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The Static Lattice Model of Hardy and Bullough applied to the Noble Metals to calculate Divacancy Interaction Energies and Relaxations

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Abstract

The discrete lattice method of Hardy and Bullough (1967) and Bullough and Hardy (1968) is applied to the noble metals to obtain estimates of the relaxations around a vacancy and of the near neighbour divacancy interaction energy. Accuracy is improved on earlier work by use of a point-formula integration technique. It is found that the soft phonon spectrum of gold leads to large relaxations and a divacancy interaction energy which is about half the single vacancy formation energy. It is therefore concluded that the model is too simplistic to describe the single and divacancy situations in gold, and may also not be accurate for copper and silver, though for the lighter elements the results are better.

Introduction

The model used here (Hardy and Bullough 1967) is a lattice statics model where the ions are considered to behave harmonically, and relaxations in the vicinity of two defects are taken as the vector sum of the relaxation from each individually. The boundary conditions are made periodic, so the defect(s) is(are) contained in a periodic superlattice, the separation between the periodic images of the defect being taken to be sufficiently large that interactions between the defect and images are negligible.

The interaction potential between ions in the present model (Bullough and Hardy 1968) is taken to arise only through the force constants, which are obtained (via the method of long waves) from experimental elastic constants, and the transverse acoustic mode frequency at the (100) zone face centre (the X point). Thus the potential itself is not and does not need to be determined explicitly, though there are clear limitations in neglecting things such as the electronic contribution to the elastic constants* and many-body interactions. Also the effect of the Coulomb interaction is diminished since it is known to contribute only a small fraction of the dynamical matrix compared with the short-ranged interactions between ions (Fuchs 1936). Though, naturally, the Coulomb interaction will be screened in the noble metals it is not clear that it plays little role in defect relaxations. Also, interactions are only taken to first and second neighbours, on the assumption that third neighbour force constants are small.

* Note, however, that use of experimental elastic constants suggests that electronic contributions are implicit in the potential, but these contributions will not give the correct relaxation behaviour unless treated explicitly, via for example a jellium model.

Although the model described here contains the advantages of a discrete description of the crystal structure (over the elastic theories which ignore structure), as Hardy and Bullough (1967) explain in detail, it is really the simplest discrete model calculation for a defect system and, as such, one must question its general validity, despite its advance on elastic models of defects. The purpose of this paper is to study this point in some detail for the application of the model to the noble metals. In order to avoid numerical errors, an improved method of Brillouin zone integration is introduced. On comparison with the previous results of Bullough and Hardy (1968) and Miller and Heald (1975) for the data that are available, better agreement is found with the original results of Bullough and Hardy than with those of Miller and Heald (who gave ion displacements only). These discrepancies may be due to differences in the parameters used to simulate the potential as well as to numerical error.

Table 1. Calculated ionic displacements and vacancy pair interaction energies for noble metals

Here: (1) the nearest neighbour displacements (1ND) and second nearest neighbour displacements (2ND) shown are radial displacements in units of the length of a side of the unit cube, and hence they are twice those of Bullough and Hardy (1968); (2) the errors shown are taken from the calculated differences of displacements of all ions with the same initial distance from the origin; (3) the vacancy pair interaction energies E_{2v} are given in units of electron volts. The Monte Carlo calculations were done in double precision while the others were done in single precision

Method	Metal	1ND (% error)	2ND (% error)	E_{2v} (% error)
Monte Carlo	Cu	0·0174 (3)	0·0021 (37)	−0·100 (7)
method	Ag	0·0191 (3)	0·0052 (4)	−0·165 (4)
(5000 points)	Au	0·028 (3)	0·017 (2)	−0·605 (5)
19-point	Cu	0·0171 (0·5)	0·0018 (6)	−0·097 (0·1)
formula	Ag	0·0190 (0·5)	0·0048 (4)	−0·159 (0·08)
(4864 points)	Au	0·028 (0·6)	0·018 (2)	−0·607 (0·05)
Bullough and	Cu	0·0170	0·0022	−0·093
Hardy (1968)	Ag	—	—	—
results	Au	—	—	—
Miller and	Cu	0·0156	0·0016	—
Heald (1975)	Ag	0·0198	—	—
results	Au	0·0226	—	—

Calculations

A computer program has been written to estimate displacements of ions around a vacancy and the interaction energy between pairs of vacancies using the method described by Hardy and Bullough (1967) and Bullough and Hardy (1968). The calculation is for face-centred cubic structured metals. The data used as input for the three noble metals were the same as those quoted by Miller and Heald (1975), though for copper the slightly more accurate data of Bullough and Hardy were used. There are slight variations in values given by these authors and those quoted elsewhere (e.g. by Sinha 1966; Kittel 1968; Lynn *et al.* 1973), but to enable comparison with the earlier work these differences were ignored.

