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Volume of Self-Interstitials in Metals**

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Abstract

A new approach to compute the relaxation volume of self-interstitials in metals is developed which requires only information about the symmetry of the crystal and the interstitial as well as elastic moduli and their pressure derivatives. The method consists of first evaluating the increase in volume of a coordination polyhedron when an interstitial is inserted. Second, non-linear elastic contributions as obtained by Zener's approach are added. The computed values are in good agreement with measured relaxation volumes.

1. Introduction

Relaxation volumes for self-interstitials have been measured only for very few metals, namely those listed in Table 1. Rather elaborate and costly experiments are required to obtain this parameter. In the physical foundation of high-temperature radiation damage, this parameter is of fundamental importance as it is directly related to the preferential absorption of interstitials at dislocations. The latter is considered to be the primary cause for radiation-induced void formation and creep. It is therefore desirable to develop theoretical means to obtain this important parameter for a variety of metals and alloys for which the experimental methods are not well suited. In the present paper a simple theoretical method is developed to evaluate the relaxation volume of self-interstitials. We apply it to elastically isotropic materials under the assumption that the self-interstitial is a spherical inclusion. In spite of these rather drastic simplifications the computed values agree closely with the measured relaxation volumes. It is therefore expected that future refinements which eliminate these simplifications will further improve the predictive capability of the present theoretical approach.

Earlier theoretical evaluations of the relaxation volumes of point defects relied mainly on either the lattice statics method initiated by Kanzaki (1957) and pioneered by Hardy (1960) and others [for further references see, e.g., the review by Heald (1977)], or on computer simulation work as, for example, carried out by Johnson (1966). The former method requires an extensive list of lattice coupling parameters, whereas the latter is based on a suitably chosen interatomic potential.

When large lattice distortions occur, as in the case of self-interstitials, the Kanzaki method breaks down as recently demonstrated by Schober

Table 1. Measured Relaxation Volumes of Self-Interstitials in Metals*

| Metal | (V^R/Ω) | Experimental Method |
|-------|----------------|---------------------|
| Al | 1.9 ± 0.4 | lattice parameter |
| | 1.9 ± 0.4 | Huang scattering |
| | 1.7 ± 0.4 | diffuse scattering |
| Cu | 1.3 ± 0.3 | lattice parameter |
| | 1.5 ± 0.3 | Huang scattering |
| | 1.4 ± 0.3 | diffuse scattering |
| Mo | 1.1 ± 0.2 | lattice parameter |
| | 1.1 ± 0.2 | Huang scattering |
| Pt | 2.0 ± 0.3 | lattice parameter |

*According to the compilation of Schilling (1978).

and Ingle (1980). This is due to the fact that the lattice coupling parameters actually vary with increasing lattice distortions.

On the other hand, computer simulations must either be carried out with a large number of atoms, or the simulated lattice region around the point defect must be properly matched to an elastic continuum. In either case, elaborate computational methods are required to search for the configuration of the defect-containing lattice with the minimum energy.

It has been pointed out by Schober and Ingle (1980) for the case of a self-interstitial that the nearest neighbor displacements depend mainly on the packing of the atoms, whereas the long-range displacement field depends on the strength and shape of the interatomic potential around the equilibrium interatomic distance. This insight has inspired the following new method for the evaluation of the relaxation volume of self-interstitials.

The next-nearest neighbors of a self-interstitial form an oversized inclusion whose volume would be determined by the most efficient packing of spheres if the inclusion were not constrained by the surrounding matrix. As this misfitting polyhedron, containing at its center the interstitial, is inserted in the crystal lattice, a volume change results which is composed of two contributions. The first contribution arises from the linear elastic response of the medium and can be obtained from the work of Eshelby (1956). The second represents a non-linear elastic correction which can be evaluated according to Zener's (1942) perturbation approach.

In the following sections, the above program is carried out in detail for the self-interstitial in both bcc and fcc crystals.

2. Volume of the Distorted Coordination Polyhedron

The self-interstitial, or for that manner any point defect, is surrounded by next-nearest neighbor atoms which form the coordination polyhedron. When the point defect is replaced by a regular lattice atom, the perfect, or regular coordination polyhedron (RCP) possesses a volume V_0 . However, when the point defect is contained within the next-nearest neighbor polyhedron, this distorted coordination polyhedron (DCP) would have a volume V_d if it were not constrained by the surrounding crystal. In the following, this volume V_d of the unconstrained DCP will be evaluated and compared with the volume V_0 of the RCP.

