Technical Report No. 9
Contract Nonr 177-(00)
NR 017-417

THE DISTORTION OF A CRYSTAL BY POINT IMPERFECTIONS

J. D. Eshelby
Department of Physics
University of Illinois
Urbana, Illinois

July, 1953

U. S. Navy Department
Office of Naval Research
Washington, D. C.

Abstract

The expression $\underset{\sim}{u} = c\ \underset{\sim}{r}/r^3$ (where c is a constant) sometimes assumed for the displacement around a point imperfection (interstitial or substitutional impurity, lattice vacancy) gives a non-zero stress at the surface of the solid. The additional 'image displacement' necessary to insure that this stress vanishes is usually neglected, but may be important. For example, it accounts for from 30 to 50 per cent of the volume change produced by such defects. This and other effects of the image term are discussed. Miller and Russel have pointed out that a point imperfection near the center of a sphere the apparent volume change deduced from measurements of the x-ray lattice constant is greater than the geometrical volume change. It is shown that the reverse is true when the defect is near the surface, and that for a large number of defects scattered uniformly through the sphere the geometrical and x-ray expansions are equal. This result is true with or without the image term, but to establish the equality of geometrical and x-ray expansions for a body of arbitrary shape the image terms must be included.

The contributions of the image term to various phenomena are different and so they cannot be merely absorbed in the 'strength' c of the imperfection.

Introduction

As a model for the distortion of a crystal lattice by a substitutional or interstitial atom or a vacant lattice site a number of authors have taken a center of dilatation in an isotropic elastic continuum. In many cases calculations have been made using the elastic displacement appropriate to a center of dilatation in an infinite medium. This displacement cannot be correct since it would give a non-vanishing stress at the free surface of the body. It is convenient to regard the actual displacement as the sum of the displacement in an infinite medium and an 'image' displacement due to the perturbing effect of the boundary.

It is the object of this paper to show that the image term cannot be neglected in certain applications. In particular, if it is omitted the volume change due to one or more point singularities will be underestimated by a factor of 1.5 for metals or 1.8 for alkali halides. Again, if the effects of the free boundary are ignored, any non-spherical body uniformly filled with point singularities would suffer a change of shape as well as a change of size. When the boundary effect is taken into account there is a change of volume without change of shape. Moreover, for this case, a calculation of the change of x-ray lattice constant gives a result consistent with the geometrical deformation only if the image displacements are included. Thus, unusually, the boundary effects simplify the problem instead of complicating it.

2. A Point Singularity in an Infinite Body

The elastic displacement due to a center of dilatation

in an infinite medium is[1]

[1] A. H. Love, Mathematical Theory of Elasticity. (Cambridge University Press, 1924).

$$\underset{\sim}{u}^{\infty} = c\frac{\underset{\sim}{r}}{r^3} = -c\ \mathrm{grad}\left(\frac{1}{r}\right) \qquad (1)$$

where c is a constant, the 'strength' of the singularity. (We use the affix ∞ to emphasize that (1) is only valid in an infinite medium). The displacement has the same form as the field of an electrostatic point charge. The real justification for taking (1) as a rough description of the elastic field of a point imperfection in an infinite crystal which has been idealized as a homogeneous isotropic elastic continuum is that it is the only spherically symmetrical displacement which satisfies the equations of elasticity and does not increase with r. Still, it is convenient to have some sort of detailed elastic model. As a model of an interstitial or substitutional atom we might take an elastic sphere of radius $(1+\varepsilon)r_0$ forced into a spherical hole of radius r_0 in an infinite block of the same material. It is easy to show that for $r > r_0$ the displacement is given by (1) with $c = \varepsilon r_0^3(1+\sigma)/3(1-\sigma)$ and that for $r < r_0$ there is a uniform compression. (σ is Poisson's ratio). The surface of the hole suffers an outward displacement c/r_0^2, increasing the volume within it by $4\pi c$.

This model must not be taken too literally. The lattice constant of gold is increased by a little dissolved silver. The misfitting sphere model would suggest that therefore a little

dissolved gold would decrease the lattice constant of silver, and this is not true. All that we can hope for is that a particular type of singularity in a particular matrix will be characterized by a constant c which can be used consistently to describe various phenomena.

Again, a foreign atom in a lattice exerts forces on its neighbors differing from the 'standard' forces they would experience in the perfect lattice. When we assimilate the lattice to a continuum the standard forces are absorbed in the elastic properties of the medium, but the additional forces due to the imperfection are still outstanding. Hence as an alternative to the sphere-in-hole model we may take a cluster of point forces to represent a point lattice imperfection in the elastic approximation. For a sufficiency symmetrical relation of the interstitial or substitutional atom and the lattice, the forces will be equivalent to three equal 'double forces without moment' at right angles. The displacement will then be of the form (1) which can be considered[1] as due to a distribution of body force

$$\underset{\sim}{F}(\underset{\sim}{r}) = -12\pi cK\,\underset{\sim}{\text{grad}}\,\delta(r) \qquad (2)$$

(K is the bulk modulus).

