PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Asymptotic Interaction Energy between Pairs of Point Defects in Cubic Metals

J. W. FLOCKEN*
University of Nebraska, Department of Physics, Behlen Laboratory, Lincoln, Nebraska 68508

(Received 23 July 1969)

We have calculated the asymptotic interaction energies between pairs of interstitial Cu atoms in Cu and between pairs of vacancies in Al, Na, and K. These calculations were performed using the asymptotic equations of the method of lattice statics. The exact method of lattice statics is based on the Fourier transformation of the direct-space equilibrium equations for a "supercell" of the lattice containing one defect surrounded by a large number of host atoms. The asymptotic interaction energies were compared with the corresponding results obtained from the exact method of lattice statics. This comparison indicates that elasticity theory cannot be used to obtain strain-field interaction energies for defects nearer than at least 26 or 27 neighbors from each other, and is probably not truly valid until much larger interdefect separations are considered. This result places a heavy restriction on the use of elasticity theory in practical defect-interaction calculations.

I. INTRODUCTION

When two defects are present in a crystal, each defect modifies the strain-field displacements of the host atoms produced by the other. Hence, the strain-field contribution to the formation energy of the defect pair is different from the sum of the contributions of the individual strain fields to the formation energies of the isolated defects. This energy difference manifests itself as an "indirect" energy of interaction between the two defects, as opposed to any direct energy bonds which may exist, and depends only on the relaxed configuration of the host atoms in the presence of the defect pair. We refer to this indirect potential as the strain-field interaction energy. If no direct interaction exists between two defects, as is the case for widely separated defects in metals or uncharged defects in the alkali halides, the strain-field interaction will be the dominant one and will play a decisive role in determining the stability of a given pair of defects.

The classical approach to calculating the strain-field interaction energy involves the use of continuum elasticity theory in which each defect is represented as a distribution of body forces. The interaction energy is then defined in terms of the dilatation produced by the first defect at the position of the second in the presence of the stresses produced by the second defect, and vice versa. However, it has been pointed out repeatedly[1–4] that classical elasticity theory does not give reliable values for strain-field displacements until one is much farther from the defect than had previously been assumed. Since the interaction energy calculations are based explicitly on the results of the displacement calculations, they must inherently contain the same restrictions.

Hardy and Bullough[5,6] have applied the method of lattice statics to obtain an expression for the interaction energy between a pair of similar defects in a lattice having cubic symmetry. The method of lattice statics is based on the Fourier transformation of the $3N\times3N$ direct-space equilibrium equations for a "supercell" containing N host atoms and one defect. The result of this transformation is a set of N 3×3 decoupled equations in reciprocal space, each of which can be solved for one of the Fourier amplitudes of the direct-space displacement field. By imposing periodic boundary conditions across the faces of a supercell having the same symmetry as the primitive lattice cell, one ensures the existence of only N independent wave vectors $\mathbf{q}$ contained within the first Brillouin zone (FBZ). This is equivalent to solving the problem for a superlattice of defects with one defect per supercell. Once the Fourier amplitudes have been determined, the direct-space displacement field can be found by Fourier inversion. However, the Fourier amplitudes are often a more convenient set of generalized coordinates than the direct-space displacements and, in the case of the interaction energy, it is a simple matter to perform the entire calculation in reciprocal space.

The lattice statics expression for the interaction energy can be used to obtain the strain-field interaction between all but very close defects, for which the interdefect spacing is determined by direct interactions between the defects. For very widely separated defects, the interaction energy is determined entirely by Fourier amplitudes evaluated in the long-wavelength limit. We have shown[4] that in this limit, the expressions for the Fourier amplitudes are identical to the corresponding equations of elasticity theory. Hence, the asymptotic lattice statics expression for the interaction energy should be the same as that predicted by continuum elasticity.

Hardy and Bullough[5] have treated the asymptotic interaction energy between similar cubic defects in an

---

* Present address: University of Nebraska at Omaha, Omaha, Nebraska.

[1] R. Bullough and J. R. Hardy, Phil. Mag. **17**, 833 (1968).

[2] J. W. Flocken and J. R. Hardy, Phys. Rev. **175**, 919 (1968).

[3] J. W. Flocken and J. R. Hardy, Phys. Rev. **177**, 1054 (1969).

[4] J. W. Flocken and J. R Hardy, Phys. Rev. (to be published).

[5] J. R. Hardy and R. Bullough, Phil. Mag. **15**, 237 (1967).