(a) Bcc Lattice

The RCP for the bcc lattice is simply the elementary cubic cell shown in the upper half of Figure 1. Its volume is

$$V_0 = a_0^3 = (2^3/3^{3/2}) d_0^3 = 2\Omega \quad , \quad (1)$$

where a_0 is the lattice parameter, d_0 the nearest neighbor distance, and Ω the volume per atom. If the central atom in the cubic cell is now replaced by a dumbbell interstitial oriented along a $\langle 011 \rangle$ direction, it causes the RCP to be distorted as indicated in the lower half of Figure 1.

In order to compute the volume V_d of the unconstrained DCP we assume that any two atoms in this polyhedron must have a separation distance no shorter than d_0 . This requirement reflects the steep repulsive part of any realistic interatomic potential. Within this single constraint the volume V_d can be found as follows.

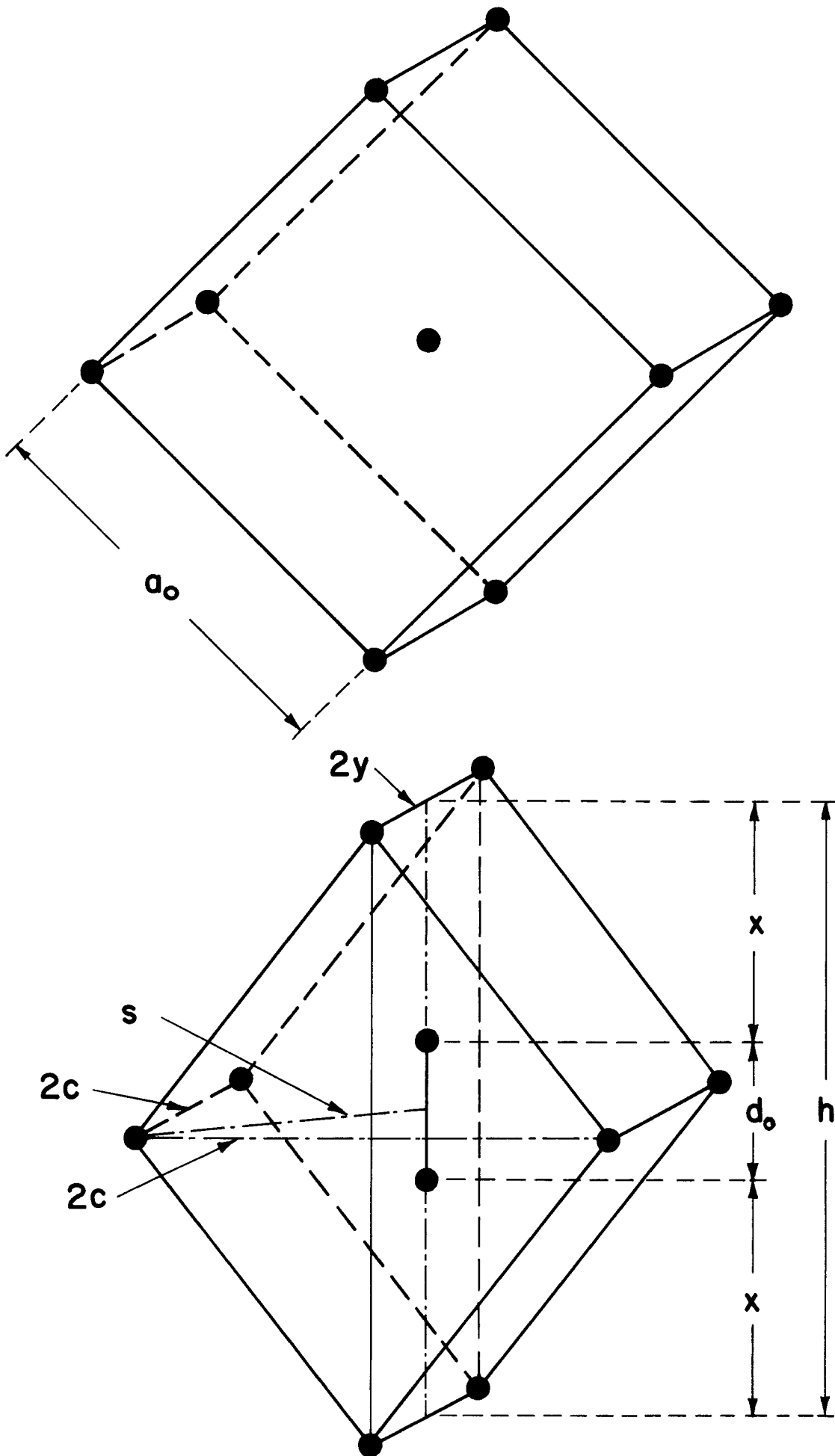


Fig. 1. The regular and the distorted coordination polyhedron in the bcc lattice.

