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Self-Interstitial in Hexagonal Close-Packed Metals

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Different symmetry configurations for an interstitial in a hexagonal close packed lattice are studied. Their stabilities are discussed and calculations are performed by means of an interatomic potential which reproduces some properties of Mg. The defect lattice eigenfrequencies and eigenvectors are calculated within the Einstein and a cluster approximation.

Es werden verschiedene Symmetriekonfigurationen für eine Zwischengitterstörstelle in einem hexagonal dichtgepackten Gitter untersucht. Ihre Stabilitäten werden diskutiert und Berechnungen mit einem interatomaren Potential durchgeführt, das einige Eigenschaften von Mg widergibt. Die Eigenfrequenzen und Eigenvektoren des Defektgitters werden in der Einsteinnäherung und einer Clusternäherung berechnet.

1. Introduction

This paper belongs to a series devoted to studying the point defect configurations in h.c.p. lattices [1 to 4]. In [1] two different interstitial configurations are discussed and interatomic potentials which reproduce some Mg properties are deduced. Also in [1] and [4] the vacancy configuration and dynamics are studied, while [2] is devoted to the Frenkel pair stability and [3] to the Green function for h.c.p. Mg. Based on the radiation recovery stages Seeger and Gösele [5] claim the feasibility of a dumbbell interstitial in Cd. Also in [6] this one is found by computer simulation as the stable configuration in Mg. Huang scattering measurements and theoretical studies of the technique have been performed recently for point defects in h.c.p. metals [7 to 10]. The conclusions on point defect locations and structures based on these measurements depend on the study of the defect statics. In this paper we try to clarify and supplement some of the previous theoretical and experimental results. We shall first discuss the defect symmetry and some computer simulation results will be shown later.

2. Interstitial Symmetry

The defect lattice must belong to a point symmetry subgroup of the perfect lattice group with origin at the defect site. By examining the perfect lattice symmetry one can foresee several locations for an interstitial that will relax the environment to a local extremum in the configurational energy. A schematic representation of the h.c.p. lattice is shown in Fig. 1. The lattice is composed by a pile-up of dense basal planes which become mirror symmetry planes. Two different rotation axes of order 3 perpendicular to the basal plane can be identified (C_3 and C_3' in Fig. 1). An inversion centre (I) is located over the axis C_3. A rotation axis of order 2 and perpendicular to C_3 joins two nearest neighbour points I. The axes C_3 and C_3' are also at the intersection of three mirror planes perpendicular to the basal one. At the intersection of the mirror planes that contain C_3' with the above-mentioned axes of order 2 another inversion centre (I′ in Fig. 1) exists. An atom located at either of those inversion

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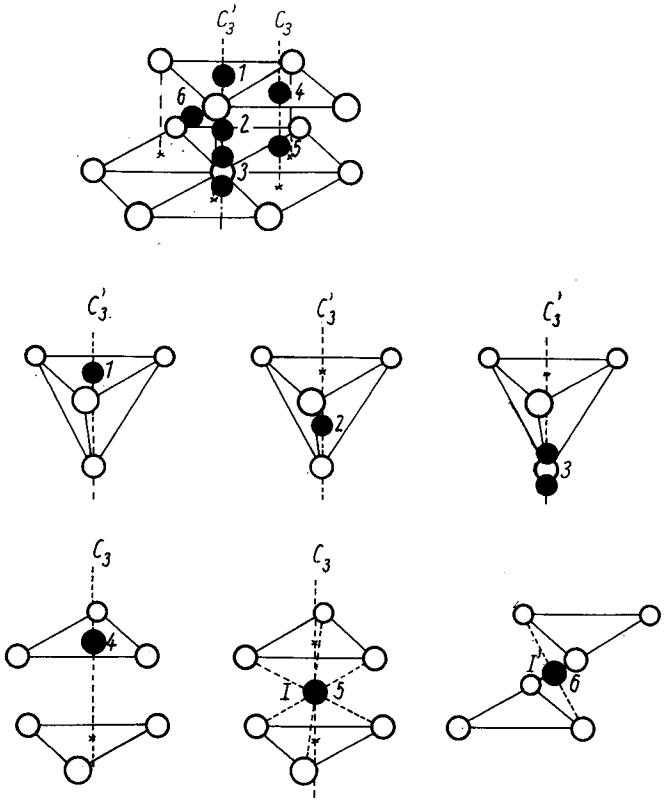