In a less symmetrical case (e.g. carbon in iron) the cluster of forces will be equivalent to three unequal double forces without moment and the resulting displacement will be more complicated than (1). However, it is probably not justifiable to introduce this refinement without at the same time considering the anisotropy of the material, and we shall not consider it further.

The displacement (1) can be produced by heating a point of the elastic medium, assumed to be non-conducting. This can be seen by imagining that the misfit in the first model was produced by heating a sphere with originally no misfit, or in terms of the second model by noticing that the thermal stress[2] due to a temperature distribution T ( ) is the same as the stress produced by

---

[2] S. Timoshenko, Theory of Elasticity, McGraw-Hill Book Co., Inc., New York, N. Y. 1934.

---

a density of body force proportional to grad T, which for the hot spot T = const ∂( ) would be of the form (2). This analogy will be useful in discussing a body containing a large number of imperfections.

In general the stress associated with a displacement $\underset{\sim}{u}$ whose Cartesian components are u_1, u_2, u_3 is

$$p_{ij} = \lambda \delta_{ij} \operatorname{div} \underset{\sim}{u} + \mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \qquad (3)$$

where λ and μ are Lame's constants. From the electrostatic interpretation it is at once clear that the divergence and curl of (1) vanish, so that the stress produced by the singularity when in an infinite body is simply

$$\overset{\infty}{p}_{ij} = 2\mu \frac{\partial \overset{\infty}{u}_i}{\partial x_j} . \qquad (4)$$

3. A Point Singularity in a Finite Body with a Stress-Free Surface.

Consider now a center of dilatation in a finite body with

a free surface. First mark out the surface S of the proposed body in an infinite block of material and introduce the singularity. The displacement is given correctly by (1). Across any surface element of S there is a stress* $p_{ij}n_j dS$, where $\underset{\sim}{n}$ is the normal to S. Thus if we remove the material outside S the displacement will

---

* Throughout the paper we use the convention that a repeates suffix is to be summed over the values 1, 2, 3.

---

continue to be $\underset{\sim}{u}^{\infty}$ only if we apply a distribution of surface traction $p_{ij}n_j$ to S. Removing this distribution to give a body with a stress-free surface is equivalent to applying an additional distribution $-p_{ij}n_j$. The elastic state will then be given by

$$\underset{\sim}{u} = \underset{\sim}{u}^{\infty} + \underset{\sim}{u}^{I}, \quad p_{ij} = p_{ij}^{\infty} + p_{ij}^{I} \tag{5}$$

where the image stress p_{ij}^{I} is the stress which surface tractions $-p_{ij}n_j$ would produce in the body and the image displacement $\underset{\sim}{u}^{I}$ is is related to p_{ij}^{I} by (3). p_{ij}^{I} is clearly free of singularities within S and satisfies

$$(p_{ij}^{I} + p_{ij}^{\infty}) \; n_j = 0 \text{ on S.} \tag{6}$$

Unlike $\underset{\sim}{u}^{\infty}$, $\underset{\sim}{u}^{I}$ has in general a non-vanishing divergence.

If the surface traction and surface displacement are prescribed (they are not, of course, independent) the elastic field inside the body can be found by integration. When only the surface traction is given, we need the appropriate elastic Green's function, known for only a few simple shapes. Since we know the image traction

$p_{ij}n_j$ but not $\underset{\sim}{u}^I$ on S we cannot in general calculate the image field in the body.

The change in volume of the solid can be divided into parts ΔV^∞ and ΔV^I arising from the two terms in (5). We have at once

$$\Delta V^\infty = \int_S \underset{\sim}{u}^\infty \cdot \underset{\sim}{n}\, dS = 4\pi c , \tag{7}$$

the integral being, according to (1), c times the solid angle subtended by the surface at the singularity. This result can be seen at once for the sphere-in-hole model: When the sphere is inserted, the volume of the hole increases by $4\pi c$, and since $\operatorname{div} \underset{\sim}{u}^\infty = 0$ outside the hole, this increase is transmitted unchanged to S. Again for the ideal mathematical singularity for which (1) holds for all $\underset{\sim}{r}$ we have strictly not $\operatorname{div} \underset{\sim}{u}^\infty = 0$ but rather

$$\operatorname{div} \underset{\sim}{u}^\infty = -c\,\nabla^2(1/r) = 4\pi c\,\delta(r), \tag{8}$$

with a delta-function of expansion at $r = 0$. A formal volume integration gives (7).