The DCP may be viewed as two wedges joined at their rectangular base. The dumbbell axis lies within this common base plane, as shown in Figure 1. With the notation for the various distances indicated in this figure, we find for the DCP the volume

$$V_d = \frac{1}{3} hc (4y + 2c) \quad . \quad (2)$$

Note that the distance $2y$ is not necessarily equal to the distance $2c$. From simple geometric considerations and the requirement that all near-neighbor distances must be equal to or greater than d_0 , the following relationships are derived:

$$x^2 + y^2 = d_0^2 \quad (3)$$

$$2x + d_0 = h \quad . \quad (4)$$

These equations apply to the interatomic distances in the plane containing the dumbbell axis. For atoms on the perpendicular plane, the following relationships must hold:

$$s^2 + (d_0/2)^2 = d_0^2 \quad (5)$$

$$2c^2 = s^2 \quad . \quad (6)$$

It follows from these two equations that $2c = (3/2)^{1/2} d_0 > d_0$. Thus, the

atoms in the plane perpendicular to the dumbbell axis touch both atoms of the self-interstitial, but not each other.

With Eqs. (3) and (4) we can express the volume V_d of the DCP as a function of only one unknown, say, x . Then, Eq. (2) gives

$$V_d(x) = \frac{2}{3} c [2(d_0^2 - x^2)^{1/2} + c][2x + d_0] \quad , \quad (7)$$

and we determine x such as to give the minimum value for V_d . The requirement $dV_d/dx = 0$ gives the equation

$$4x^2 + d_0 x - 2d_0^2 = d_0^2 (3/8)^{1/2} (1 - x^2/d_0^2)^{1/2} \quad (8)$$

which has the solution

$$x_0 = 0.6684071 d_0 \quad . \quad (9)$$

For this value of x the distance

$$2y = 1.488 d_0 \quad , \quad (10)$$

and is therefore not smaller than d_0 as are all other interatomic distances.

The minimum value of the DCP is then

$$V_d(x_0) = 2.0034 d_0^3 \quad (11)$$

so that the change in the volume of the coordination polyhedron upon formation

of a $\langle 011 \rangle$ dumbbell interstitial is equal to

$$\Delta V = V_d(x_0) - V_0 = 0.3012 V_0 = 0.6418 \Omega \quad . \quad (12)$$

(b) Fcc Lattice

The coordination shell of nearest-neighbor atoms in a fcc lattice forms a cubo-octahedron shown in the upper half of Figure 2. One may view this RCP as composed of a rectangular prism with a base area of d_0^2 and a height of a_0 plus four pyramids with rectangular bases attached to the sides of the central prism. The pyramids have each a base area of $(a_0 d_0)$ and a height of $(d_0/2)$. Hence, the volume of the RCP is

$$V_0 = \frac{1}{2} a_0^3 + \frac{2}{3} a_0 d_0^2 = (5/3) \sqrt{2} d_0^3 \quad . \quad (13)$$

Upon introduction of a $\langle 001 \rangle$ dumbbell interstitial the central prism of the RCP will acquire a new base area of $2y^2$ and a new height of h . Furthermore, the height of the attached pyramids assumes a new value s . As a result, the volume of the DCP becomes

$$V_d = 2(2x + d_0)[d_0^2 - x^2 + (2^{3/2}/3)(d_0^2 - x^2)^{1/2} s] \quad , \quad (14)$$

which depends on the two unknown parameters x and s . These two parameters are, however, not independent if we want to maintain at all times interatomic distances no less than d_0 . Nor is V_d in this case an analytic function of either s or x around its minimum value. In fact, to find the minimum of V_d with the constraint that all interatomic distances be no less than d_0 , will