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

isotropic lattice. In this case, the first term in the energy expansion vanishes, as predicted by elasticity theory. The lowest-order nonvanishing term is found to fall off as $1/R^5$, where R is the interdefect separation distance, a result which has only recently been obtained from an elasticity theory approach due to Seims.[7]

In the present paper, we will be concerned with the asymptotic strain-field interaction between pairs of defects in anisotropic materials. We will show that for this case the first term in the interaction energy expansion does not vanish but falls off as $1/R^3$ in any given direction, as in the theory of continuum elasticity. For anisotropic materials, the various terms in the energy expansion cannot be treated analytically as they can for isotropic materials. Moreover, the manner in which the second-order terms in the expansion depend upon the form of the generalized forces, makes it impossible to evaluate them in a general way for a variety of materials and defect types. We will therefore confine our discussion to the first term in the expansion, which we assume to be the dominant one for most materials.

We have evaluated the interaction energy in the asymptotic limit for a set of defect types and lattice models for which exact lattice statics calculations have also been done. By comparing the results of exact lattice statics calculations with the corresponding results obtained from the asymptotic theory, we can gain some insight as to the conditions under which continuum elasticity can be justifiably applied.

In Sec. II, we state the important points of the lattice statics approach to determining the interaction energy in the long-wavelength limit. In Sec. III, we will use this approach to find the interaction energy between widely spaced pairs of interstitial Cu atoms in Cu and between pairs of widely separated vacancies in Al, Na, and K. In Sec. IV, we compare the asymptotic interaction energy results with those obtained using the exact theory of lattice statics. Section V is devoted to a summary of our results and conclusions.

II. ASYMPTOTIC INTERACTION ENERGY BETWEEN PAIRS OF POINT DEFECTS IN AN ANISOTROPIC CRYSTAL

The derivation of the lattice statics expression for the interaction energy between two similar point defects has been given by Hardy and Bullough[5] as

$$E=-\frac{1}{N}\sum_{\mathbf{q}} \mathbf{F}^{-\mathbf{q}}(\mathbf{V}^{-\mathbf{q}})^{-1}\mathbf{F}^{\mathbf{q}} \cos\mathbf{q}\cdot\mathbf{R} \qquad (1)$$

for a pair of defects separated by a vector $\mathbf{R}$ within a supercell containing N host atoms. The summation is over the N distinct wave vectors $\mathbf{q}$ in the FBZ. $\mathbf{F}^{\mathbf{q}}$ is the generalized force array associated with a given defect type and is given in terms of the direct-space forces $\mathbf{F}^l$ exerted by the defect on the surrounding host atoms by

$$F_\alpha{}^{\mathbf{q}}=\sum_l F_\alpha{}^l \exp(-i\mathbf{q}\cdot\mathbf{r}^l),$$

where $\mathbf{r}^l$ is the perfect lattice position vector of the lth neighboring atom to the defect. α refers to one of the axes of a set of Cartesian coordinates having the defect at the origin and axes along the $\langle 100\rangle$ directions in the crystal.

The matrix $\mathbf{V}^{-\mathbf{q}}$ in Eq. (1) is the Fourier transform of the direct-space force constant matrix $\mathbf{V}_{\alpha\beta}{}^{0l}$ and is given by

$$V_{\alpha\beta}{}^{-\mathbf{q}}=\sum_l V_{\alpha\beta}{}^{0l} \exp(i\mathbf{q}\cdot\mathbf{r}^l).$$

The components of the perfect lattice position vector, $\mathbf{r}^l$ can be expressed as integral multiples of "a"; half of the cubic unit cell side. Hence, in the limit as the wave vector $\mathbf{q}$ tends to zero, the expression for the interaction energy given by Eq. (1) can be expanded in a power series in the variable $|\mathbf{q}|a$.

Since the generalized forces are odd functions of qa and the $\mathbf{V}^{-\mathbf{q}}$ matrix is an even function of qa, we may expand these matrices in the forms

$$\mathbf{F}^{-\mathbf{q}}=\{\mathbf{F}^{-\mathbf{q}}\}_1+\{\mathbf{F}^{-\mathbf{q}}\}_3+\{\mathbf{F}^{-\mathbf{q}}\}_5+\cdots$$

and

$$\mathbf{V}^{-\mathbf{q}}=\{\mathbf{V}^{-\mathbf{q}}\}_2+\{\mathbf{V}^{-\mathbf{q}}\}_4+\{\mathbf{V}^{-\mathbf{q}}\}_6+\cdots.$$

The subscripts on the various terms in the expansions indicate the orders of qa contained in each of these terms. Using this notation, the first term in the interaction energy expansion is

$$E\cong-\frac{1}{N}\sum_{\mathbf{q}} \{\mathbf{F}^{-\mathbf{q}}\}_1[\{\mathbf{V}^{-\mathbf{q}}\}_2]^{-1}\{\mathbf{F}^{\mathbf{q}}\}_1 \cos\mathbf{q}\cdot\mathbf{R}. \qquad (2)$$

As we mentioned earlier, this term vanishes for pairs of similar cubic defects in an isotropic material and the lowest-order nonvanishing expression must be obtained from the next two terms in the expansion, which are both of the same order in qa. These terms can be evaluated analytically, though the process is tedious and complicated. The interaction energy term in Eq. (2) cannot be evaluated analytically for a general direction in an anisotropic material and we must perform these calculations numerically on a computer.

