33831

THEORY OF DIFFUSE X-RAY SCATTERING BY INTERSTITIALS
IN bcc METALS

by

Roy Benedek and P. S. Ho

June 1973

Cornell University

Ithaca, New York 14850

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Report #2034

Issued by

The Materials Science Center

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THEORY OF DIFFUSE X-RAY SCATTERING BY INTERSTITIALS IN bcc METALS

Roy Benedek
Department of Materials Science and Engineering
Cornell University
Ithaca, New York 14850
P. S. Ho
IBM Watson Research Center
Yorktown Heights, New York 10598

Abstract

Starting with a Green's function lattice statics approach, recently developed by the authors, an expression is derived for the diffuse x-ray scattering cross section of interstitials in cubic metals. Numerical calculations have been performed, based on interatomic potentials for Tungsten, for the six possible geometrical configurations of an intrinsic interstitial in a bcc metal. The relevance of such calculations to the problem of determining the stable form of the interstitial is discussed.

Introduction

The question of which geometrical configuration an intrinsic interstitial assumes in a metal is a fundamental one for the field of radiation damage. However, it has not been satisfactorily answered even for the relatively well understood fcc metals.

For a bcc crystal, symmetry considerations suggest six possible configurations. Of these, three (tetrahedral, octahedral, $\langle 100 \rangle$ split) give rise to long range displacement fields of tetragonal symmetry, two ($\langle 111 \rangle$ split crowdion, activated crowdion) to fields of trigonal symmetry, and one ($\langle 110 \rangle$ split) to a field of orthorhombic symmetry. It is generally believed that the $\langle 110 \rangle$ split configuration is the most likely to occur. In a calculation for α -iron (1) based on an empirical interatomic potential this was found to be the stable configuration. Other calculations (2), however, have indicated that a slightly altered potential can result in a different stable configuration. At present, theory alone seems unable to resolve this question.

Of the experimental probes of point defect symmetry the most direct are i) strain field induced image contrast observed in the field ion microscope (3) and ii) x-ray diffuse scattering (4). It is the latter which we would like to discuss in the present paper.

To make use of the information which may be provided by scattering measurements one must have a theoretical model for predicting the intensity profiles for the different configurations. In the usual Born approximation this involves the calculation of the crystal structure factor. The calculation of this structure factor for an interstitial in a bcc metal is complicated by the large relaxation of near neighbor atoms. A modified Green's function approach proposed recently (5) by the authors is appropriate for dealing with this difficulty.

In section II the Green's function equations for lattice equilibrium are very briefly reviewed. In section III a relation is derived for the scattering cross section. Numerical calculations for six bcc interstitial configurations, based on interatomic potentials for Tungsten, are discussed in section IV.

II. Green's Function Equations

In this section the Green's function approach to the calculation of lattice distortion around interstitials is outlined. A fuller discussion may be found in reference (5).

Consider a crystal containing an isolated interstitial atom. In the spirit of the harmonic approximation of lattice dynamics, one writes the crystal energy as

$$\Phi = \Phi_0 - \sum_{l\alpha} F_\alpha(l) u_\alpha(l) + 1/2 \sum_{\substack{l\alpha \\ l'\beta}} \phi_{\alpha\beta}(l, l') u_\alpha(l) u_\beta(l') \quad (2.1)$$

Here $F_\alpha(l)$ (the force on the l^{th} atom in the α direction) and $\phi_{\alpha\beta}(l, l')$ (the dynamical matrix) are expansion coefficients; the displacement $\vec{u}$ is defined

$$u_\alpha(l) = \begin{cases} r_\alpha(l) - R_\alpha(l), & l \text{ within core} \\ r_\alpha(l) - R_\alpha(l), & \text{remainder of crystal} \end{cases}$$

The interstitial "core" includes n_c atoms displaced by large amounts (say $.05a$, where $2a$ is the lattice constant) from their normal lattice sites. Typically, for an interstitial in a bcc crystal the core consists of 10-30 atoms (5). The quantity $\vec{R}(l)$ is a preliminary estimate of the equilibrium position of the l^{th} core atom (5). The core may be thought of as consist-

ing of n_c "interstitials" located at sites $\vec{R}(l)$ and $n_c - 1$ "vacancies" at the normal lattice sites $\vec{R}(l)$ within the core.

It is convenient to decompose

$$\phi_{\alpha\beta}(l, l') = \frac{\partial^2 \phi}{\partial u_\alpha(l) \partial u_\beta(l')}$$

into two contributions:

$$\phi = \phi^0 - \delta\phi$$

ϕ^0 is the dynamical matrix of a perfect lattice into which are placed non-interacting atoms at sites $\vec{R}(l)$. $-\delta\phi$ is the change in ϕ occurring when core-core and core-lattice interactions are "turned on" and lattice-core vacancy interactions are "turned off" (5).