The program was checked by recalculating the results of Bullough and Hardy (1968) for copper and the displacements for all the noble metals quoted by Miller and Heald (1975). Reasonable agreement was obtained, though calculation of displacements for all the nearest and next nearest neighbours of the vacancy showed

some variation in shift, indicating some measure of computational error in my program. (All nearest neighbours should shift by the same distance, and likewise for next nearest neighbours.) It was found that the use of a 19-point integration formula (Davis and Rabinowitz 1975) gave more accurate results for a given computation time than the random number Monte Carlo calculation used in the previous studies. With the 19-point formula, good results (as shown in Table 1) were obtained for 4864 points in half of the Brillouin zone (instead of 1/48 of the zone for convenience). These results suggest that some caution is required in using the previously obtained value, particularly when looking at displacements of other than next nearest neighbours. It was also found, however, that the value of the two-vacancy interaction energy in the nearest neighbour case varied only a few per cent for more than 1000 random numbers (for the same zone as above), indicating that the interaction energy is not very sensitive to the accuracy of the calculated displacements.

Some results for copper, silver and gold obtained by using the two integration methods are shown in Table 1 where they are also compared with the earlier results. It will be noted that use of the 19-point formula generally improves accuracy considerably over the Monte Carlo method.

Table 2. Physical parameters for noble metals used in calculations

Here a is the lattice parameter and w_t is the TA phonon mode for the X point of the first Brillouin zone. The data from columns 2, 3, 4, 5 and 10 were used as input to the calculations. The values for silver and gold are from Miller and Heald (1975) while the values for copper, which basically agree with those of Miller and Heald, are more accurate data taken from Bullough and Hardy (1968)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
	Elastic constants[A]			w_t	Calculated force constants[B]				a
Metal	c_{11}	c_{12}	c_{44}	(THz)	A_1	A_2	B_1	B_2	(Å)[C]
Cu	1·70	1·23	0·75	5·068	66983·0	−559·4	−4494·6	162·6	3·61
Ag	1·24	0·935	0·46	3·41	52974·0	779·5	−3941·5	−903·5	4·08
Au	1·86	1·57	0·42	2·75	73020·0	5327·7	−7973·2	−3728·0	4·07

[A] In units of 10^{12} dyn cm^{-2} ≡ 10^{11} Pa. [B] In units of dyn cm^{-1} ≡ 10^{-3} N m^{-1}. [C] 1 Å ≡ 10^{-10} m.

Results

A striking difference between the results for copper and silver and those for gold is the large vacancy pair interaction energy in the latter case: six times that of copper and about half the measured single vacancy formation energy (Gorecki 1974). This is, of course, accompanied by much larger displacements of the surrounding ions. In fact, the displacements are so large (3% of the unit cell length or ~6% of the nearest neighbour distance) that one must question whether it is valid to use Bullough and Hardy's method in this case, and whether corrections from changes in the density of the electron gas in the region of the defect will not be large. This is possible though it has not yet been studied in detail. The assumption of the additivity of strains is also in question for gold, and a much more detailed analysis is needed.

Despite the above reservations, it is nevertheless clear that the divacancy binding energy in gold is much larger than in copper and silver. This suggests that vacancy clusters may form more readily in gold than in the other noble metals. However, it should be emphasized that further factors such as vacancy mobility, thermal emission and other stress fields will enter the complete description of cluster formation.

The reasons for some of the differences between copper and silver and gold are illustrated in Table 2 where the respective values of the first and second neighbour axial and tangential force constants A_1, A_2, B_1, B_2 (calculated from the shown experimental elastic constants c_{11}, c_{12} and c_{44} using the long wave method) and w_t are shown for all three materials. It will be noted that the largest difference in the input data is in the value of the TA mode frequency w_t, which for gold is about half that of copper. The gold lattice is therefore much softer and larger relaxations are possible, and are indeed found in the calculations (Table 1). It should also be noted that there are differences between the elastic constants used by Sinha (1966) and those used in the present work. Although these differences are small, the force constants calculated from them differ considerably, particularly the tangential components (B_1 and B_2). It is also interesting to note that gold has much larger next nearest neighbour force constants than copper, so a two-neighbour model as used here for gold may also be inappropriate on this ground.

Conclusions

The general conclusion from this work is that, with the large displacements around the vacancy in gold, due to the softer lattice than copper, and the large second neighbour force constants, it is not clear that the approximations inherent in Bullough and Hardy's method are entirely valid for such cases, and a more detailed analysis of relaxation, formation and interaction energies is therefore required. For the lighter elements such as copper and aluminium the method appears to be much more satisfactory, though the above doubts must persist to some extent.

The computer program used in this study is available for anyone interested in it.

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