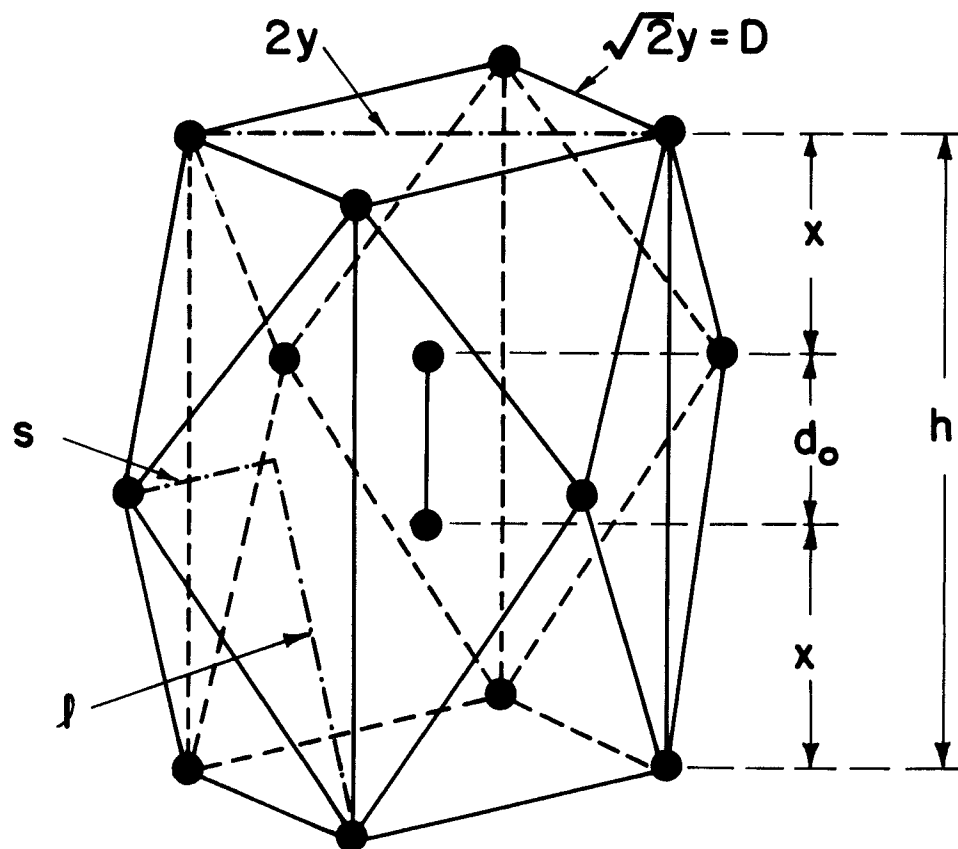
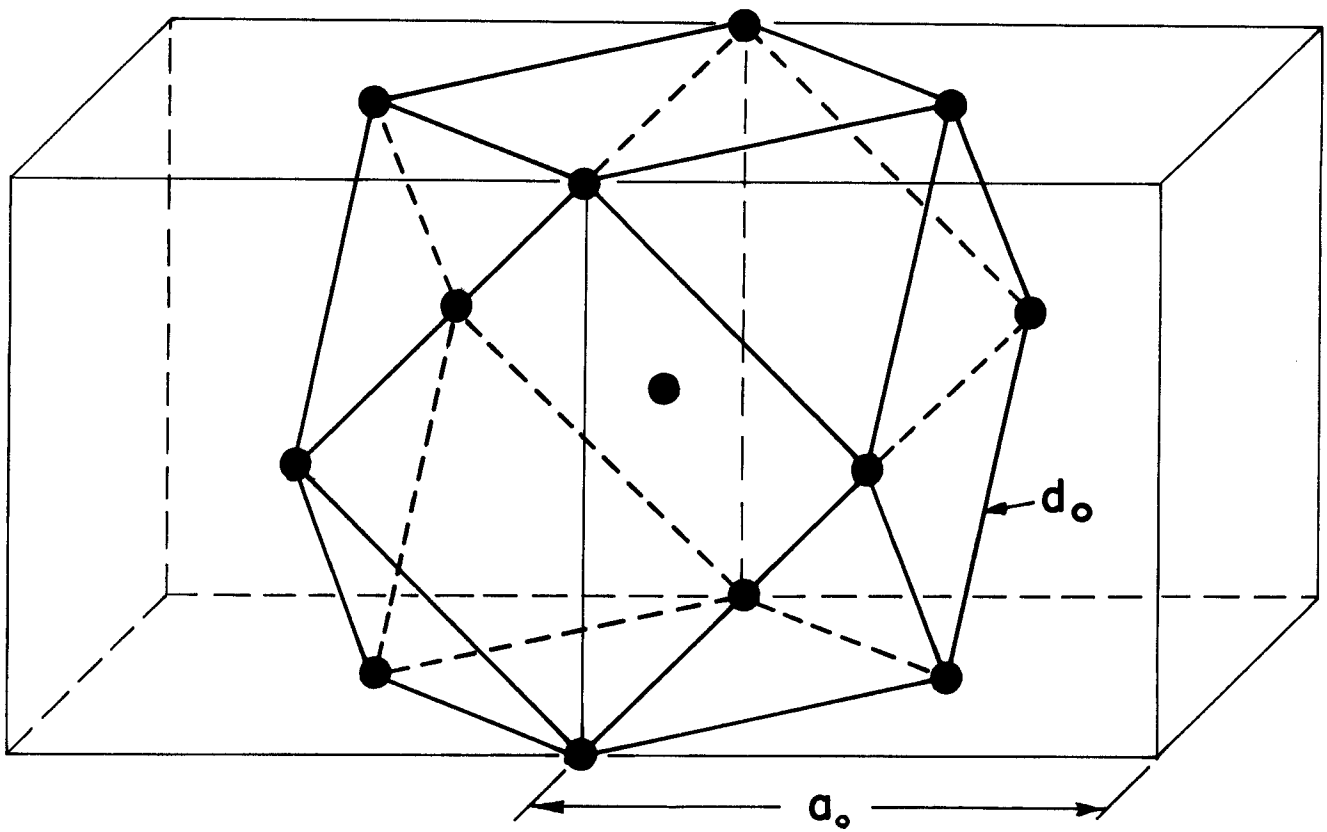


