A screening based study of impurity-dynamics in metals

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Abstract. The dynamics and energetics of a light impurity (hydrogen) embedded in metals (Al, Cu, and Ni) are studied using a phenomenological 'local' oscillator potential experienced by it as a result of its screened interaction with the host ions. Calculations of the migration energy of hydrogen in the above mentioned metals are reported.

Keywords. Screening; impurity; migration energy.

1. Introduction

The problem of dynamics and energetics of an impurity dissolved in metals is of enormous interest from scientific as well as technological point of view (Friedel 1952; Daw and Baskes 1984; Puska and Nieminen 1984; Fukai and Sugimoto 1985; Norskov and Besenbacher 1987). We report a new model for the calculation of localized dynamics and the associated energetics of light impurities in metals and its results for hydrogen in Al, Cu and Ni. Earlier such calculations were carried out using a jellium model (Popovic *et al* 1976; Larsen and Norskov 1979; Mannienand and Nieminen 1979; Kahn *et al* 1990; Craig 1983; Estrieher and Meier 1983; Solt *et al* 1983) by treating the interaction of the host with the electronically screened impurity as a first order perturbation, which was recognized later as so considerable that it is beyond the perturbative limits (Larsen and Norskov 1979; Mannienand and Nieminen 1979; Kahn *et al* 1980; Estrieher and Meier 1983). Hence non-perturbative calculations, with spherical approximation for the potential due to ions, were carried out (Mannienand and Nieminen 1979; Kahn *et al* 1980; Parrot and Rasolt 1981; Craig 1983). *Ab initio* calculations using the local density approximation and super cell approach were also carried out for hydrogen in aluminium (De Vita and Gillan 1991, 1992). The effect of lattice relaxation around the impurity was, however, considered in a very few limited attempts (Puska and Nieminen 1984; De Vita and Gillan 1991) alone.

In this work, we have treated an impurity embedded in a metal mainly through the screened interaction between the impurity and host ions. Lattice relaxations around the impurity are calculated and used to estimate the heat of solution and migration energy of hydrogen in aluminium, copper and nickel. The screening-dependent impurity-dynamics is discussed in §2, §3 outlines the calculation of lattice relaxation around the impurity, in §4 the results derived are discussed and finally, in §5 the conclusions are presented.

2. Screening and impurity-dynamics

Calculations of modes and frequencies of an impurity embedded in a metal involves determination of the dynamical matrix, consisting of screened interaction elements

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between the impurity and host ions. This screened interaction can be considered within the adiabatic approximation owing to the heavy mass of the nuclei relative to the valence electrons (Harrison 1979) and hence the impurity ion can be thought of as moving in the screened Coulombic potential field constituted by all the host ions in the metal. To get a clear understanding of how the above field at an arbitrary point (say, P) due to the host ions would affect the impurity ion (say, i) situated away from P , the above field must be transformed into a function of the radial coordinates centred at the mean position of the impurity ion. We can readily accomplish this by using the well-known transformation procedure of Lowdin (1956), which for radial contributions is

$$f(a, r_i) = \frac{1}{2\pi a r_i} \int_{|a-r_i|}^{a+r_i} r_j f(a, r_j) dr_j, \quad (1)$$

where a is the radial distance between the mean position of the impurity ion and the j th host ion and r_i the radial distance of the point P from the impurity site i . The function $f(a, r_i)$ on the left of (2), represents the spherically averaged function $f(a, r_j)$ from the host ion site as measured from the impurity site i in terms of the corresponding local radial coordinate r_i . Using the repulsive screened Coulombic potential for f and the impurity-host ion distance, say, R_{ij} , for a , (1) finally yields the 'local' potential 'as experienced' by the impurity ion at a point P of radial distance r_i in its immediate vicinity, (i.e. for $r_i < R_{ij}$), of the form

$$V_{ij}(r_i) = A_{ij} + v_{ij}(r_i), \quad (2)$$

where

$$A_{ij} = z_i z_j e^2 \frac{\exp(-bR_{ij})}{R_{ij}}, \quad (3)$$

and

$$v_{ij}(r_i) = A_{ij} \left(\frac{b^2 r_i^2}{3!} + \frac{b^4 r_i^4}{5!} + \dots \right), \quad (4)$$

where $z_i e$ is the charge of the impurity ion and $z_j e$ that of the i th host ion and b the screening constant which depends upon the valence electron concentration. In the above (2), A_{ij} represents the average screened repulsive (short-range) interaction between the impurity (i) and the host ion (j) with respect to their mean positions separated by a distance R_{ij} whereas $v_{ij}(r_i)$ is a phenomenological 'local' oscillator potential experienced by the impurity in its immediate vicinity. The impurity-electron interaction, on the other hand, is beyond the long wavelength limit, and hence needs to be treated by the first-principles calculations such as the local density approximation. This is of long range nature and does not contribute to the small oscillations of the impurity ion. However to account for the full pair potential, this impurity-electron interaction (attractive part) must be added to the contribution obtained by summing over j (i.e. all the host ion sites) in (2).