Although we cannot find the image deformation in detail, we can find ΔV^I with the help of the rule that the volume change of a body subjected to a distribution of surface traction $\underset{\sim}{T}$ per unit area is

$$\frac{1}{3K}\int_S \underset{\sim}{r}\cdot\underset{\sim}{T}\, dS = \frac{1}{3K}\int_S x_i p_{ij} n_j\, dS \tag{9}$$

where p_{ij} is the stress produced by $\underset{\sim}{T}$ and K is the bulk modulus. For

$$\int x_i p_{ij} n_j\, dS = \int \frac{\partial}{\partial x_j}(x_i p_{ij})\, dv = \int p_{jj}\, dv = 3K\int \operatorname{div} \underset{\sim}{u}\, dv, \tag{9'}$$

since $\partial x_i / \partial x_j = \delta_{ij}$ and in elastic equilibrium $\partial p_{ij} / \partial x_j = 0$.

To find ΔV^I we must put $p_{ij} n_j = p^I_{ij} n_j = -p^\infty_{ij} n_j$ with p^∞_{ij} from (4). But the operator $x_i (\partial / \partial x_i)$ applied to $u^\infty_k = c x_k / r^3$ merely multiplies it by -2. Hence the integral (9) is equal to the integral (7) times $4\mu/3K$ and so

$$\Delta V^I = 4\pi c \frac{2(1-2\sigma)}{1+\sigma} \tag{10}$$

Thus the total volume change on introducing a center of dilatation of strength c into any homogeneous isotropic body with a stress-free surface is

$$\Delta V = \Delta V^\infty + \Delta V^I = \gamma \Delta V^\infty = 4\pi c \gamma \tag{11}$$

where the constant

$$\gamma = 3 \frac{1-\sigma}{1+\sigma} \tag{12}$$

is about 1.5 for metals ($\sigma \sim 1/3$) and 1.8 for alkali halides ($\sigma \sim 1/4$). This result has already been given by Seitz[2a].

[2a] Frederick Seitz, Rev. Mod. Phys. 18, 384 (1946)

It is also implicit in the known result for the interaction energy of a center of dilatation and an external hydrostatic pressure[2b]: This energy is the product of ΔV and the hydrostatic pressure.

[2b] See, for example, J. D. Eshelby, Phil. Trans. Roy. Soc. A 244, 87 (1951)

If in (9') we take p_{ij} to be any state of purely internal stress, so that the surface integral is zero we arrive at the known result that the volume of a body is unaffected by internal stresses provided Hooke's law is valid. The volume expansion we have calculated is not in disagreement with this. Consider the hole-in-sphere model of section 2, and suppose for clearness that ε is negative. Then the unstrained state is a body with a spherical hole of radius r_o containing a sphere of radius $r_o(1 - |\varepsilon|)$ and an unoccupied volume $4\pi r_o^3 |\varepsilon| = 4\pi |c| \gamma$. In the strained state the surfaces of the hole and sphere have been drawn together and welded. Since the total volume of material is unchanged, the volume enclosed by the outer surface must have decreased by an amount equal to the volume eliminated between sphere and hole. This simple derivation does not supersede our more elaborate treatment since to relate the expansion to stress effects arising from the imperfections we need to know something about $\underset{\sim}{u}^{\infty}$ and $\underset{\sim}{u}^{I}$ separately. If there are departures from Hooke's law, the volume change of the material is not quite zero: this is discussed in section 6.

4. The Deformation produced by a Large Number of Singularities

If there are a number of singularities in the body we have

$$\underset{\sim}{u}^{\infty}(\underset{\sim}{r}) = \sum_{n} c_n \frac{\underset{\sim}{r} - \underset{\sim}{r}_n}{|\underset{\sim}{r} - \underset{\sim}{r}_n|^3} \qquad (13)$$

with summation over all imperfections. The image stress p_{ij}^{I} is that stress which has no singularities within S and on S annuls the surface traction calculated from (13). $\underset{\sim}{u}^{I}$ is the associated displacement.

If the defects are all alike we have

$$\Delta V/V = 4\pi\gamma\, c\, f\, /\Omega \qquad (12')$$

where f is the atomic fraction of defects and Ω is the volume per atom of the matrix.

Of special interest is the case where there are a large number of identical centers spread through the volume, with an approximately uniform density of n centers per unit volume. Here we can also say something about the change of shape if we allow ourselves to replace the actual distribution by a continuous distribution of infinitesimal centers with the same total strength per unit volume. (We shall try to justify this below). If as before the body is embedded in an infinite matrix this averaged displacement is clearly

$$\underset{\sim}{u}^{\infty} = cn \int_V \frac{\underset{\sim}{r}}{r^3}\, dv \qquad (14)$$

at any rate outside S. (It is not at once clear that we can give any meaning to the average displacement in a medium riddled with singularities.)