Fig. 1. Interstitials in an h.c.p. structure

centres I and I′, configurations 5 and 6, respectively, in Fig. 1, will relax the lattice to a configuration extremum in energy which maintains the inversion symmetry round the interstitial site. A symmetry determined position of zero force over the extra atom can be found also at the intersection of the basal plane with the axes C_3' (configuration 1) and C_3 (configuration 4). On the other hand, there will exist an energy extremum for a configuration with the interstitial over the axis C_3' and located somewhere between basal planes. The lattice symmetry imposes that the interstitial remains on that axis, but its final location along it depends on the interatomic forces (configurations 2 and 3 in Fig. 1). Other configurations with less symmetry than those 1 to 6, sketched in Fig. 1, may exist in the lattice depending on the interatomic potential. We want again to point out that "apparent similarity between the lattice defects in face-centred cubic and hexagonal close-packed metals may lead to oversight of some relevant differences imposed by the crystal symmetry" [1]. Seeger and Gösele [5] in analogy to the nomenclature introduced by Seeger et al. [11] for f.c.c. metals denote as octahedral interstitial O what we called in [1] hexagonal and tetrahedral T what we called trigonal; they also discuss the dumb-bell configuration derived from the octahedral site (H_O) and the one from the tetrahedral (H_T). However, a dumb-bell interstitial will be favoured by the lattice symmetry when its axis agrees with a rotation axis, which is itself- perpendicular to a mirror plane where the lattice site to be shared by two atoms is located. This implies that the only dumb-bell allowed by the h.c.p. lattice symmetry is H_T which is the one shown as configuration 3 in Fig. 1.

3. Interstitial Stability

For the above discussed configurations 1 to 6, the lattice may be relaxed to achieve zero forces between the atoms, i.e., to be at a local extremum in energy. However, a zero force configuration may still correspond to a local maximum in the energy for some directions in the configurational space. Computer simulation techniques for defects in metals [12 to 15] generally relax the lattice by steps of atomic displacements in directions determined only by the forces, first derivatives of the energy, over the atoms at the previous relaxation step. If the initial configuration is such that at a given site, for example at the site where an extra atom is located, the defect lattice symmetry determines the force over an atom located there to be zero, this condition of zero force is maintained during the relaxation process. In this case the relaxation program minimizes the energy for a configurational space with the implicit restriction of not moving the atom from that position. The final configuration may, however, be unstable when the whole configurational space is considered and second derivatives of the energy must be examined to ensure stability under infinitesimal distortions. The force constant matrix,

$$\Phi_{\alpha\beta}(l, l') = \frac{\partial^2 \Phi^*}{\partial u_\alpha(l)\, \partial u_\beta(l')} \tag{1}$$

must be constructed; l stands for the atom l at its relaxed location, Φ^* is the potential energy of the defect lattice, and $u_\alpha(l)$ the displacement of l from its location into the defect lattice in the direction α. The eigenvalues and eigenvectors of Φ will correspond, respectively, to the square of the normal mode frequencies and to the vibration pattern [16]. A negative eigenvalue corresponds therefore to an unstable mode.

Even if some periodicity in the defect lattice is assumed, the force constant matrix Φ is too large for explicitly finding all its eigenvalues. The most common approximation is allowing for lattice vibrations of a single atom at a time and taking the remaining lattice as fixed at its relaxed configuration (Einstein approximation); i.e., a set of three eigenvalues is obtained for each atom which converge to the Einstein perfect lattice modes for atoms far away from the main distortion. If the configuration is stable the eigenvalues for the interstitial and those for any lattice atom must be positive. However, collective modes may dominate over localized ones and a positive set of eigenvalues in the Einstein approximation is not enough to ensure stability. A cluster of atoms round the interstitial may be allowed to vibrate within a fixed matrix. The eigenvalues of the force constant matrix for relatively large clusters can be calculated and the cluster stability may be studied. This method for studying the defect stability will be called the "cluster method" in what follows.

Some computer simulation results for the six interstitial configurations of Fig. 1 will be reported here. We have performed the computer simulation of a h.c.p. lattice with the rigid sphere c/a ratio and held together by the empirical potential of [1] which reproduces some Mg properties. The defect lattice has been numerically relaxed as described in [1] until a configuration extremum in energy is achieved, this entails that the interatomic forces calculated at the so-called "region I" for that configuration are zero within the numerical error. The stability of the configuration has been studied as discussed previously. In Table 1 we report the eigenfrequencies calculated within the Einstein approximation for the interstitial. Configurations 1 to 5 are doubly degenerated for vibrations perpendicular to the c-axis with frequency $\omega_\perp$. Configuration 6 has no eigenvector in the c-axis direction and the interstitial 3 eigenfrequencies are single. For the dumb-bell (configuration 3) both the Einstein eigenfrequencies of a single atom among the two which share the vacant site (shown as "per 1 atom" in Table 1) and the ones (shown as "per 2 atoms") of the cluster of two

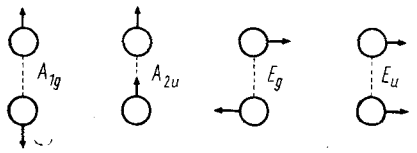

Fig. 2. Vibration modes of a dumb-bell according to Dederichs and Zeller [17]

atoms are reported. The corresponding modes "per 2 atoms" are sketched in Fig. 2. The unstable frequencies calculated for a cluster of atoms near neighbours to the interstitial are also reported in Table 1, as well as the size of the cluster, the eigenfrequency degeneracy, and the square of the component of the unitary unstable eigen-