Fig. 2. The regular and the distorted coordination polyhedron in the fcc lattice.

require either nonlinear programming methods or physical intuition. The present problem lends itself to the latter approach.

Let us consider the transformation of the RCP into the DCP as a gradual process. The height of the attached pyramids is reduced from its initial value ($d_0/2$) in the RCP to a smaller value determined by the fact that the atom on the apex of each pyramid touches both atoms which form the dumbbell. In this manner, a maximum number of atoms remain in contact in the DCP, and the height of the pyramids has to satisfy the two equations

$$s = [d_0^2/4 - xd_0 - x^2/2]^{1/2} \quad (15)$$

$$s = (3/4)^{1/2} d_0 - [(d_0^2 - x^2/2)]^{1/2} \quad (16)$$

These two equations have the solution

$$x = 0.2 d_0 \quad \text{and} \quad s = \sqrt{0.03} d_0 \quad (17)$$

In the resulting DCP with x and s as given above, the corner atoms of the central prism base are no longer in contact as their interatomic distance is now equal to $D = 1.3856 d_0$. On the other hand, the prism height has become slightly shorter, i.e. $h = 1.4 d_0 = 0.98995 a_0$. For this configuration, the DCP has the volume

$$V_d = 3.136 d_0^3 = 4.4350 \Omega \quad (18)$$

so that the volume change of the interstitial-containing polyhedron is

$$\Delta V = 1.10164 \Omega \quad . \quad (19)$$

We note that there exist 33 nearest neighbor pairs with an interatomic distance of d_0 in this DCP compared to 36 pairs in the RCP. This reduction in the number of contacting pairs is due to the fact that $D > d_0$.

Let us therefore investigate another configuration of the DCP in which D remains equal to d_0 upon introduction of the self-interstitial. Now the apex atoms of the pyramids no longer contact the atoms on the corners of the central prism, though they contact both dumbbell atoms. The number of contact pairs is only 25, and $x = d_0/\sqrt{2}$, $s = 0.3660 d_0$. The volume of the DCP becomes $V_d = 3.5924 d_0^3$, and the volume change is $\Delta V = 1.2620 \Omega$.

We see that this configuration of the DCP gives a larger volume change and a smaller number of contacting pairs and presumably a weaker bonding. The configuration leading to the volume change of Eq. (19) is therefore the most tightly packed and the strongest bound DCP around the $\langle 001 \rangle$ dumbbell interstitial in the fcc lattice.

