0) neighbor, Johnson's results are consistently lower than the corresponding lattice statics results by amounts which vary from 5 to 11%.

There are three possible sources of discrepancy which might explain the differences between our displacements and those obtained by Johnson. First, the method of lattice statics is exact only within the harmonic approximation. If the anharmonic terms in the potential are large, this would explain a large disagreement in the two sets of results shown in Table IV. Second, Johnson has applied elasticity theory at the boundary of a spherical crystallite containing 530 host atoms which must therefore have a radius of $8\,a$. According to the results of Figs. 3–5, this is much too close to the defect for elasticity theory to be valid. Finally, our interatomic potential is not identical to that used by Johnson. However, we have only used the potential for

zone II in our calculations; that potential is identical in form to the one used by Johnson.[5] In fact, the only real difference is that our zone II is about 0.05 Å wider than that used by Johnson and, moreover, the nearest neighbor relaxes inward only 0.003 Å inside the zone boundary used by Johnson. Under these circumstances, it is not likely that the difference between the direct-space

TABLE III. Defect strength, dilatation, and relaxation energy associated with a vacancy in iron.

Strength parameter G	-1.619×10^{-12} dyn cm
Dilatation[a]ΔV	-0.080 at. vol.
Relaxation energy	-0.195 eV

[a]Formation volumes are those shown plus 1 at. vol.

TABLE IV. Comparison of atomic displacements obtained by lattice statics to those obtained by Johnson.

Neighbor		Atomic displacements $(2\,a)$		
		ξ_1	ξ_2	ξ_3
111	Ref. 9	$-0.014\,75$	$-0.014\,75$	$-0.014\,75$
	Present work	$-0.016\,10$	$-0.016\,10$	$-0.016\,10$
200	Ref. 9	$0.025\,65$	0.0	0.0
	Present work	$0.026\,79$	0.0	0.0
220	Ref. 9	$-0.003\,05$	$-0.003\,05$	0.0
	Present work	$-0.003\,205$	$-0.003\,205$	0.0
222	Ref. 9	$-0.004\,95$	$-0.004\,95$	$-0.004\,95$
	Present work	$-0.005\,565$	$-0.005\,565$	$-0.005\,565$
311	Ref. 9	$0.001\,75$	$0.001\,5$	$0.001\,5$
	Present work	$0.001\,588$	$0.001\,504$	$0.001\,504$
400	Ref. 9	$0.003\,3$	0.0	0.0
	Present work	$0.003\,019$	0.0	0.0

and lattice statics results can be attributed to the modification of the interatomic potential.

The importance of anharmonic effects in the lattice statics calculations can be measured in terms of their contribution to the interaction be-tween the host atoms at the $(1, 1, 1)$ and $(2, 2, 2)$ neighbor positions. This is obviously the strongest direct interaction between host atoms in the vicin-ity of the defect since it is a direct "push" between the two atoms acting along a radius line from the defect. When one compares the exact interaction between these atoms to an approximate interaction obtained by truncating beyond the quadratic term in the Taylor expansion of the interatomic poten-tial, the difference between the two potentials is only about 0.4%. It is doubtful that such small anharmonic contributions could account for the 5–10% discrepancies in strain-field displacements, which we are seeking to explain.

We must, therefore, conclude that the most likely source of these discrepancies is the invalid application of elasticity theory in the direct-space calculations. If we use the first- and second-neighbor displacements of Ref. 9 to compute a value for the defect-strength parameter G from Eq. (11), the value obtained is fully 10% lower than that used in the lattice statics calculations. Such a "weakening" of the defect would be expected if the elastic regime were assumed to be valid closer to the defect than is actually true and would therefore result in correspondingly lower values for the displacements of all of the host atoms about the defect.

Beeler[10] has used Johnson's interatomic poten-tial and lattice program to compute interaction energies of a number of vacancy pairs in α iron. His results are the same as those quoted by Johnson[5] for the $(1, 1, 1)$, $(2, 0, 0)$, and $(3, 1, 1)$ divacancies and would presumably be the same for other divacancies. Beeler's results are com-pared with those obtained by lattice statics in Table V. The strain-field interactions for the $(1, 1, 1)$ and $(2, 0, 0)$ vacancy pairs are masked by strong direct interactions, so that comparison between the two sets of results is fairly good. We agree, in particular, that the second-nearest-neighbor configuration has the highest binding energy, and that the nearest-neighbor and fourth-nearest-neighbor vacancy pairs are the only other configurations with significant binding energies. There are, however, significant differences for most of the remaining interaction energies.