The matrix product $[\{\mathbf{V}^{-\mathbf{q}}\}_2]^{-1}\{\mathbf{F}^{\mathbf{q}}\}_1$ in Eq. (2) is actually the Fourier amplitude $\mathbf{Q}^{\mathbf{q}}$ in the limit $\mathbf{q}\sim 0$ and we have shown in a recent paper[4] that

$$\mathbf{Q}_\alpha{}^{\mathbf{q}}=[C_s a^2/P(\mathbf{k})v]k_\alpha\{Ek^4+Fk_\alpha{}^2k^2+Hk_\beta{}^2k_\alpha{}^2\}, \qquad (3\text{a})$$

where $\mathbf{k}\equiv\mathbf{q}a$ and v is the volume of a unit cell. $P(\mathbf{k})$ is the determinant of the $\mathbf{V}^{-\mathbf{q}}$ matrix and is given by

$$P(\mathbf{k})=Dk^6+Bk^2(k_1{}^2k_2{}^2+k_2{}^2k_3{}^2+k_1{}^2k_3{}^2)+Ak_1{}^2k_2{}^2k_3{}^2. \qquad (3\text{b})$$

The constants in Eqs. (3a) and (3b) are functions of the three independent elastic constants for a cubic host

---

[7] R. Seims, Phys. Status Solidi **30**, 645 (1968).

lattice and are given by

$$\begin{aligned}A&=(C_{11}-C_{12}-2C_{44})[(C_{11}-C_{44})(C_{11}+C_{12})\\&\qquad-2(C_{12}+C_{44})^2],\\B&=C_{44}(C_{11}+C_{12})(C_{11}-C_{12}-2C_{44}),\\D&=C_{11}C_{44}^2,\\E&=C_{44}(C_{11}-C_{12}-C_{44}),\\F&=C_{44}(C_{12}-C_{11}+2C_{44}),\\H&=(C_{11}-C_{12}-2C_{44})^2.\end{aligned}$$

The constant C_s in Eqs. (3) comes from the limiting expression

$$\{\mathbf{F}^q\}_1=C_s\begin{bmatrix}k_1\\k_2\\k_3\end{bmatrix}\tag{4}$$

for the generalized force array of the defect type under consideration. It can be evaluated in terms of the strength parameter G of the defect, in terms of which

$$C_s=-iG/a.$$

The strength parameter is, in general, a tensor, the elements of which are given by a prescription due to Hardy[8]

$$G_{\alpha\beta}=\sum_l F_\alpha{}^l r_\beta{}^l$$

in terms of the Cartesian components of the direct-space position vector $\mathbf{r}^l$ and the direct-space forces $\mathbf{F}^l$ exerted by the defect. For a cubic defect, the off-diagonal elements of $\mathbf{G}$ vanish and all of the diagonal elements are the same. Hence, we represent the defect strength for this case as a scalar G.

Carrying out the remaining matrix multiplication in Eq. (2), and converting the sum over wave-vector space to an integral, we have

$$E=\frac{C_s^2}{(2\pi)^3a}\underset{\text{FBZ}}{\iiint}\frac{Ek^6+Fk^2(k_1^4+k_2^4+k_3^4)+3Hk_1^2k_2^2k_3^2}{P(\mathbf{k})}\times\cos(\mathbf{k}\cdot\mathbf{L})d^3k\,,\tag{5}$$

where $\mathbf{L}\equiv\mathbf{R}/a$.