3. Relaxation Volume of Self-Interstitials

The relaxation volume V^R of a self-interstitial is defined as the volume increase of a finite and perfect crystal upon forming an interstitial by the addition of one extra atom. According to the well-known procedure of Eshelby (1956), one imagines that the volume expansion occurs as the result of the following steps. First, remove from the perfect crystal a RCP. Second, insert in this unconstrained polyhedron the interstitial and let it expand freely by the volume ΔV . The resulting DCP no longer fits into the original cavity. Therefore, in the third step, apply appropriate surface loads to both the DCP and the cavity. These loads are selected such that they are equal but

opposite on the DCP and the cavity, and of such magnitude and direction that the elastically compressed DCP and the elastically dilated cavity become equal in size and shape. In this step, both the DCP and the surrounding matrix are assumed to have the same, constant elastic moduli. After insertion of the DCP a state of internal stress exists in the solid compatible with these fictitious loads.

The well-known theorem in linear elasticity asserts now [see Eshelby (1956)] that the volume change of the finite crystal upon insertion of the inclusion is equal to the unconstrained volume change ΔV .

However, due to the large elastic distortions around the interstitial, nonlinear elastic effects produce an additional volume change δV , so that

$$V^R = \Delta V + \delta V \quad . \quad (20)$$

The evaluation of δV can be accomplished with the second-order elasticity results derived by Zener (1942), Seeger and Haasen (1958), Toupin and Rivlin (1960), and by Schoeck (1979). According to Schoeck, the additional volume change is given by

$$\delta V = \frac{\partial U^R}{\partial p} - \frac{U^R}{K} \quad (21)$$

where K is the bulk modulus, p the external hydrostatic pressure and

$$U^R = \frac{1}{2} c_{ijkl} \int \epsilon_{ij} \epsilon_{kl} \, dV \quad (22)$$

is the relaxation or strain energy associated with the internal strain field.

ϵ_{ij} is due to the linear elastic theory, where the elastic moduli $c_{ijkl}(p)$ are now assumed to depend on the pressure.

4. Results

In order to facilitate the further evaluation of δV , two simplifications are made in the present paper. First, we assume that the crystal is elastically isotropic. Second, we approximate the internal strain field ϵ_{ij} by that of a spherical inclusion with the same misfit volume ΔV . The strain energy associated with a spherical inclusion is given by

$$U^R = \frac{2K\mu}{3K + 4\mu} \frac{\Delta V^2}{\Omega} \quad (23)$$

where μ is the isotropic shear modulus. Using Eq. (21) we obtain finally

$$\delta V/\Omega = \left[3 \frac{K}{\mu} \left(\frac{d\mu}{dp} - \frac{\mu}{K} \right) + 4 \frac{\mu}{K} \left(\frac{dK}{dp} - 1 \right) \right] \frac{2\mu K}{[3K + 4\mu]^2} \left(\frac{\Delta V}{\Omega} \right)^2 \quad (24)$$

where $(d\mu/dp)$ and (dK/dp) are the pressure derivatives of the shear and bulk modulus, respectively.

Using the compilation of Guinan and Sternberg (1974) for the pressure derivatives of isotropic elastic constants, the relaxation volume V^R was computed, and the results are listed in Table 2. Values in brackets are based on estimates of the elastic properties. It is seen that relaxation volumes for bcc metals are smaller by roughly a factor of two as compared to the interstitial relaxation volumes in fcc metals. This difference is strictly due to the volume change ΔV . Bcc lattices have a more open structure and can more easily accommodate the interstitial as compared to fcc lattices. The

Table 2. Theoretical Values of Relaxation Volumes for Self-Interstitials^(*)