The comparison already made with thermal expansion suggests that a body uniformly filled with infinitesimal centers of dilatation will, like a uniformly heated solid, expand uniformly. The following is a formal proof. We first show that the displacement given by the volume integral (14) can be duplicated outside S by a distribution of body force over S of uniform magnitude

$$p = K\,\Delta V/V = 4\pi cn\gamma K$$

per unit area and directed along the outward normal at each point. A point force F in an infinite medium produces a displacement

$$\underset{\sim}{u} = A\frac{\underset{\sim}{F}}{r} + B\frac{\underset{\sim}{r}(\underset{\sim}{r}\cdot\underset{\sim}{F})}{r^3}, \quad B = 1/16\pi\mu(1-\sigma),$$

$$A = (3-4\sigma)B$$

at a vector distance $\underset{\sim}{r}$ from it. Each element of the surface contributes a force $d\underset{\sim}{F} = p\,\underset{\sim}{n}\,dS$ and the net displacement is

$$u_i = \phi\int_S \left\{\frac{A}{r}\delta_{ij} + \frac{B}{r^3}x_i x_j\right\} n_j\, dS$$

$$= \phi\int \frac{\partial}{\partial x_j}\{\}\, dv = \phi(A-B)\int \frac{x_i}{r^3}\, d\tau = u_i^{\infty}$$

Suppose now that S is marked out in an infinite medium, that the uniform distribution of infinitesimal centers of dilatation is introduced and that a layer of body force equal and opposite to that just described is distributed over S. The combined effect of these last two steps gives zero displacement outside S and leaves S its original shape and size. If the unstrained matrix is now cut away, the elastic state of the body bounded by S is unchanged, but the layer of body force becomes a hydrostatic pressure p acting on the surface. When this is removed S undergoes the uniform expansion

$$\ddot{u}_i = \frac{4}{3}\pi\, n\, c\, \gamma\, x_i \qquad (15)$$

Though $\underset{\sim}{u}^{\infty} + \underset{\sim}{u}^{I}$ represents a uniform expansion, $\underset{\sim}{u}^{\infty}$ and $\underset{\sim}{u}^{I}$ separately do not, except for a spherical body. Thus omission of the image terms in addition to giving a volume change lacking the factor γ (which could be absorbed in the usually unknown constant c) would also give a non-uniform expansion.

Suppose, for example, that S is an ellipsoid with axes a, b, c. Then $\bar{u}^{\infty} = -$ cn grad φ where

$$= 1/2\ (D - Ax_1 - Bx_2 - Cx_3) \qquad (16)$$

with the usual notation for the potential of an ellipsoid. Thus if image terms are neglected, the ellipsoid becomes another ellipsoid with semi-axes $a + \Delta a$, etc., where

$$\frac{\Delta a}{a} = cnA, \quad \frac{\Delta b}{b} = cnB, \quad \frac{\Delta c}{c} = cnC\ . \qquad (17)$$

Since $A + B + C = 4\pi$ the volume change agrees with (7). As an example, if $a:b:c = 2:1:1$ then $A:B:C = 2:1:1$ very nearly. This departure from uniform expansion, if it existed, would be hard to detect by macroscopic measurements, but as we shall see below, there is an exactly similar effect on the lattice constants determined by x-ray diffraction, and this would be easily observable.

We must now try to justify replacing the sum (13) by the integral (14). Just this question arises when we replace the field of a set of gravitating or electrified particles by the field of a continuous body. This kind of problem can be attacked in various ways, none completely satisfying; the following seems a plausible line for the elastic case.

The observable macroscopic displacement at a point of a body in which the displacement fluctuates on a microscopic scale is essentially the displacement of the centroid of a region large compared with the scale of the fluctuations. It is therefore reasonable to define the gross (or macroscopic) displacement at a

point as the average of the actual (microscopic) displacement taken over the volume of a sphere whose radius R is large enough to contain many fluctuations, but is small compared with the dimensions of the body.

Let us find the gross displacemt $\underset{\sim}{\bar{u}}^{\infty}$ corresponding to (14) for a point inside the body. The volume integral over the sphere R of the displacement due to a singularity at $\underset{\sim}{r}$ relative to its center is equal to the attraction on a charge c at $\underset{\sim}{r}$ produced by a distribution of charge of unit density filling the sphere, i.e. $4/3\ \pi c\underset{\sim}{r}$ if $r < R$ and $4/3\ \pi cR^3\underset{\sim}{r}/r^3$ if $r > R$. Thus

$$\underset{\sim}{\bar{u}}^{\infty} = \frac{c}{R^3}\sum_{r_n<R}\underset{\sim}{r}_n + c\sum_{r_n>R}\frac{\underset{\sim}{r}_n}{r_n^3}$$

As R increases and becomes reasonably large compared with $\eta^{-1/3}$ the first term should be small, being proportional to the position vector of a large number of points taken at random in a sphere. At the same time, as R increases it becomes more and more reasonable to replace the second term by an integral since the distance of each singularity from the point at which their effects are summed is large compared with the mean distance between them. We thus reach (14) but with a sphere of radius R about the point of observation excluded from the integration. However, by a known result of potential theory (14) is unaltered by this omission provided the sphere lies wholly within S.