This integral can be evaluated by techniques similar to those used in Ref. 4 and, whenever possible, we will use the notation of that paper. We first make a coordinate transformation which puts the vector $\mathbf{R}$ along the polar axis of the new set of coordinates. The vector $\mathbf{k}$ can be expressed in terms of the polar angle θ and the azimuthal angle ϕ by equations of the form

$$k_\alpha{}^2=k^2g_\alpha(\cos\theta,\phi)\,,\tag{6}$$

where the g_α are functions of $\cos\theta$ and ϕ and, as before, α refers to a component of the original set of Cartesian axes. We then define a function

$$X(\cos\theta,\phi)\equiv\frac{E+F(g_1{}^2+g_2{}^2+g_3{}^2)+3Hg_1g_2g_3}{D+B(g_1g_2+g_2g_3+g_1g_3)+Ag_1g_2g_3}\,,\tag{7}$$

and make use of the fact that

$$\nabla_L{}^2\cos\mathbf{k}\cdot\mathbf{L}=-k^2\cos\mathbf{k}\cdot\mathbf{L}\,,\tag{8}$$

where

$$\nabla_L{}^2=\frac{\partial^2}{\partial L_1{}^2}+\frac{\partial^2}{\partial L_2{}^2}+\frac{\partial^2}{\partial L_3{}^2}\,.$$

Substituting Eqs. (7) and (8) into Eq. (5), we obtain

$$E=-\frac{C_s^2}{(2\pi)^3a}\nabla_L{}^2\underset{\text{FBZ}}{\iiint}X(\cos\theta,\phi)\times\cos(kL\cos\theta)\,dk\,d\cos\theta\,d\phi\,.\tag{9}$$

We assume that for widely separated defects the main contributions to this integral will come from a region near the origin in wave-vector space. We therefore insert a convergence parameter of the form $e^{-\epsilon k}$ into the integrand, extend the k integral to infinity, and evaluate the integral in the limit as $\epsilon\to0$. The k integration then results in a δ function the argument of which is $\cos\theta$. The resulting integral is

$$E=-\frac{C_s^2}{8\pi^2a}\nabla_L{}^2\frac{1}{|\mathbf{L}|}\int_0^{2\pi}\int_{-1}^{1}X(\cos\theta,\phi)\times\delta(\cos\theta)\,d(\cos\theta)\,d\phi\,,$$

and, integrating over $\cos\theta$ we obtain,

$$E=-\frac{C_s^2}{8\pi^2a}\nabla_L{}^2\int_0^{2\pi}\frac{X(0,\phi)}{|\mathbf{L}|}d\phi\,.\tag{10}$$

The remaining integral over ϕ cannot be evaluated analytically, in general, for an anisotropic crystal and we must resort to evaluating it on a computer. The parameter ϕ is independent of L so that we may take the operator $\nabla_L{}^2$ inside the integral and perform the necessary derivations analytically. After a good deal of algebraic manipulation, one obtains an analytic form for the integrand of Eq. (10) for a given $\mathbf{L}$ and one can then evaluate the resulting expression numerically.

III. APPLICATIONS

We have calculated the interaction energy in the asymptotic limit between pairs of interstitial Cu atoms in Cu and between pairs of vacancies in Al, K, and Na. The force constants and direct-space forces $\mathbf{F}^l$ were taken from the lattice statics calculations of Bullough and Hardy[1] for vacancies in Al, and from our own calculations for interstitial Cu atoms in Cu [5] and for vacancies in Na and K, for which the K(1) and Na(1) lattice models of Ref. 3 were used.

Since the interaction energy term which we have evaluated falls off as $1/R^3$ in any given direction, we have chosen to represent our results as interaction energies between a defect at the origin and a similar defect situated on a sphere of radius "a." One can find

---

[8] J. R. Hardy, J. Phys. Chem. Solids 29, 2009 (1968).