| Metal | Structure | $\kappa^{(+)}$ | $\mu^{(+)}$ | $d\kappa/dp$ | $d\mu/dp$ | v^R/Ω |
|-------|-----------|----------------|-------------|--------------|-------------|--------------|
| Ag | fcc | 1.03 | 0.298 | 6.12 | 1.4 (1.45) | 1.81 (1.83) |
| Al | fcc | 0.76 | 0.261 | 4.42 | 1.8 (1.75) | 1.86 (1.84) |
| Au | fcc | 1.73 | 0.28 | 6.29 | 1.05 (1.1) | 1.69 (1.72) |
| Ca | fcc | 0.167 | 0.074 | 2.7 | (1.2) | (1.49) |
| Cr | bcc | 1.62 | 1.15 | 4.89 | (1.4) | (0.88) |
| Cs | bcc | 0.021 | (0.0065) | 3.17 | (1.2) | (0.80) |
| Cu | fcc | 1.37 | 0.477 | 5.48 | 1.35 (1.45) | 1.75 (1.79) |
| Fe | bcc | 1.66 | 0.819 | 5.29 | 1.8 | 0.91 |
| Ir | fcc | 3.63 | 2.21 | 4.83 | (3.4) | (2.26) |
| K | bcc | 0.033 | 0.009 | 3.96 | 0.79 (0.8) | 0.76 (0.76) |
| Li | bcc | 0.121 | 0.0385 | 3.53 | 0.42 (0.59) | 0.70 (0.73) |
| Mo | bcc | 2.63 | 1.25 | 4.4 | 1.5 (1.6) | 0.85 (0.86) |
| Na | bcc | 0.0674 | 0.0198 | 4.69 | 0.8 (0.78) | 0.76 (0.76) |
| Nb | bcc | 1.71 | 0.376 | 6.91 | 0.53 (0.63) | 0.76 (0.77) |
| Ni | fcc | 1.83 | 0.858 | 6.20 | 1.4 (1.8) | 1.85 (1.98) |
| Pb | fcc | 0.447 | 0.086 | 5.53 | 1.0 (1.25) | 1.63 (1.76) |
| Pd | fcc | 1.93 | 0.48 | 5.35 | 0.54 (1.4) | 1.4 (1.79) |
| Pt | fcc | 2.83 | 0.637 | 5.18 | 1.6 (1.5) | 1.9 (1.85) |
| Rb | bcc | (0.023) | (0.0063) | 3.63 | 0.72 (0.59) | 0.75 (0.73) |
| Rh | fcc | 2.87 | 1.47 | 4.50 | (2.9) | (2.13) |
| Sr | fcc | 0.116 | (0.052) | 2.76 | (0.94) | (1.41) |
| Ta | bcc | 1.93 | 0.69 | 3.15 | 1.1 (1.45) | 0.78 (0.83) |
| Th | fcc | 0.577 | 0.287 | 4.11 | 1.7 (1.5) | 1.75 (1.70) |
| V | bcc | 1.57 | 0.481 | 3.5 | (0.94) | (0.77) |
| W | bcc | 3.10 | 1.60 | 3.95 | 2.3 (1.9) | 0.92 (0.88) |
| Yb | fcc | 0.149 | 0.0806 | 2.2 | (1.4) | (1.46) |

(*) Numbers in brackets are based on estimates rather than measured elastic properties.

(+) Elastic constants are in units of MPa.

nonlinear elastic contribution δV further accentuates this difference as $\delta V \sim (\Delta V)^2$.

When compared to the few measured values in Table 1 with their associated uncertainties, the theoretically derived values of V^R according to the present method are in remarkably good agreement. The values for fcc metals are, however, on the high side, whereas the values for bcc metals appear to be on the low side. Further refinements of the present method, namely by the use of anisotropic elasticity and the correct non-spherical strain field ϵ_{ij} of the restrained DCP, are therefore expected to improve the predictive capability of the theory.

5. Conclusions

A simple method was developed to compute the relaxation volume of self-interstitials in cubic metals. This method consists of determining first the unconstrained volume increase ΔV of a coordination polyhedron formed by the nearest neighbor atoms of an inserted dumbbell interstitial. Added to this volume increase is a contribution arising from nonlinear elastic effects which can be easily evaluated according to Zener's formula for volume changes produced by internal stresses. The results obtained with this method are, even after further simplifications of the theory, in good agreement with experimental values. Only macroscopic properties such as elastic constants and their pressure derivatives are required for the computations.

This is contrast to the theories of point defects based on discrete lattice models [Heald (1977)] or on the electron theory of metals [Evans (1977)]. Although the latter theory represents the most fundamental approach to obtain point defect properties, it has been applied with success only to vacancies in simple metals. The present method, being an extension of the

continuum models of Eshelby (1956), appears to be restricted to the evaluation of the relaxation (or formation) volume of point defects for which the electron redistribution plays a minor role in evaluating V^R . For example, if the central atom in the RCP of a fcc lattice is removed to create a vacancy, no volume change results and $\Delta V = 0$. Since the DCP has the same volume as the RCP, the vacancy relaxation volume would also be zero. It is clear from this example, that the electron redistribution is the major cause for the volume change when a vacancy is formed. In contrast, the most efficient packing of atoms together with the nonlinear elastic deformation of the lattice appear to be the major factors which determine the relaxation volume of self-interstitials in metals.

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