Having defined the gross displacement we can calculate a gross stress from it with the aid of (3). This should be the true

macroscopic stress, i.e. it should give correctly the surface traction required to prevent relative motion of the faces of a macroscopic cut made in the material.

We can obviously generalize these results to a distribution of imperfections in which is a function of position. The microscopic u is still given by but the gross displacement is

$$\underset{\sim}{u}^{\infty} = c \int_V \frac{n(\underset{\sim}{r})\, \underset{\sim}{r}}{r^3}\, dv \qquad (18)$$

and in the averaging process we must have $n^{-1/3} \ll R \ll n^{-1/3}$ $\left|\text{grad } (n^{-1/3})\right|$.

The gross or microscopic p^{I}_{ij} is the stress produced by surface tractions $-p^{\infty}_{ij}n_j$ calculated from (13) or (14, 18). These two surface tractions will differ by rapidly fluctuating quantities with a 'wave-length' of the order of $n^{-1/3}$ whose effect will be confined to a surface layer of the same order. Thus in the bulk of the material the image quantities are efficiently smoothed by St. Venant's principle whether we smooth the infinity quantities or not, and we need not distinguish between their gross and microscopic values.

5. The Effect of Point Singularities on the X-ray Diffraction Pattern

Miller and Russel[3] originally suggested that there is a

---

[3] P. H. Miller, Jr., and B. R. Russel, J. Appl. Phys. 23, 1163 (1952).

---

difference between the geometrical volume change of a crystal containing imperfections and the volume change deduced from the change of

x-ray lattice constant. They calculate that for a uniform distribution of point imperfections the latter should be about twice the former.[4] Huang[5] found that they were equal. These authors omit

---

[4] They have since withdrawn this factor. P. H. Miller, Jr. and B. R. Russel, J. Appl. Phys.

[5] K. Huang, Proc. Roy. Soc. A190, 102 (1947).

---

image effects. Miller and Russel calculate the image effect for a single imperfection at the center of a sphere. They take a collection of such spheres with the interstices filled up to represent a body containing many imperfections and argue that the image effect is negligible because the surface traction across these spheres is by no means zero. As we have seen, the effect of the image term on the volume change can be taken into account quite generally, and we shall find that the same is true for its effect on the x-ray lattice constant.

For an undisturbed crystal the scattering power plotted in reciprocal space will be a set of patches with their maxima at the points of the reciprocal lattice. If the crystal is distorted by external forces or internal imperfections the patches will be displaced and deformed. We may regard the new maxima as defining a new reciprocal lattice and we can then speak of the deformation of the reciprocal lattice corresponding to a deformation of the crystal.

Let the position of a point of the crystal or reciprocal lattice before and after distortion be

$$\underset{\sim}{r} = L_i \underset{\sim}{a}_i, \qquad \underset{\sim}{r} + \Delta\underset{\sim}{r} = (L_i + \Delta L_i)\,\underset{\sim}{a}_i$$

and

$$\underset{\sim}{B} = h_i \underset{\sim}{b}_i, \qquad \underset{\sim}{B} + \Delta\underset{\sim}{B} = (h_i + \Delta h_i)\,\underset{\sim}{b}_i$$

Miller and Russel derive the following relation valid within a region around the origin of reciprocal space which decreases as the degree of crystal distortion increases:

$$\Delta h_i \, A_{ij} = - h_i \, B_{ij} \qquad (j = 1,2,3) \qquad (19)$$

where

$$A_{ij} = L_i \, L_j, \qquad B_{ij} = \Sigma \, \Delta L_i \, L_j,$$

Σ implying summation over all points of the crystal lattice. We have simplified equations (1, 2, 3) in reference 3, appendix 1, by taking the origin at the lattice point nearest the center of gravity of the crystal: then the sums ΣL_i will differ from zero by integers small compared with the number of atoms in the crystal and may be neglected. Equation (19) has the solution

$$\Delta h_i = - h_k \, C_{ki}, \qquad C_{ki} = B_{kj} \, A^{-1}_{ji} \qquad (20)$$

where A^{-1}_{ij} is the matrix reciprocal to A_{ij}. C is not in general symmetric even if B_{ij} is. Thus (20) is an infinitesimal affine transformation in reciprocal space. In other words the reciprocal lattice points are shifted as if they were embedded in am imaginary elastic continuum which undergoes a deformation in which all the strain and rotation components

$$e_{ij} = \frac{1}{2} \left(\partial \Delta h_i / \partial h_j + \partial \Delta h_j / \partial h_i \right) = \frac{1}{2} \left(C_{ij} + C_{ji} \right)$$

$$\omega_{ij} = \frac{1}{2} \left(\partial \Delta h_i / \partial h_j - \partial \Delta h_j / \partial h_i \right) = - \frac{1}{2} \left(C_{ij} - C_{ji} \right)$$

are in general different from zero and constant from small h_i. This implies, for example, that from x-ray measurements of the position of low-order spots alone, a distorted cubic crystal could not be distinguished from an unstrained monoclinic crystal slightly misoriented.

