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Abstract. The vibrational behaviour of vacancies in bcc metals is discussed with the use of the Green function method. In particular the local densities of states of the first and second neighbours of the vacancy, the atoms most affected by the defect, in α-Fe, Mo and W have been calculated. The local density of states of the first neighbours is shifted to lower frequencies as compared to host spectra whereas the local spectra of second neighbours in Mo and W are little affected by the defect; in α-Fe the second neighbour spectrum shifts to higher frequencies. However, in all three metals the local spectra of neighbours of the vacancy do not show any resonance or localized modes. The local spectra of neighbours have been utilized to calculate formation entropy and thermal mean-square displacements. The obtained values for formation entropy using the local density of states approach are similar to those found by other methods.

1. Introduction

The study of dynamics of irradiation-produced point defects, vacancies and self-interstitials is of fundamental importance in an understanding of physical properties of irradiated metals [1]. The study of dynamics not only provides direct interpretation of some of the physical properties but also elucidates aspects of the general problem of radiation damage in these metals. In this context in most of the recent studies on the dynamics of point defects in metals, the focus of attention has been on self-interstitials [2] while less attention has been paid to the dynamics of vacancies in metals though they are expected to play an equally important role in the interpretation of various properties of the irradiated metals, and also the structures of vacancies are simpler than those of the interstitials.

   The earlier studies [3, 4] of vacancies in metals were mostly concerned with their static properties, such as energies and relaxations around the vacant site, and only a few of them have discussed the dynamical aspects of vacancies. Land and Goodman [5] carried out an investigation of the vibrational effects of vacancies in cubic metals with short-ranged forces using a molecular approximation. Their result for copper showed the appearance of a mode slightly above the maximum frequency of the crystal which they regarded as a local mode. On the other hand, Hatcher *et al* [6] have used the Green function method to discuss the vibrational behaviour of vacancies in Cu and α-Fe and have found that no local mode appears. Therefore, from the above inconclusive result on the dynamical aspects of the vacancies, it has been felt that more work is needed to obtain further insight and understand the vibrational behaviour of vacancies in metals. Quite recently Blah and Ram [7] have discussed the vibrational behaviour of vacancies in Mo.

Another aspect which plays an important role in the study of vacancies is the choice of an appropriate potential suitable for the distorted region round the vacant site. From our experience with vibrational properties of self-interstitials in α-Fe, Mo and W and their neighbours in Mo [8, 9], using the Green function method, it has been felt that the potential constructed by Johnson and Wilson (JW) [10] provides a reasonable description of dynamical properties of point defects in these metals. Therefore, in this paper the JW potential is used to study the vibrational behaviour of the vacancies in three normal bcc metals, α-Fe, Mo and W, and calculate the local density of states of the atoms surrounding the vacancy. The local density of states is used to calculate dynamical properties such as formation entropy and mean square displacements of the concerned atoms. The calculation of formation entropy for vacancies is important in more than one way: a knowledge of formation entropy enables one to determine the concentration of vacancies and to calculate the self-diffusion constant in metals; and, in view of the non-availability of any reliable experimental value of formation entropy for vacancies, a theoretical calculation of its value is worthwhile. As a matter of fact, an accurate determination of defect parameters, formation energies and entropies is quite essential for the interpretation of the self-diffusion data in irradiated metals. While the static properties of the defect determine the formation energy, the dynamical properties determine the formation entropy. It is the study of the dynamics of the defects which facilitates an accurate determination of the formation entropy, its temperature dependence and the vibrational contribution to formation energy [11]. It is not surprising, therefore, that most of the earlier work on the vibrational properties of vacancies in metals was concerned with the calculation of formation entropy. Earlier calculations of formation entropy of vacancies in bcc metals include those by Burton [12] who obtained values ranging from $2.2k$ to $2.6k$ for bcc metals.

We have calculated the local density of states of the first and second neighbours of vacancies in α-Fe, Mo and W by two methods: (i) by using the JW potential consistently, i.e., for the calculation of perfect lattice Green's functions and the changes in force constants in the vacant site and (ii) by following the procedure used in the earlier work regarding self-interstitials [8, 9] where a perfect lattice is described by phonons measured in neutron scattering experiments [13–15] while the force constants near the vacancy are found from JW potentials and they are scaled by the nearest neighbour force constant in the lattice dynamic model. From the local frequency spectra of the first and second neighbours of the vacancy, the vacancy formation entropy can be calculated easily since the change in frequency spectrum of the lattice is closely related to the local frequency spectra of the neighbours. The vacancy formation entropy is calculated both for the case of the relaxed lattice and for the case of the unrelaxed lattice. It is expected that the formation entropy for the unrelaxed lattice will be smaller than that of the relaxed case.