The equilibrium condition $\partial\phi/\partial u_\alpha(l) = 0$ leads to the relation

$$u_\alpha(l) = \sum_{l', \beta} G_{\alpha\beta}(l, l') F_\beta(l') \\ \equiv GF \quad (2.2)$$

where the Green's function satisfies the Dyson equation

$$G = G^0 + G^0 \delta\phi G \quad (2.3)$$

Here $G^0 = (\phi^0)^{-1}$ is the perfect lattice Green's function. Substituting eq. (2.3) into (2.2) one obtains the alternate form

$$u = G^0 (F + \delta\phi u) \\ \equiv G^0 F^* \quad (2.4)$$

where F^* is the so-called Kanzaki force. It is easily shown (8) that $\vec{F}^*(l) = 0$ for core atoms.

The reduction of eq. (2.2) or (2.4) to a form suitable for numerical computation is explained in detail in reference 5.

III. Diffuse Scattering Cross Section

The cross section for x-ray (or neutron) scattering by a dilute random array of cN interstitials may be written as (4)

$$\frac{d\sigma}{d\Omega} = \frac{cN}{n} \sum_{j=1}^n |\vec{f}(\vec{q}) \cdot \vec{s}^j(\vec{q})|^2 \quad (3.1)$$

Here $\vec{f}(\vec{q})$ is the atomic scattering factor (assumed the same for all atoms), n is the number of possible orientations of the defect, and

$$\vec{s}^j(\vec{q}) = \sum_l \exp\{-i\vec{q} \cdot (\vec{r}^j(l) - \vec{R}_0)\}$$

is the structure factor at scattering vector $\vec{q}$ associated with the j^{th} orientation. $\vec{R}_0$ is the center of mass of the defect.

It is useful to divide the structure factor into 2 parts one of which corresponds to the interstitial core and the other to the rest of the lattice:

$$S(\vec{q}) = S_c(\vec{q}) + S_L(\vec{q})$$

The displacements of atoms included in the second term are small ($\approx 0.05a$) and therefore the exponential may be expanded:

$$\begin{aligned} S_L(\vec{q}) &= \sum_{\vec{l}}' \exp\{-i\vec{q} \cdot (\vec{R}(\vec{l}) - \vec{R}_0)\} \\ &= \sum_{\vec{l}}' \exp\{-i\vec{q} \cdot (\vec{R}(\vec{l}) - \vec{R}_0)\} \exp(-i\vec{q} \cdot \vec{u}(\vec{l})) \\ &\approx \sum_{\vec{l}}' \exp\{-i\vec{q} \cdot (\vec{R}(\vec{l}) - \vec{R}_0)\} (1 - i\vec{q} \cdot \vec{u}(\vec{l})) \end{aligned} \quad (3.2)$$

The prime indicates that core atoms are not included in the summation. Using eq. (2.4) one may write

$$\begin{aligned} &\sum_{\vec{l}}' \vec{u}(\vec{l}) \exp\{-i\vec{q} \cdot (\vec{R}(\vec{l}) - \vec{R}_0)\} \\ &= \sum_{\vec{l}}' \sum_{\vec{l}'} G^0(\vec{l} - \vec{l}') F^*(\vec{l}') \exp\{-i\vec{q} \cdot (\vec{R}(\vec{l}) - \vec{R}_0)\} \\ &= G(\vec{q}) F^*(\vec{q}) - \vec{A}(\vec{q}) \equiv \vec{Q}(\vec{q}) - \vec{A}(\vec{q}) \end{aligned} \quad (3.3)$$

where

$$\begin{aligned} G_{\alpha\beta}(\vec{q}) &= \sum_{\vec{l}'} (\phi_{\alpha\beta}^0(\vec{l} - \vec{l}'))^{-1} \exp\{-i\vec{q} \cdot (\vec{R}(\vec{l}) - \vec{R}(\vec{l}'))\} \\ &\equiv (\phi_{\alpha\beta}^0(\vec{q}))^{-1} \end{aligned} \quad (3.3a)$$

$$\begin{aligned} \Delta_{\alpha}(\vec{q}) &= \sum_{\vec{l}}'' \sum_{\vec{l}', \beta} G_{\alpha\beta}^0(\vec{l} - \vec{l}') F_{\beta}^*(\vec{l}') \exp\{i\vec{q} \cdot (\vec{R}(\vec{l}) - \vec{R}_0)\} \\ &\equiv \sum_{\vec{l}}'' \vec{d}_{\alpha}(\vec{l}) \exp\{-i\vec{q} \cdot (\vec{R}(\vec{l}) - \vec{R}_0)\} \end{aligned} \quad (3.3b)$$

and

$$F_{\alpha}^*(\vec{q}) = \sum_{\vec{l}'} F_{\alpha}^*(\vec{l}') \exp\{-i\vec{q} \cdot (\vec{R}(\vec{l}') - \vec{R}_0)\} \quad (3.3c)$$