It should be pointed out that Eq. (8) for the strain-field interaction energy is only an approx-imation, involving the lowest-order term in the energy expansion. However, it is certain that any difference in the defect-strength parameters

TABLE V. Comparison of interaction energies with those of Beeler.

Neighbor	Ref. 10 interaction energy (eV)	Lattice statics interaction energy (eV)
111	−0.131	−0.14
200	−0.195	−0.25
220	0.027	0.041
311	−0.051	−0.046
222	0.009	0.027 2
400	0.028	0.041
331	0.009	0.014
420	−0.011	−0.006
422	−0.014	−0.011 5
511	−0.004	−0.002
333	0.002	0.009
440	−0.001	0.003
531	−0.005	−0.001
600	0.002	0.004
442	−0.000	0.003 8
444	−0.001	0.003 3
800	−0.002	0.000 38

used in the space calculations and the lattice statics calculation will lead to much greater dis-crepancies in the strain-field interaction energy, since it is essentially the square of the strength parameter tensor which is used in this calculation.

V. SUMMARY

We have applied the method of lattice statics to the calculation of the lattice distortion produced by a vacancy in α iron and have also obtained the strain-field interaction energy between pairs of such defects. We have used the strain-field dis-placements to calculate the volume change and relaxation energy associated with single vacancies in α iron.

The exact lattice statics displacements were compared directly with the corresponding results of the asymptotic theory and with results obtained by means of a semidiscrete calculation.[5] The conclusions drawn from these comparisons con-firm the results of earlier lattice statics inves-tigations of point defects in metals,[1−4] which show that calculations based on a semidiscrete model of the crystal are unreliable as a means of predicting the strain-field properties of the imperfect lattice.

This is especially significant in the case of point defects in α iron, since the interatomic po-tentials of this material are relatively short-range in nature and much stronger than those of most other bcc metals. One must therefore con-clude that the long-range approach to the asymp-totic limit found for bcc metals is due largely to the open nature of such a structure rather than

being significantly dependent upon the range of the interatomic potential.

The method of lattice statics, on the other hand, is exact within the harmonic approximation, which is shown to be quite valid for the present calculations. It appears, therefore, that the only consistent method of calculating the direct-space forces due to the defect and hence the strain-field displacements and associated parameters is the method of lattice statics. Certainly, it would seem that any strain-field properties obtained as

a result of direct-space calculations in any of the bcc metals should be reappraised using the lattice statics approach.

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Dynamics of Disordered Alloys and Glasses*

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A formalism is presented for the calculation of the spectrum of normal modes of a disordered solid by means of a perturbation theory that takes a mean-field model as its unperturbed system. A transformation is used that allows the long-range correlations in the low-frequency vibrational modes to be accurately taken into account. In the special case of a random substitutional alloy, a result is found which reduces to those of other workers when the limit of small mass difference of the constituents or low concentration is taken. Some aspects of the application of the theory to amorphous systems are also discussed.

I. INTRODUCTION

The topic of the dynamics of disordered systems is at present a rather fragmented area of theoretical physics, in that the concepts that have been developed to discuss one type of disordered solid are only rarely applicable to other systems. A calculation of the spectrum of vibrational modes of a substitutional alloy, for example, may be attempted in a perturbation theory in which the phonon modes of a pure material form the unperturbed states. The results may then be expressed as a

power series in either the concentration of one element of the alloy[1] or the difference in mass of the two elements.[2] Such methods, however, cannot readily be applied to glasses or other materials that are lacking in long-range order, in that there is then no obvious Brillouin zone to limit the wave numbers of whatever phonon spectrum is chosen to represent the unperturbed system; in other words, there is no one-to-one correspondence between the atomic sites in the glass and in any perfect periodic lattice except in the special case of one-dimensional systems. The most fruitful ap-