2. Local density of states

We use the Green function method [16] to obtain the local density of states of neighbours of a vacancy. The local density of states can be expressed in terms of the Green function of the defect lattice. The vacancy is taken at the origin and its interaction with the first and second neighbours is modelled by missing springs to these atoms which are then relaxed to new positions. This results in modifications of force constants between neighbouring atoms. The remaining atoms of the host crystal beyond second neighbours are assumed to be unperturbed.

The Green function for the defect lattice is given by

$$\left(\Phi - M\omega^2\right)G(\omega) = 1 \tag{1}$$

while that of the ideal lattice is

$$\left(\overset{\circ}{\Phi} - \overset{\circ}{M}\omega^2\right)\overset{\circ}{G}(\omega) = 1 \tag{2}$$

where Φ is the force constant in a relaxed lattice and $\overset{\circ}{\Phi}$ that of the ideal lattice while every quantity pertaining to an ideal lattice is indicated by $^\circ$.

By using (1) and (2) we can express the defect Green function G in terms of the ideal lattice Green function $\overset{\circ}{G}$ as

$$G(\omega) = \overset{\circ}{G}(\omega)\left[1 + V(\omega)\,\overset{\circ}{G}(\omega)\right]^{-1} \tag{3a}$$

where

$$V(\omega) = \Delta\Phi + \overset{\circ}{M}\omega^2 \text{ and } \Delta\Phi = \Phi - \overset{\circ}{\Phi}. \tag{3b}$$

The Green function $G(\omega)$ is used to obtain the local density of states of an atom l in the α-direction in the defect lattice as

$$Z_\alpha(l,\,\omega) = \frac{2\omega M}{\pi}\,\operatorname{Im} G_{\alpha\alpha}(l,\,l;\,\omega). \tag{4}$$

The local density of states provides an elegant way to discuss those properties of the solids which do not depend on the atom–atom correlations in the lattice. Further, all the thermodynamic properties of the crystal can be expressed in terms of the local spectra of all the atoms. The local density of states is particularly useful in those situations where a defect mode, resonant or localized mode, is dominated by the vibration of the defect only: since, then, such modes are easily identified as resonant-type peaks in the local spectrum of the defect.

2.1. Formation entropy

The production of a vacancy increases the entropy of the crystal and this increase in entropy is known as the vacancy formation entropy. The vacancy formation entropy is closely related to the local density of states of the neighbours of the vacancy, especially to those of the first and second neighbours. The formation entropy of the vacancy may be calculated in terms of the change in the frequency spectrum in the presence of the vacancy. Leaving apart a negligible small electronic contribution, the vibrational contribution to the entropy is given by [16]

$$S = k\sum_s \sigma\left(\omega_s,\,T\right) \tag{5a}$$

with

$$\sigma(\omega,\,T) = \frac{\hbar\omega/kT}{\exp(\hbar\omega/kT) - 1} - \ln\left[1 - \exp(-\hbar\omega/kT)\right]. \tag{5b}$$

In the classical limit of high temperatures, the expression for $\sigma(\omega,\,T)$ reduces to

$$\sigma(\omega,\,T) = 1 - \ln(\hbar\omega/kT). \tag{6}$$

With the use of the total frequency spectrum, the entropy is expressed as

$$S = k\int_0^\infty \sigma(\omega,\,T)Z(\omega)\,\mathrm{d}\omega \tag{7}$$

whereas the formation entropy is given by

$$S_{1V}^F = k \int_0^\infty \sigma(\omega, T) \Delta z(\omega) \, d\omega \qquad (8)$$

where $\Delta z(\omega)$ is the change in frequency spectrum due to a single vacancy.

The change in frequency spectrum can be expressed in terms of the generalized phase shift π times the integrated density of states [16]. However, in the present work we will utilize a local representation of the total spectrum to express the formation entropy in terms of local frequency spectra of all the atoms in a defective lattice as well as an ideal lattice so that

$$S_{1V}^F = 3k \int_0^\infty \sigma(\omega, T) \sum_l \left\{ z(l, \omega) - \overset{\circ}{z}(l, \omega) \right\} d\omega. \qquad (9)$$

For a weakly perturbing defect like the vacancy we expect the local frequency spectra of only a few neighbouring atoms to be significantly different from that of the host spectrum.