The summation with respect to $\vec{l}'$ in eqs. (3.3a,b,c) is over a perfect lattice while the double prime in eq. (3.3b) indicates a summation over the n_c core vacancies. The quantities $\vec{d}(\vec{l})$ may be referred to as "virtual" displacements since they pertain to the core vacancies and are not related to the real displacements $\vec{u}(\vec{l})$. Substituting eq. (3.3) into eq. (3.2) one obtains

$$\begin{aligned} S_L(\vec{q}) &= \sum_{\vec{l}}' \exp\{-i\vec{q} \cdot (\vec{R}(\vec{l}) - \vec{R}_0)\} - i\vec{q} \cdot \vec{Q}(\vec{q}) \cdot F^*(\vec{q}) + i\vec{q} \cdot \vec{A} \\ &= \sum_{\vec{l}}'' \exp\{-i\vec{q} \cdot (\vec{R}(\vec{l}) - \vec{R}_0)\} (-1 + i\vec{q} \cdot \vec{d}(\vec{l})) - i\vec{q} \cdot \vec{Q}(\vec{q}) \end{aligned}$$

For a split interstitial pair located at $\pm \vec{R}_I$ the core term $S_c(\vec{q})$ may be written

$$S_c(\vec{q}) = 2\cos(\vec{q} \cdot \vec{R}_I) - 1 + \sum_l \exp\{-i\vec{q} \cdot (\vec{R}(l) + \vec{u}(l))\} \quad (3.4)$$

Finally, combining eqs. (3.2) and (3.4) one obtains

$$S(\vec{q}) = S_1(\vec{q}) + S_2(\vec{q}) + S_3(\vec{q}) \quad (3.5)$$

where

$$\begin{aligned} S_1(\vec{q}) &= 2\cos(\vec{q} \cdot \vec{R}_I) - 1 \\ S_2(\vec{q}) &= \sum_l \exp\{-i\vec{q} \cdot (\vec{R}(l) - \vec{R}_0)\} \\ &\quad \cdot (\exp\{i\vec{q} \cdot (\vec{R}(l) - \vec{R}(l) + \vec{u}(l))\} - 1 + i\vec{q} \cdot \vec{d}(l)) \\ S_3(\vec{q}) &= -i\vec{q} \cdot \vec{Q}(\vec{q}) \end{aligned}$$

Equation (3.5) is similar to an expression obtained by Eisenriegler (7a), who studied scattering by the $\langle 100 \rangle$ split configuration in Cu. Eisenriegler's work, however, is not based on a unified lattice statics treatment, such as we have presented here.

The term $S_1(\vec{q})$ corresponds to the interstitial itself. The second term accounts for the near neighbor shells (the interstitial core) which are displaced by large amounts from their normal lattice sites. $S_3(\vec{q})$ includes the contribution of the long range part of the lattice distortion field and is associated with the so-called Huang scattering (6) near reciprocal lattice vectors.

$S_3(\vec{q})$ varies as $1/(q-G)^2$ (apart from angular dependence) when $\vec{q}$ is near a nonzero reciprocal lattice vector $\vec{G}$. Far away from reciprocal lattice vectors $S_3(\vec{q})$ becomes negligible and the terms $S_1(\vec{q})$ and $S_2(\vec{q})$ dominate the scattering.

Trinkaus (7) has shown that knowledge of the surfaces of constant scattering intensity in the Huang regime ($\vec{q} \rightarrow \vec{G}$) would allow one to distinguish between interstitials of tetragonal, trigonal and orthorhombic symmetry in cubic crystals. If, for example, such an analysis revealed the interstitial to be tetragonal this would still leave unanswered the question of which of the three possible configurations having this symmetry was responsible. Additional information, particularly concerning the atoms in the immediate vicinity of the interstitial, may be obtained by studying the scattering far from reciprocal lattice vectors. Therefore, in order to make a complete identification of the interstitial it

is important to study the scattering over a wide region of reciprocal space.