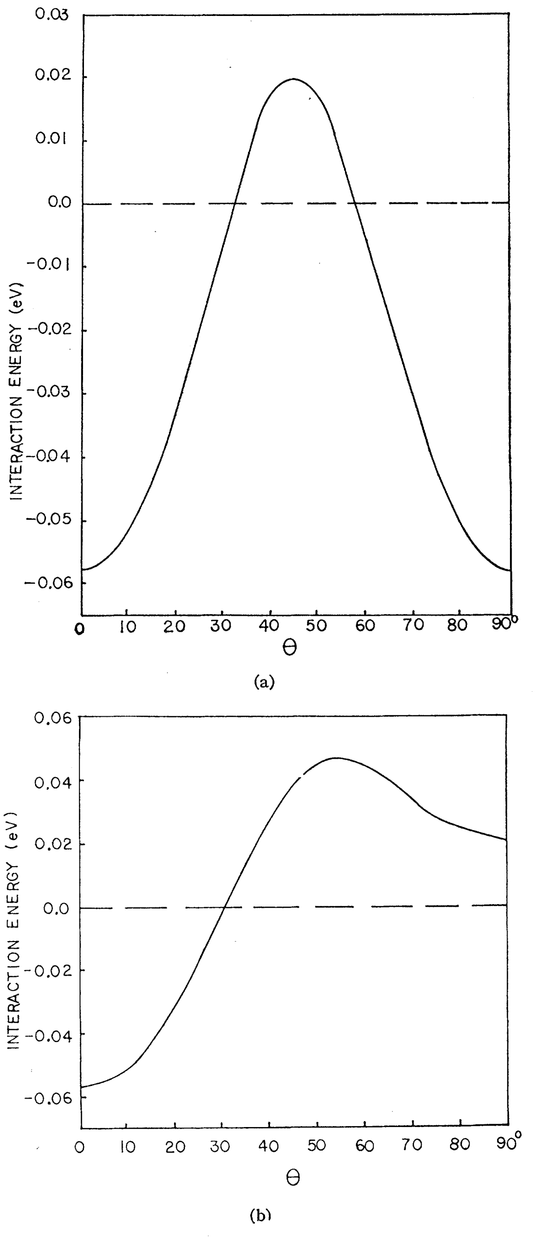

FIG. 1. (a) Asymptotic interaction energy profile in the first quadrant of the (001) plane for vacancy pairs Al. (b) Asymptotic interaction energy profile in the first quadrant of the $(0\bar{1}1)$ plane for vacancy pairs Al.

the interaction energy between two defects at any separation distance R in a given direction, simply by scaling our results by a factor of $(R/a)^3$.

Interaction energies have been computed at 2.5° intervals in the (0,0,1) and $(0,\bar{1},1)$ planes. Only the first quadrant of each of these profiles is shown, since the entire profile can be generated by mirror reflection of the first quadrant in the x and y axes.

The integral over ϕ in Eq. (10) was evaluated using Simpson's rule with 100 equal increments of ϕ. The calculations were done on an IBM 360/65 at the University of Nebraska at Lincoln.

In Figs. 1(a) and 1(b) we show the interaction energy profiles associated with vacancy pairs in Al. In Figs.

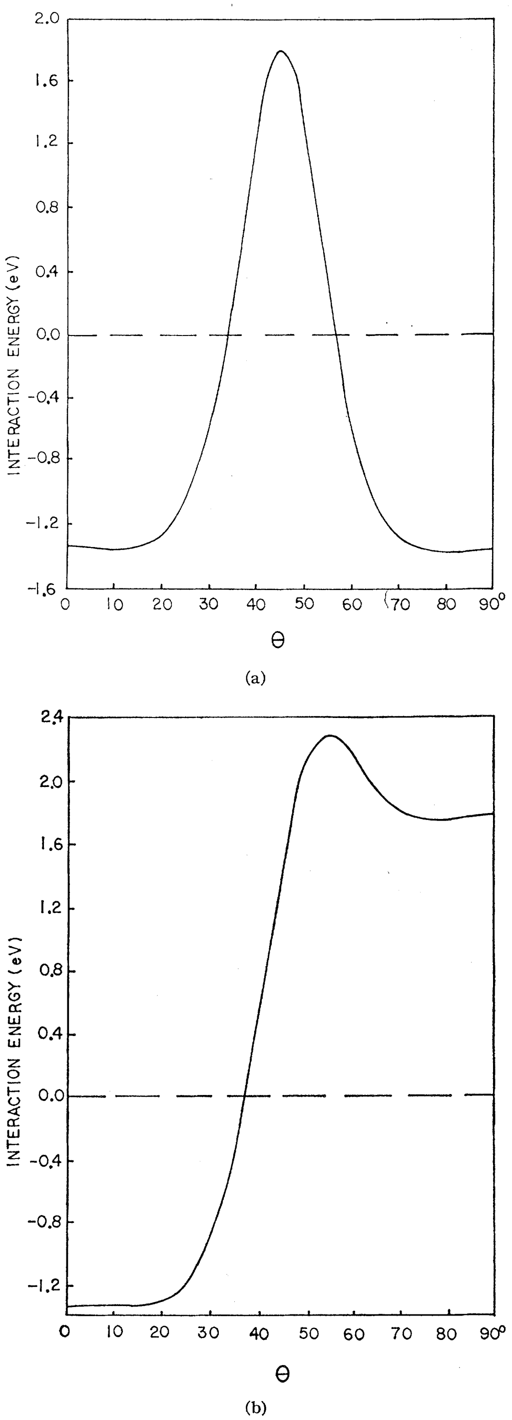

FIG. 2. (a) Asymptotic interaction energy profile in the first quadrant of the (001) plane for pairs of interstitial Cu atoms in Cu. (b) Asymptotic interaction energy profile in the first quadrant of the $(0\bar{1}1)$ plane for pairs of interstitial Cu atoms in Cu.