Following Huang we may replace the displacement expressed as a sum of the effects of the separate imperfections by an integral if the distribution is statistically uniform. This corresponds to the averaging process of the previous section, and we may put $a\Delta L_1 = u_1$. The summation may also be replaced by an integral and we have

$$A_{ij} = \frac{1}{a^5} \int_V x_i x_j \, dv, \qquad B_{ij} = \frac{1}{a5} \int_V x_i \ddot{u}_j \, dv \qquad (21)$$

But we know that when the image terms are included $\bar{u}_i$ has the form (15), so that $A_{ij} = \frac{4\pi}{3} n c$ B_{ij} and (20) has the solution

$$\frac{\Delta h_1}{h_1} = \frac{\Delta h_2}{h_2} = \frac{\Delta h_3}{h_3} = -\frac{4}{3} \pi n c \gamma$$

(The A_{ij} are the products of inertia of the crystal and det (A_{ij}) could only vanish if the moment of inertia of the crystal about some axis were zero.) Thus the reciprocal lattice contracts uniformly in the way we should expect for a crystal which had suffered the uniform expansion (15).

This simple result would be destroyed if the image terms were omitted. We should have

$$B_{ij} = -\frac{cn}{a^5} \int_V x_i \frac{\partial \varphi}{\partial x_j} \, dv$$

where

$$\varphi = \int_V dv/r$$

is the potential of the specimen if filled with charge of unit density. For an ellipsoidal crystal φ is a quadratic function of the coordinates (eqn. (16)), and it follows that $-\Delta h_1/h_1$, $-\Delta h_2/h_2$, $-\Delta h_3/h_3$ are equal respectively to the three quantities (17). In this case the (incorrect) deformation of the reciprocal lattice agrees with the (incorrect) macroscopic deformation with image effects omitted. For a body of arbitrary shape this is no longer true, since there is no simple relation between A_{ij} and B_{ij}. X-ray measurements would indicate that the cubic unit cell had become monoclinic, and its change of volume would bear no simple relation to the change in volume of the crystals calculated with or without image effects. These complications are implicit in Huang's calculations. Each of the two terms his expression (I) is, in electrostatic language, the sum of the potentials of a set of parallel dipoles. Such a sum taken over a large finite region in an infinite distribution of dipoles is ultimately independent of the size of the region but depends on its shape and the relative position of the point of observation within it. Inclusion of the image terms adds a layer of surface charge which just annuls these variations. Thus Huang's (I) does not represent a uniform expansion [illegible] for a sphere, for the latter the expansion lacks a factor [illegible] in the [illegible] of the [illegible] reciprocal lattice [illegible] (II) and (III) [illegible]

eventually eliminated with the help of his equation (18) in which also c must be replaced by $c\gamma$ the final result is unaffected.

Miller and Russel found by calculating the $\Sigma L_i \Delta L_i$ numerically that for a single singularity at the center of a sphere the expansion deduced from x-rays was 2.5 times the geometrical expansion. They deduce from this that there should be a similar difference (with the factor reduced from 2.5 to about 2) when there are a large number of imperfections distributed at random.

The previous discussion indicates that this is incorrect, but does not show exactly how the discrepancy arises. This discrepancy exists whether image terms are introduced or not (though introducing them would reduce the factor from 2 to $(1 + \gamma)/\gamma$) and for simplicity we omit them in the following discussion.

Let us find the effect of a single imperfection at a point $\underset{\sim}{\xi}$ relative to the center of a spherical crystal of radius R. We can save calculations by finding the dilatation of the reciprocal lattice and not its detailed distortion. Putting $\bar{u}_i = c(x_i - \xi_i)/\left|\underset{\sim}{x} - \underset{\sim}{\xi}\right|$ in (21) we find after some manipulation

$$\frac{\Delta V^{\infty}}{V} = -\frac{\partial \Delta h_i}{\partial h_i} = \frac{15}{4\pi}\frac{c}{R^5}\left(1 + \xi_i \frac{\partial}{\partial \xi_i}\right) \int_V \frac{dv}{\left|\underset{\sim}{x} - \underset{\sim}{\xi}\right|}$$

The integral is the gravitational potential at $\underset{\sim}{\xi}$ in a solid sphere of unit density and has the value $\frac{2}{3}\pi(3R^2 - \xi^2)$. Thus

$$\Delta V^{\infty} = 10\pi c\,(1 - \xi^2/R^2) \qquad (22)$$

If we exclude from the integration a sphere of radius r_0 about ξ a term $-r_0/R$ must be introduced inside the bracket. Since r_0 can presumably be taken of atomic dimensions we shall omit it.