Essentially all existing experimental work (reviewed recently by Dederichs (4)) has been concerned with scattering in the Huang regime since this is the most intense part of the diffuse scattering.

In the next section numerical calculations for the six possible interstitial configurations in Tungsten, taken as a typical refractory bcc metal, are discussed.

IV. Numerical Calculations

Recently (5,8) the authors have calculated lattice distortion fields for interstitials in Tungsten using the Green's function approach outlined in section II. Parameters obtained from these calculations may now be used to calculate the structure factor using eq. (3.5) and the quantity

$$I(\vec{q}) = \frac{1}{n} \sum_{j=1}^n |S_j^j(\vec{q})|^2 = \frac{1}{n} \sum_{j=1}^n I_j(\vec{q}) \quad (4.1)$$

related to the scattering intensity.

Before discussing the detailed results some general features may be noted. The peaks and valleys in the function $I(\vec{q})$ are related to maxima, minima and nodes in the structure factor. If the n orientations of the interstitial are equivalent (for a given direction in reciprocal space) the sum in eq. (4.1) reduces to a single term. Examples of such a situation are i) interstitials of tetragonal symmetry for $q=(\xi\xi\xi)$, ii) interstitials of trigonal symmetry for $q=(\xi00)$. These special directions in reciprocal space will be referred to as "singlet" directions with respect to the corresponding configurations.

The function $I(\vec{q})$ along singlet directions has the same nodes as the structure factor $S(\vec{q})$. Since the latter may possess several nodes between, say, the origin and the first reciprocal lattice vector, singlet intensity curves generally exhibit large and rapid oscillations. Doublet and triplet curves (i.e. along directions for which 2 and 3 nonequivalent orientations, respectively, contribute to equation (4.1)) generally have no nodes and show oscillations of smaller amplitude than singlet curves. Table I lists the types of intensity profiles along three directions in reciprocal space corresponding to interstitials of tetragonal, orthorhombic and trigonal symmetry.

TABLE I

This table lists the terms entering the intensity profile $I(\vec{q})$ along three directions in reciprocal space for the three interstitial symmetry types in bcc crystals. Each profile is labeled singlet, doublet or triplet according to the number of terms it contains. $I_{[hkl]} = |S^{[hkl]}(\vec{q})|^2$ in the square of the structure factor for a defect oriented in the $[hkl]$ direction.

Symmetry Configuration	Tetragonal <100> Split Tetrahedral Octahedral	Orthorhombic <110> Split	Trigonal <111> Split <111> Activated Crowdion
$\vec{q}$			
$\xi 0 0$	DOUBLET	DOUBLET	SINGLET
$I(q)$	$\frac{1}{3} I_{[100]} + \frac{2}{3} I_{[001]}$	$\frac{1}{3} I_{[011]} + \frac{2}{3} I_{[110]}$	$I_{[111]}$
$\xi \xi 0$	DOUBLET	TRIPLET	DOUBLET
$I(q)$	$\frac{1}{3} I_{[001]} + \frac{2}{3} I_{[100]}$	$\frac{1}{6} I_{[110]} + \frac{1}{6} I_{[\bar{1}10]} + \frac{2}{3} I_{[011]}$	$\frac{1}{2} I_{[111]} + \frac{1}{2} I_{[\bar{1}11]}$
$\xi \xi \xi$	SINGLET	DOUBLET	DOUBLET
$I(q)$	$I_{[100]}$	$\frac{1}{2} I_{[110]} + \frac{1}{2} I_{[1\bar{1}0]}$	$\frac{1}{3} I_{[111]} + \frac{2}{3} I_{[11\bar{1}]}$

Now we consider some of the detailed results. Fig. 1 shows plots of $I(q)$ for tetragonal and orthorhombic interstitials up to the second reciprocal lattice vector in the $[100]$ direction. The steep rise in the vicinity of the 200 and 400 reciprocal lattice points is characteristic of the Huang scattering. The slight asymmetry of the peaks ($I(2+|\epsilon|, 0, 0) > I(2-|\epsilon|, 0, 0)$) may be attributed to the positive dilatation due to interstitials (4). None of the curves are singlets so that the intensity is nonzero everywhere. The sharp cusplike minimum of the <100> split interstitial occurs because the two contributing structure factors have nodes

at nearly the same point.

The question arises as to what extent calculated intensity profiles are sensitive to the interatomic potential used in the lattice distortion calculation. Fig. 2 illustrates the results for the $\langle 110 \rangle$ split interstitial using two widely differing potentials (described in reference (5)). The numerical correspondence is not exact, however, qualitatively the two curves have similar features. This was found to hold true for the other configurations as well. Other than those appearing in fig. 2, all of the plots are based on calculations using a Tungsten potential derived by Johnson and Wilson (9).