Table 1
Eigenfrequencies and eigenvectors

configuration	Einstein approximation		cluster approximation				remarks
	$\omega_{\parallel}^2$ (10^{26} s^{-2})	$\omega_{\perp}^2$ (10^{26} s^{-2})	ω_{in}^2 (10^{26} s^{-2})	$\lvert e^D(\omega_{in})\rvert^2$ $\lvert e_{\parallel}^D\rvert^2$	$\lvert e_{\perp}^D\rvert^2$	cluster size (number of atoms)	
1	−1.87	−8.59	$-11.89^{(2)}$ $-7.05^{(1)}$	0.0 0.7249	0.8710 0.0	27	
2 trigonal [1]	24.91	13.73	stable (E_f = 1.1 eV)				*)
3 dumb-bell	per 1 atom 15.43	2.94					**)
	per 2 atoms		$-0.85^{(2)E_u}$	0.0	0.3622 × 2 = 0.7244	58	
	$20.84^{A_{2u}}$ $10.04^{A_{1s}}$	3.90^{E_u} 1.99^{E_g}	$-0.62^{(2)E_g}$	0.0	0.3985 × 2 = 0.7970		
4	11.01	10.34	$-1.32^{(2)}$	0.0	0.1279	23	
5 hexagonal [1]	4.12	−6.97	$-1.15^{(1)}$ $-11.14^{(2)}$	0.7389 0.0	0.0 0.8394	31	
6	29.52, 10.41, 10.09		stable (E_f = 1.3 eV)				***)

$\omega_{\parallel/\perp}$ Eigenfrequency corresponding to an eigenvector parallel/perpendicular to the c-axis.
ω_{in} Unstable frequency for a cluster round the defect. The frequency square value is reported with the degeneracy as a superscript (n).
$|e^D(\omega_{in})|$ Modulus of some components of the eigenvector corresponding to the eigenfrequency ω_{in}.
$|e_{\parallel/\perp}^D|^2$ Square of the component corresponding to the interstitial in the normalized eigenvector projected into a direction parallel/perpendicular to the c-axis.
E_f Formation energy.
*) The interstitial is located at a distance of $0.793a$ from the lattice atom in the c-direction which has displaced $0.264a$ from its perfect lattice position.
**) The atoms that share the vacant lattice site are separated by $0.828a$ and they perform unstable displacements with symmetry A, E, etc. [17] (superscript at the frequency values).
***) Three single eigenvalues are obtained for the Einstein eigenfrequencies.

vector mode corresponding to the interstitial atom. The latter should give an idea of the localization in the interstitial of the kinetic energy that gains the system when it displaces harmonically towards equilibrium. For the dumb-bell the addition of the components for both atoms at the core is reported.

4. Discussion

The self-interstitial configuration and stability have been discussed and calculations performed by using the empirical potential of [1]. The difference between the stability results obtained by the Einstein approximation and by the cluster one can be seen in Table 1. It can be seen that some configurations calculated by using the above-mentioned potential are already unstable within an Einstein approximation (configurations 1 and 5), while others (3 and 4) only appear as unstable when the eigenfrequencies for a relatively big cluster round the interstitial are studied.

It is interesting to see that for example the two unstable configurations 1 and 4, where the extra atom is located in both cases at the centre of a triangle of lattice atoms at the basal plane, differ so significantly in their instability; i.e., more unstable modes appear for 1 and they are more localized in the interstitial than for configuration 4. The dumb-bell interstitial appears as unstable in our calculation, however its stability may depend critically on the potential (see Dederichs and Zeller [17]). As reported in [1] the trigonal configuration involves a very large displacement of the atom located in the c-direction with respect to the interstitial and the final configuration, although it has not the dumb-bell symmetry, it is not very far from it.

Among the two stable configurations reported in Table 1 (2 and 6), the trigonal one [1] (configuration 2) is the most stable. It has a formation energy of 1.1 eV which is smaller than the one of 1.3 eV calculated for the interstitial located at the centre of inversion I′ (configuration 6). The first value is slightly smaller than the one reported in [1] due to a larger relaxation obtained via some improvements in the numerical program. These results reaffirm our previous conclusions in [1], which have been wrongly denied by Sahu et al. [6]; the trigonal interstitial is the most stable configuration for a h.c.p. lattice held together by the empirical potential of [1] and the hexagonal one is unstable. One must conclude that some configurations of defects in metals reported in the literature as stable may be unstable in the sense discussed above, but this instability remains undetected when only first derivatives of the energy needed for the numerical method are analysed.

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