Apart from the vibrational contribution to the formation entropy, the contribution due to image forces is also taken into consideration for a relaxed lattice. The displacements due to image forces for vacancies lead to a homogeneous contraction of the lattice and hence to the strengthening of the force constant, i.e., a negative contribution to formation entropy. The volume change caused by image forces is [16]

$$\Delta V^{Im} = \frac{2}{3} \frac{1 - 2p}{1 - p} \Delta V \qquad (10)$$

where ΔV is the total volume change and p is the Poisson ratio.

The change in formation entropy due to volume relaxation is obtained from the thermodynamic relation

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V = -V \left(\frac{\partial P}{\partial V} \right)_T \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = K\beta \qquad (11)$$

where K is the isothermal bulk modulus and β the volume expansion coefficient. The change in formation entropy due to image forces is

$$\Delta S_{1V}^F (\text{image}) = K\beta \Delta V^{Im}. \qquad (12)$$

3. Calculated results and discussion

We have calculated the local density of states of the neighbours of the vacancies in three normal bcc metals, α-Fe, Mo and W, with the Green function method. To calculate the local density of states of atoms near a vacancy we have evaluated the force constants in the vicinity of the vacant site as also the ideal lattice Green function $\overset{\circ}{G}(\omega)$. The vacancy is described by zero coupling to its neighbours. For calculation of $\overset{\circ}{G}(\omega)$, two sets of force constants have been used: (i) calculated force constants based on the JW potentials and (ii) force constants obtained from the experimental-based phonons fitted to the Born–von Karman force models. Therefore, in this case two sets of Green's functions $\overset{\circ}{G}(\omega)$ are obtained with the help of the modified Gilat–Raubenheimer method [17]. For calculation of matrix elements of Φ in a relaxed lattice, the static displacements of first and second neighbours of the vacancy are taken from molecular dynamics calculations of Taji *et al* [18] which give inward displacements of first neighbours and outward displacements of second neighbours away from the vacant site along the coordinate axes. The atoms falling in the cluster of first and second neighbours of the vacant site take up new equilibrium

positions, while other atoms beyond the second neighbours are considered to be in their perfect lattice positions. With new equilibrium positions of atoms in the defect space we have eight new distances between these atoms. Using the JW potential, the force constants A_i, B_i $(i = 1, 8)$ are calculated at the new equilibrium interatomic distances, as also are the perfect lattice force constants A_0^i, B_0^i $(i = 1, 2)$ when the perfect lattice Green functions $\overset{\circ}{G}(\omega)$ are calculated by using force constants obtained from Born–von Karman fits to measured phonons in neutron scattering experiments; the force constants determined on the basis of the JW potential are scaled by A_0^1 which is the nearest neighbour force constant in the ideal lattice occurring in the phonon model. This means that the force constants calculated on the basis of the JW potential are scaled according to the measured phonon force model. This type of procedure is essential for ensuring consistency between phonons used in the calculation of Green's functions and the used force constant changes in the defect space.

The local densities of states of the first and second neighbours of the vacancy in all three metals are calculated both for the unrelaxed lattice and for the relaxed lattice by using the JW potential phonons and also by using the experimental phonons. However, in the unrelaxed case no significant change in the local density of states of the first and second neighbours of the vacancy as compared to that of the host lattice atom is expected, while in the relaxed case significant changes are expected. The obtained local densities of states of first and second neighbours of the vacancy in a relaxed lattice, when the phonons are calculated from the JW potential, are shown in figures 1–3, for α-Fe, Mo and W, respectively. In the figures the host spectra are also presented in all three figures for comparison. The frequency spectrum of the first neighbour is considerably shifted to the lower frequency side of the spectrum in all cases with some weak peaks which may be treated as incipient resonances. In all cases no local modes have been found. This behaviour is explained by the loss of coupling between the vacancy and the neighbouring atom in the (111) direction. This is also in accordance with the reduced value of Einstein frequency for the atom. The result is similar to that found by Hatcher *et al* for copper [6]. However, the frequency spectrum of the second neighbour is not much different from that of the host lattice in the case of Mo and W. This shows that the vibrations of only the first neighbours of the vacancy are significantly changed compared to those of the atoms in the host lattice. In contrast to the case of Mo and W, the spectrum of the second neighbours in α-Fe shows a significant shift of the spectrum towards the higher frequencies. The local densities of states of the first and second neighbours of the vacancy using experimental phonons are similar to those presented in figures 1–3. However, the shift of local spectra of first neighbours to lower frequencies in all three metals and that of second neighbours to higher frequencies in the case of α-Fe are less compared to those for JW phonons shown in figures 1–3.