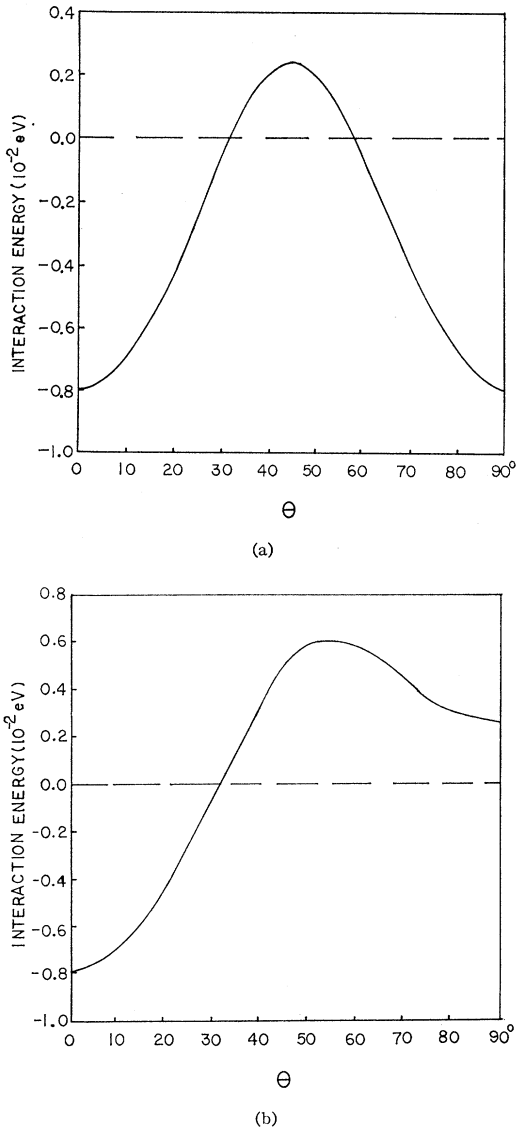

FIG. 3. (a) Asymptotic interaction energy profile in the first quadrant of the (001) plane for vacancy pairs in K. (b) Asymptotic interaction energy profiles in the first quadrant of the (0$\bar{1}$1) plane for vacancy pairs in K.

2(a) and 2(b) ,we show the corresponding profiles for pairs of interstitial Cu atoms in Cu. Figures 3 and 4 show the energy profiles for vacancy pairs in K and Na.

IV. DISCUSSION

The primary importance of the calculations which we have just described is that we may make a direct comparison of the asymptotic results shown in Sec. III with the corresponding results obtained from exact lattice statics. From this comparison we will get some idea of the distance by which two defects must be separated before one can expect to obtain reliable values of interaction energy using a continuum elasticity approach.

In Table I, we compare the exact and asymptotic interaction energies between vacancy pairs in Al. It is apparent that the asymptotic results fall far below the values predicted by exact lattice statics. This is not surprising since aluminum is nearly isotropic and, as we mentioned earlier, the term which we have evaluated in the energy expansion vanishes identically for an isotropic material.

The comparison between the exact and asymptotic lattice static results for the interaction energies associ-