Figs. 3 and 4 show several intensity profiles along the $\{110\}$ and $\{111\}$ directions, respectively. Although only two curves are shown, all of the configurations exhibit rapid oscillations in the $\{111\}$ direction. The $\langle 111 \rangle$ activated crowdion and $\langle 111 \rangle$ split crowdion (not shown) have almost indistinguishable intensity profiles. Regions of very low intensity for the crowdion configurations (as in fig. 4 between 000 and 222) are caused by destructive interference between the terms $S_1(\vec{q})$ and $S_2(\vec{q})$ (eq. 3.5).

One may remark that on the whole there is a great deal of similarity in the intensity profiles associated with the different interstitial configurations. Still, certain distinguishing features do appear, such as the sharp cusp for the $\langle 100 \rangle$ split configuration in the $\{100\}$ direction, the double minimum for the $\langle 110 \rangle$ split configuration between 110 and 220, etc.

V. Conclusions

In this paper relations are derived for the diffuse x-ray scattering cross section of interstitials in cubic materials. The formulation is based on a Green's function lattice statics treatment of the strain field due to the interstitial. In this approach the large relaxations of near neighbor atoms are properly accounted for, as well as the long range part of the strain field.

Numerical calculations of the scattering cross section have been performed for intrinsic interstitial atoms in Tungsten along three symmetry directions in reciprocal space. The results show certain distinguishing features in the scattering profiles associated with each of the six possible interstitial configurations. These features might enable one to identify the stable configuration of the interstitial from experimental

measurements of the diffuse scattering cross section. It is important to note that the general features of the calculated scattering profiles are relatively insensitive to the form of the interatomic potential.

We hope that the present study will stimulate experimental work on diffuse scattering by interstitials.

Acknowledgement

This work was supported by the United States Atomic Commission under contracts AT(11-1)-3158 and AT(11-1)-3171. Additional support was received from the National Science Foundation through the use of the technical facilities of the Materials Science Center, Cornell University. We are grateful to Professor A. Baratoff for bringing reference (7a) to our attention.

References

- (1) R. A. Johnson, Phys. Rev. 134A, 1329 (1964).
- (2) A. De Pino, Jr., D. G. Doran and J. R. Beeler, Jr., Radiation Effects 3, 23 (1970).
- (3) D. N. Seidman and K. H. Lie, Acta Metall. 20, 1045 (1972).
- (4) P. H. Dederichs, J. Phys F: Metal Phys., 3, 471 (1973).
- (5) R. Benedek and P. S. Ho, J. Phys. F: Metal Phys., accepted for publication (1973). See also V. K. Tewary, Harwell Report T.P. 388 (1969).
- (6) K. Huang, Proc. R. Soc. A 190, 102 (1947).
- (7) H. Trinkaus, Phys. Stat. Sol. b 51, 307 (1972).
- (7a) E. Eisenriegler, Crystal Lattice Defects 2, 181 (1971).
- (8) R. Benedek and P. S. Ho, Cornell University Materials Science Center Report #2013 (1973).
- (9) R. A. Johnson and W. D. Wilson in Interatomic Potentials and Simulation of Lattice Defects, P. C. Gehlen, J. R. Beeler, Jr. and R. I. Jaffee eds. (Plenum, New York, 1972)p301.

Key Words

Diffuse x-ray scattering, lattice statics, Green's function, interstitial configuration, interatomic potential, Huang scattering.

Figure Captions

FIG 1

Intensity profiles $I(\vec{q})$ between origin and 400 reciprocal lattice vector for tetrahedral, octahedral, $\langle 100 \rangle$ split and $\langle 110 \rangle$ split interstitial configurations in Tungsten.

FIG 2

Intensity profiles $I(\vec{q})$ between origin and 400 reciprocal lattice vector for $\langle 110 \rangle$ split interstitial calculated using two different interatomic potentials for Tungsten.

FIG 3

Intensity profiles $I(\vec{q})$ between origin and 220 reciprocal lattice vector for tetrahedral, octahedral, $\langle 100 \rangle$ split and $\langle 110 \rangle$ split configurations in Tungsten.

FIG 4

Intensity profiles $I(\vec{q})$ between origin and 444 reciprocal lattice vector for $\langle 111 \rangle$ activated crowdion and $\langle 110 \rangle$ split configurations in Tungsten.

Figure 1.

Figure 2.

Figure 3.

Figure 4.