The obtained local density of states is used to calculate the formation entropy S_{1V}^F of the vacancy in all three metals, α-Fe, Mo and W, with both types of phonon used and also both for the relaxed lattice and for the case of the unrelaxed lattice. In these calculations both sets of local spectra have been utilized, so it is clear that we can present four values of the formation entropy for each metal. For a relaxed lattice, the contribution to S_{1V}^F from image forces in the crystal is also taken into consideration. The image forces yield a negative contribution to S_{1V}^F, indicating a homogeneous contraction of the lattice and hence a general strengthening of the force constants in the lattice. The relaxation volumes for α-Fe and Mo are $0.05V_c$ and $0.1V_c$ respectively as quoted by Ehrhart *et al* [19], where V_c is the unit cell volume. For W we take relaxation volume equal to that of Mo, i.e., $0.1V_c$, since the measured value is not available in this case. The contributions from image forces
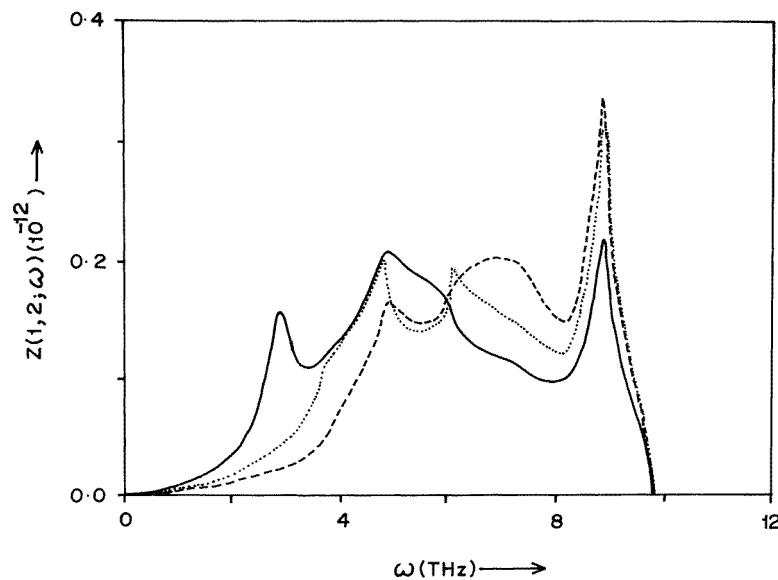
Figure 1. The local density of states of the first neighbour (——) and second neighbour (- - - -) of a vacancy and a host atom ($\cdots\cdots$) in α-Fe in the case of a relaxed lattice, with ideal phonons calculated from the JW potential.

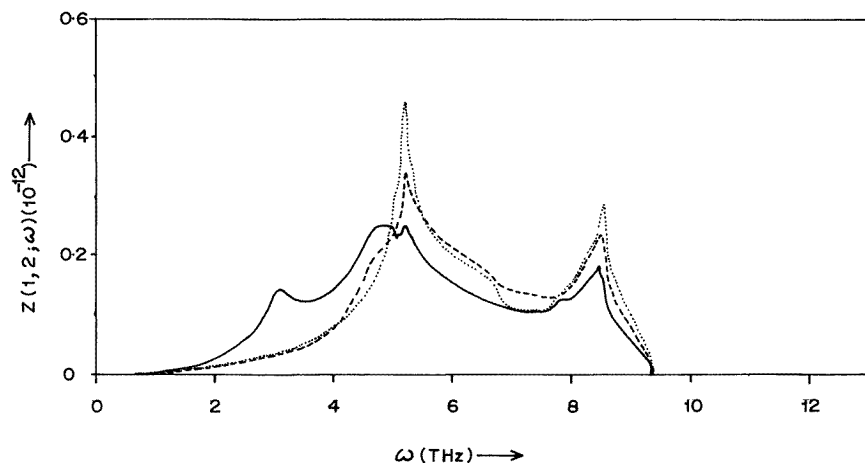**Figure 2.** The local density of states of the first neighbour (——) and second neighbour (- - - -) of a vacancy and a host atom ($\cdots\cdots$) in Mo in the case of a relaxed lattice, with ideal phonons calculated from the JW potential.