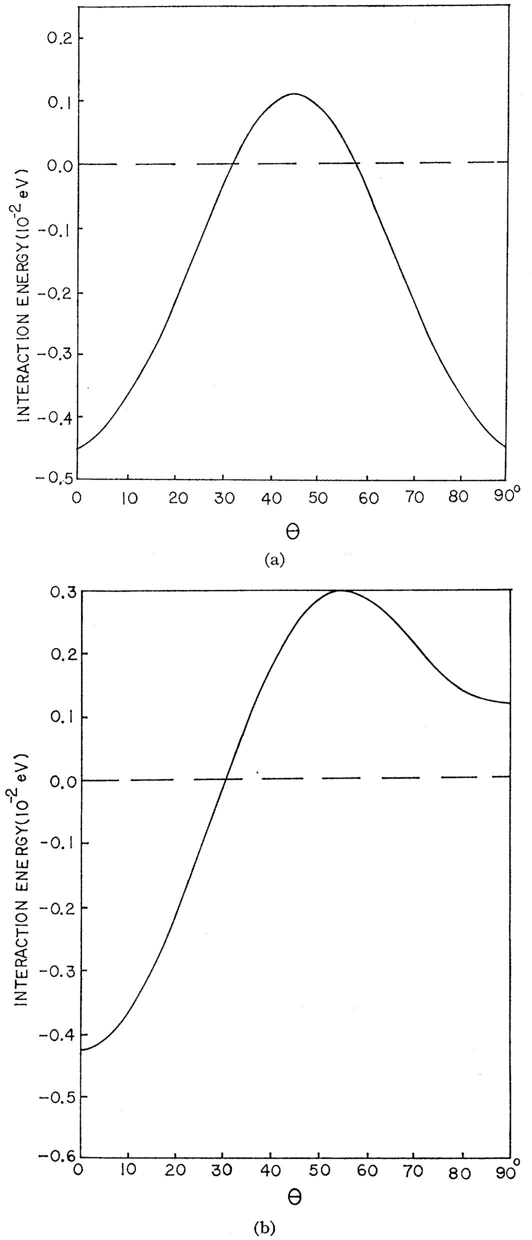

FIG. 4. (a) Asymptotic interaction energy profiles in the first quadrant of the (001) plane for vacancy pairs in Na. (b) Asymptotic interaction energy profiles in the first quadrant of the (001) plane for vacancy pairs in Na.

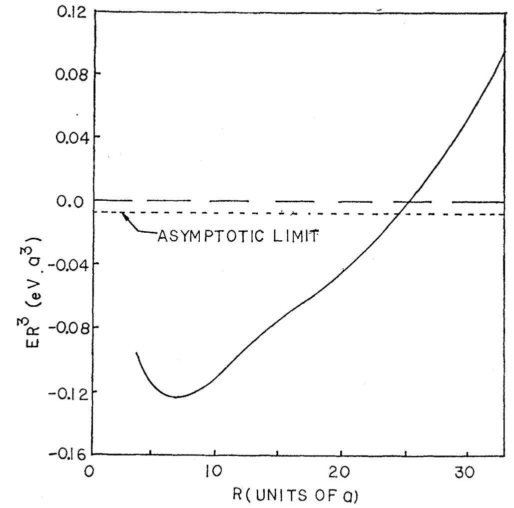

FIG. 5. ER^3 as a function of interdefect separation, R, along the ⟨100⟩ direction in K.

ated with pairs of interstitial Cu atoms in Cu is shown in Table II. The agreement between the two sets of results in this case is considerably better than for the vacancy pairs in Al. A comparison between the asymptotic and exact lattice statics calculations for the strain-field displacements induced by an interstitial Cu atom in Cu shows that the elastic regime is only valid at distances greater than about $5a$ from the defect.[2] Hence, we cannot expect the asymptotic values of the interaction energy shown in Table II to be reliable except for the (6,0,0) and (4,4,4) defect pairs, and we have reason to believe that our exact lattice statics results for the (4,4,4) defect pair are inaccurate due to the limited size of our wave-vector sample density. (A sample of 64 000 regularly spaced wave vectors was used for the exact calculations.)

In the case of the alkali metals Na and K, we have indicated in Ref. 4 that the elastic regime is only attained beyond the 26th or 27th neighbors from the defect. Valid lattice statics results for such large distances have only been computed along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions in the K(1) lattice model.

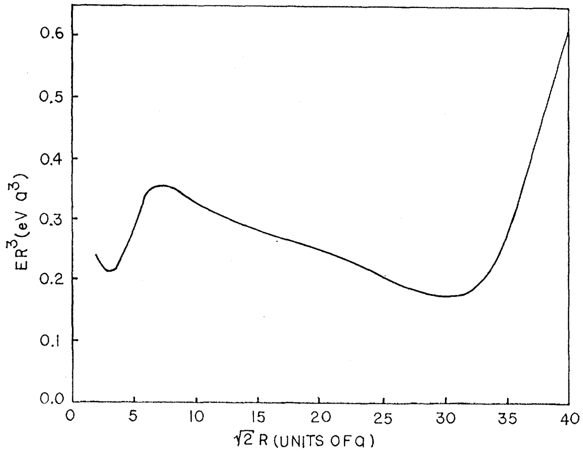

FIG. 6. ER^3 as a function of $\sqrt{2}\,R$ along the ⟨110⟩ direction in K. R is the interdefect separation.

TABLE I. Comparison of strain-field interaction energies for vacancy pairs in Al (eV).