The reason for the discrepancy now becomes clear. The expression (22) is greater or less than the geometrical ΔV^{∞} according as ξ is greater or less than $\sqrt{(3/5)}R = 0.77R$. For $\xi = 0$ it is 2.5 times the geometrical value, in agreement with Miller and Russel. If there are a large number of defects scattered at random throughout the sphere, the average contribution to ΔV^{∞} per imperfection is given by replacing ξ^2 in (22) by its mean value for all points of the sphere,

$$\overline{\xi^2} = 4\pi \int_0^R r^4\,dr \Big/ 4\pi \int_0^R r^2\,dr = \frac{3}{5} R^2 .$$

This gives a mean x-ray ΔV^{∞} of $4\pi c$, in agreement with the geometrical value (7). There seems to be nothing objectionable in the replacement of sums by integrals, and presumably Miller and Russel's summation procedure would give the geometrical value if carried out for a reasonable number of imperfections scattered throughout a sphere.

As a corollary we see that with a given number of defects the x-ray expansion depends strongly on their (non-uniform) distribution, while the geometrical expansion is, of course, independent of the distribution. Thus, for a sphere the ratio of the x-ray ΔV^{∞} to the geometrical ΔV^{∞} can be given any value between 2.5 and 0 by sweeping the defects towards the center or surface. When the two expansions are corrected for the image terms the ratio lies between $(1.5 + \gamma)/\gamma$ and $(\gamma - 1)/\gamma$.

6. Discussion

The equality of the x-ray and geometrical expansions of a crystal uniformly filled with point imperfections has a bearing on the question whether they are of Schottky or Frenkel type[3]. Revised calculations by Miller and Russel[4] gave a difference of not more than 10 to 20 per cent difference between the two expansions in place of their original factor of two. The residual difference may be partly due to the neglect of image terms.

Turning to the factor γ introduced into the expansion by the image terms it looks at first sight as if one could redefine the strength of an imperfection as c and then forget about the image effects. This is not so. The contributions to the expansion from $\underset{\sim}{u}^{\infty}$ and $\underset{\sim}{u}^{I}$ are in the ratio 1: $(\gamma - 1)$. But the ratio of their contributions to any other phenomenon will in general be quite different, since $\underset{\sim}{u}^{\infty}$ is a rapidly fluctuating function of position associated with a pure shear whereas $\underset{\sim}{u}^{I}$ is smooth except near the surface with an associated stress which is chiefly a hydrostatic pressure in a body of reasonable shape. c is thus the basic constant which we might hope to determine from measurements of one effect, and apply in calculating the value of another. The following examples illustrate this.

Nabarro[6] has discussed the hardness of dilute alloys.

---

[6] F. R. N. Nabarro, Proc. Phys. Soc. (London) 58, 669 (1946).

The hardening is due almost entirely to p_{ij}^{∞}, the slowly varying p_{ij}^{I} playing scarcely any part. He eliminates c with the help of

the observed change of lattice constant with composition but neglects the image effect. This can be put right by dividing his theoretical constant $\alpha = 0.05$ by γ before comparing it with the values deduced from experiment. The spread of the latter is too great to say if this gives any improvement.

Dexter[7] has calculated the effects of $\underset{\sim}{u}^{\infty}$ and $\underset{\sim}{u}^{I}$ on the

---

[7] D. L. Dexter, Phys. Rev. 87, 768, 1952.

---

electrical conductivity of metals. The former gives a temperature independent and the latter a temperature dependent contribution. They are of the same order at room-temperature.

Overhauser[8] has considered the modification of ratio of

---

[8] A. W. Overhauser, Phys. Rev. 90, 393 (1953)

---

diffusion by the strain due to point imperfections. The effects arising from $\underset{\sim}{u}$ and $\underset{\sim}{u}^{I}$ depend differently on temperature, and the image term may become important at high temperatures.

Zener[9] has calculated the change of shear modulus caused

---

[9] C. Zener, Acta Cryst. 2, 163 (1949).