towards the formation entropy are $-0.0909k$ for α-Fe, $-0.1738k$ for Mo and $-0.1342k$ for W. The final values of the formation entropy are presented in table 1. From table 1 it is evident that the effect of relaxation is different for different metals: for Mo and W this formation entropy increases in the relaxed lattice while for α-Fe it is reduced. The increase in formation entropy for Mo and W in the relaxed lattice is understandable, since the most affected atoms are first neighbours and their local spectra shift to the lower frequency region
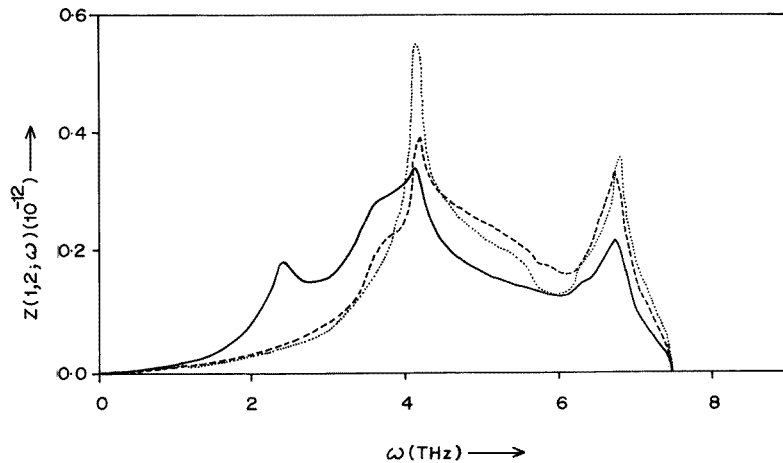
Figure 3. The local density of states of the first neighbour (——) and second neighbour (- - - -) of a vacancy and a host atom ($\cdots\cdots$) in W in the case of a relaxed lattice, with ideal phonons calculated from the JW potential.

where the density of modes in the host lattice is negligible, whereas the second neighbour spectra are not much changed in these metals. In the case of α-Fe also the first neighbour spectrum shifts to lower frequencies but the second neighbour spectrum shifts to higher frequencies which causes a reduction of formation entropy.

Table 1. Obtained vacancy formation entropy S_{1V}^F in α-Fe, Mo and W in the unit of k/atom: (a) using JW potentials consistently and (b) using experimental based phonons.

Phonons used	α-Fe	Mo	W	Remark[a]
a	2.043	1.61	1.921	u
a	1.559	2.25	3.199	r
b	1.646	1.69	2.143	u
b	1.485	1.94	2.446	r

[a] u is for unrelaxed lattice and r for relaxed lattice.

It would be of interest to compare the values of S_{1V}^F obtained in the present work with those obtained by other workers. Burton [12] has reported values from $2.2k$ to $2.6k$ for bcc metals based on an empirical relation between formation entropy and lattice relaxation due to the vacancy. This relation shows an increase in formation entropy due to inward relaxation of nearest neighbours of a vacancy. The other calculations of formation entropy in bcc metals are in α-Fe by Hatcher *et al* [6], who find a value of $2.1k$, and in all three metals by Schober *et al* [20], with a value of about $1.8k$. Schober *et al* [20] have considered a cluster of 432 atoms with a vacancy at the centre. The vacancy is modelled by missing force constants to neighbours, thus ignoring the relaxation completely. An examination of table 1 shows that our results for S_{1V}^F for a relaxed lattice are in the same range as obtained by others. As regards experimental measurements of formation entropy, Schwirtlich and Schultz [21] have derived a value of $1.5k$ for Mo on the basis of quenching and recovery experiments. The calculated values are somewhat higher than the quoted experimental

results.

We have also utilized the obtained density of states to calculate the mean square thermal displacements of first and second neighbours of the vacancy. The mean square thermal displacements of the first and second neighbours have been calculated [8, 9]. For the first neighbours the thermal displacements are larger than those for their respective host atoms while for second neighbours the thermal displacement is almost the same as that of the host atoms for Mo and W in both sets of studies. In the case of α-Fe the thermal displacements of the second neighbours are lower than that of the host. The increase in thermal displacement of the first neighbour is the result of a general shift of the spectrum to lower frequencies, whereas the decrease in thermal displacements of the second neighbours of α-Fe is accounted for by the shift of the spectrum towards higher frequencies. At high temperatures the mean square thermal displacement increases linearly with temperature T.

To summarize, the local density of states of neighbours of the vacancy shows that the vibrations of only the first neighbours are significantly changed compared to those of a host atom. The obtained value of formation entropy based on local density of states of the neighbours of the vacancy is in close agreement with the value determined using static lattice Green functions and is in reasonable agreement with the earlier calculations in the literature.

Acknowledgments

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