Neighbor	Lattice statics value	Asymptotic value
110	−0.0692	0.0143
200	−0.0245	−0.0072
211	−0.0061	0.00093
220	−0.0006	0.00080
222	−0.0033	0.00113
310	0.0048	−0.00114
330	0.0004	0.00027
400	0.0072	−0.0009
411	−0.0011	−0.00046
420	0.0002	0.00018
422	−0.0019	0.00012
433	0.0001	0.00021
440	−0.0021	0.00011
442	−0.0008	0.00016
444	0.0019	0.00014

In Fig. 5, we have plotted exact values of ER^3 versus R in the ⟨100⟩ direction for K(1). The asymptotic value, $ER^3 = -0.00796$ is shown as a horizontal dashed line. There is no apparent tendency for the energy to settle to an asymptotic limit. In Fig. 6, we show ER^3 versus $\sqrt{2}R$ along the ⟨110⟩ direction in K(1), and Fig. 7 shows ER^3 versus $\sqrt{3}R$ along ⟨111⟩. In both cases, the asymptotic limits are virtually indistinguishable from zero and the exact lattice statics results always stay well above the asymptotic limit. There are two possible sources of discrepancy between the exact and asymptotic results for K. First, we again emphasize that we are evaluating only the lowest-order term in the interaction energy. While we have every reason to expect this term to be dominant for anisotropic materials, the effect of the long-range interatomic potentials for the alkali metals, extending out to fifth neighbors, may result in a slowly converging series for the interaction energy. Second, the Fourier amplitudes which were used in the exact calculations were those appropriate to a superlattice of regularly spaced defects. (One defect for every 64 000 host atoms in the calculations along ⟨100⟩

TABLE II. Comparison of strain-field interaction energies between pairs of interstitial Cu atoms in Cu (eV).

Neighbor	Lattice statics results	Asymptotic results
200	0.4004	−0.1675
220	0.09751	0.0786
222	0.02414	0.0548
400	−0.03468	−0.0209
420	0.001636	−0.0104
422	−0.000297	−0.00281
440	0.09381	0.0980
442	0.03737	0.00824
444	0.003284	0.00687
600	−0.007348	−0.00619

and ⟨110⟩ and one defect for every 512 000 host atoms for the calculations along ⟨111⟩.) Hence, the interaction energies calculated using exact lattice statics contain contributions from the strain fields of other defects in the lattice and these contributions are known to be dominant at distances of more than 26 neighbors from a vacancy in K or Na.

Nevertheless, even if we make large allowances for the approximations inherent in our calculations, it is apparent that we cannot completely account for the discrepancies shown in Figs. 5–7, and we must conclude that the elastic regime is simply not attained within the range of interdefect distances considered here. This places a very serious restriction on the usefulness of continuum elasticity when one considers that for any reasonable concentration of defects in a lattice the migration of defects will be determined largely by defect interactions which cannot be treated by elasticity theory.

V. SUMMARY

We have applied the method of lattice statics in the asymptotic limit to the calculation of interaction energies between pairs of similar point defects in Al, Cu, Na, and K. In each case, a comparison was made between the asymptotic interaction energies and those obtained from exact lattice statics.

The asymptotic interaction energy was taken to be the lowest-order term in the energy expansion. Since this term vanishes identically for an isotropic lattice, no meaningful asymptotic results could be obtained for Al.

A comparison has been made between interaction energies in the long-wavelength limit and the corresponding results obtained from exact lattice statics for pairs of vacancies in K and Na. We conclude from this comparison that elasticity theory calculations of the strain-field interaction energies between point defects in K and Na will not yield reliable results for interdefect spacings smaller than about $27a$ from the defect, where a is half the lattice constant.

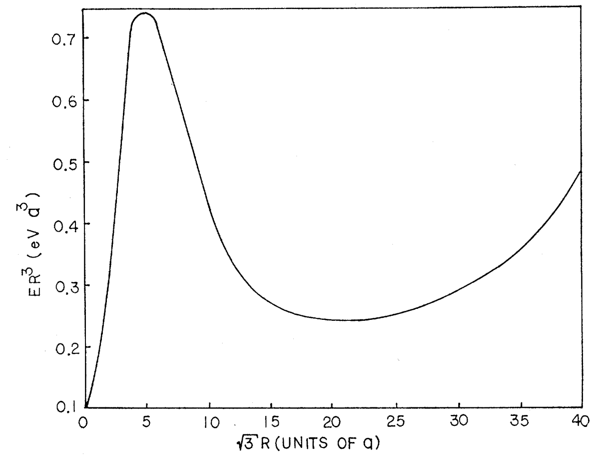

FIG. 7. ER^3 as a function of $\sqrt{3}\ R$ along the ⟨111⟩ direction in K. R is the interdefect separation.

In light of these findings, it appears to us that interaction energies obtained by any method in which elasticity theory is applied at interdefect spacings smaller than those specified above should be viewed with some suspicion. The method of lattice statics provides a natural and consistent transition from lattice theory to continuum elasticity and is thus free from the constraints imposed on the lattice in direct-space calculations and therefore, seems to present the most direct and reliable approach to the type of problem considered here.

ACKNOWLEDGMENT

The author wishes to thank Professor John R. Hardy for suggesting the problem considered in this paper and for many stimulating discussions during the course of this work.