---

by the $\underset{\sim}{u}^{\infty}$ field of point imperfections. Evidently the dilatation due to the image field should give rise to an analogous change of bulk modulus. (As we have seen $\underset{\sim}{u}^{\infty}$ produces no dilatation of the material between the imperfections.) In fact we should have a change

$$\frac{\Delta K}{K} = \frac{d \log K}{d \log V} \frac{\Delta V^{I}}{V} = \frac{d \log K}{d \log V} \, 3 \frac{\gamma - 1}{\gamma} \frac{d^{3}}{l} \qquad (23)$$

proportional to the relative change $d\ell/\ell$ of lattice constant but of opposite sign, since d log K/k log V is negative. According to a simple theory[10] verified quite well by experiment -d log K/d log V

[10] J. C. Slater, Phys. Rev. 57, 744 (1940).

is equal to $2\Gamma + 4/3$, where Γ is Grüneisen's constant. Zener's $\Delta\mu/\mu$ on the other hand depends on the shear strain energy associated with an imperfection and so is proportional to $|d\ell/\ell|$.

By an atomic calculation Dienes[11] has found that one per

[11] G. J. Dienes, Phys. Rev. 86, 228 (1952).

cent of interstitials increase the bulk modulus of copper by 6.8 per cent and of sodium by 1.9 per cent. His calculations deal in principle with what happens in the immediate neighborhood of the imperfection, so it is reasonable to suppose that they take account of $\underset{\sim}{u}^{\infty}$ and that the effects of $\underset{\sim}{u}^{I}$ should be added. The results of Dienes and Huntington and Seitz[12] suggest that we may take

[12] H. B. Huntington and F. Seitz, Phys. Rev. 61, 315 (1942).

$4\pi c/\Omega$ to be about 0.6 and 0.9 respectively for an interstitial in copper or sodium. By (12') and (23) the corresponding percentage changes for one per cent interstitials are: lattice constant 0.9 (Cu), 1.4 (Na), bulk modulus - 4.6 (Cu), - 6.9 (Na). Our calculation cannot claim any accuracy, but it suggests that the image term is important, perhaps even large enough to change the sign of $\delta K/K$.

The change of shear modulus found by Zener's argument depends on non-linear behavior in the region close to the imperfection (see below) and it is therefore in principle already included in a calculation such as Dienes' which considers the balance of interatomic forces near the imperfection.

It was pointed out at the end of section 3 that for a purely elastic model the actual volume of material was unaltered. Zener[13] has shown how in such a case the departure from Hooke's

---

[13] C. Zener, Trans. Am. Inst. Mining Met. Eng. 147, 361 (1942).

---

law gives a volume change, and we ought to consider what effect this will have on our calculations. This change has the value

$$\Delta V = -(1 + d \log K/d \log V) W_d /K$$

$$-(1 + d \log \mu /d \log V) W_s/K$$

where W_d and W_s are the total dilatational and shear strain energies associated with the internal stress. The first term can be considered as a small correction to ΔV^I corresponding to using in (9) the value of K appropriate to the lattice as expanded. The shear strain associated with the sphere-in-hole model of section 2 is $8\pi \mu c^2/r_o^3$ (of ref. 8). If we take the case of interstitials in a face-centered cubic material and put r_o equal to the distance from the interstitial to the nearest face-centered atom we have

$$\Delta V'/V = -(1 + d \log \mu / d \log V) 16\pi (\mu/K) (c/\sqrt{2})^2 f.$$

This is about one tenth of (12') for interstitials in copper. As before we take $c/\sqrt{2} \sim .05$. However, even if the ratio were

quite large our previous calculations would not be upset. Of the shear strain energy $\frac{3}{4}\mu\omega c/r_0^3$ associated with an imperfection nearly ninety percent is contained within a sphere of radius $2r_0$. Thus the correction comes entirely from an additional expansion confined to the immediate neighborhood of the imperfection. This extra volume change is transmitted to the surface by the displacement $\underset{\sim}{u}^{(\infty)}$ which must have the form (1) as soon as the elastic region is reached. Thus the effect we are considering merely 'renormalizes' the constant c in (1) and it is correct to use the modified value not only in (12') but also in discussing any other phenomenon in which only strains in the elastic region.

Point imperfections may expand the lattice by mechanisms other than misfit. Take for example an alkali halide crystal with doubly charged foreign cations in some positions together with an equal number of vacant anion sites. The continuum model is a dielectric with positive and negative charges embedded in it. Round each there is an elastic stress field due to electrostriction. The dilatation is large near a change and falls off rapidly with distance. The stress field is essentially that of a center of dilatation. A rough calculation suggests that its strength is of the same order as for a reasonable degree of misfit. It is of the same sign for both positive and negative charges. Again, if atoms of different valency are introduced substitutionally into a metal the resulting change in the number of electrons in the conduction band will produce a change of lattice constant quite apart from any misfit effects.

It is not the aim of this paper to advocate the elastic approach, but to show that when it is used, neglect of the presence of the free surface may lead to qualitative untidinesses (such as non-uniform deformation by a uniform distribution of defects) and quantitative errors which may be important.