3. Estimation of lattice relaxation

The force constant and hence the dynamical matrix corresponding to the interaction between the impurity and host ions can be directly obtained with the help of (2), from

which the lattice relaxation of the host ions can, in turn, be calculated. The force exerted by the impurity on the j th host ion can be written as (Puska and Nieminen 1984)

$$\vec{F}_j = [\phi] \vec{u}_j, \quad (5)$$

where $[\phi]$ is the dynamical matrix of the unperturbed lattice in presence of the impurity and $\vec{u}_j$ is the displacement of the j th ion. Hence we get for the lattice relaxation

$$\vec{u}_j = [\phi]^{-1} \vec{F}_j. \quad (6)$$

Lattice relaxation beyond the second nearest neighbours with respect to the impurity is found to be very small and hence neglected in the present calculations. Incorporating this lattice relaxation, the vibrational energy of the impurity is estimated based upon (2).

4. Results and discussion

The frequency of the local vibrational motion of the impurity is found to be a strong function of the screening constant (b) and vanishes under the limit $b \rightarrow 0$. This implies that the vibrational motion of the impurity depends primarily upon the short range screened interaction of the impurity ion with the host lattice ions. The energy change in the host metal due to the introduction of an impurity is equal to the energy associated with the impurity in its environment. Before getting trapped within the potential well formed out of lattice relaxation, the impurity is in its Bloch state of the periodic bulk, and the lowest energy of this Bloch state is equal to the energy possessed by the impurity prior to the lattice relaxation. Thus the total energy difference for the impurity between the relaxed and the unrelaxed conditions of the lattice gives the impurity binding energy (ϵ_{imp}) at the interstitial sites. In the present calculations, since the change of energy due to lattice relaxation for the impurity–electron interaction is much smaller than that of the impurity–host ions interaction, the former is neglected to the first approximation. An estimate of the heat of solution of the impurity can be obtained if the free atom energy of the impurity is subtracted from the above said

Figure 1. Variation of ϵ_{imp} for H in Al (interstitial: octahedral to tetrahedral sites).

Table 1. Migration energy of H, in metals.

Metal	Migration energy (eV)		
	Theory		Experiment
	Present	Previous(De Vita and Gillan 1992)	
Al	0.22	0.20(for 16 atom cluster) 0.15(for 27 atom cluster)	0.47 at 600 K (Eichenauer and Pebler 1957)
Cu	0.34	—	0.40 (Katz <i>et al</i> 1971)
Ni	0.32	—	0.41 (Trian 1976)

binding energy and this is obtained in the present method for a hydrogen in aluminium at the octahedral (interstitial) site as ~ 0.76 eV. An earlier theoretical report of this quantity is ~ 0.94 eV (De Vita and Gillan 1992), whereas, the corresponding experimental values reported are ~ 0.83 eV (Ransley and Neufeld 1948) and ~ 0.66 eV (Eichenauer 1968).

Figure 1 displays the variation of ϵ_{imp} calculated at various positions of the impurity (hydrogen) in the interstitial region, along the diagonal direction of the fcc aluminium from an octahedral site to the next tetrahedral site and this agrees well with the earlier theoretical prediction of De Vita and Gillan (1992). The impurity migration energy obtained as the height of the barrier with respect to its minimum (cf. figure 1) is ~ 0.22 eV, whereas that of De Vita and Gillan (1992) is, 0.20 eV for 16-atoms cluster and ~ 0.15 eV for 27-atoms cluster in which calculation, they considered periodically repeated hydrogens, while the present results are for a single localized hydrogen (infinite dilution). The hydrogen migration energy in aluminium, nickel and copper resulting from the present approach is listed in table 1, and compared with similar values in the literature, fairly good agreement is evident. The difference between experimental and theoretical results is mainly because the experimental values correspond to high temperature (Eichenaur and Pebler 1957; Katz *et al* 1971) whereas the present calculations have not considered the temperature effects.

5. Conclusions

It is shown that the treatment of repulsive screened interaction between the impurity and the host ions within the adiabatic limit could describe phenomenologically the local dynamics of the impurity. Comparison of the present results for hydrogen in aluminium, nickel and copper with those of the *ab initio* calculations and experiments emphasizes strongly that the contribution to the energetics of the impurity is predominantly due to the screened interaction between the impurity and host ions.

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