Electronic structure of hydrogen in Al

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Abstract. The impurity induced charge density of proton in Al is calculated by solving the Schrödinger equation self-consistently. The lattice contribution and the lattice dilation are included through spherical solid model potential and Blatt correction, respectively. The proton is kept at an octahedral site. The resulting phase shifts have been used to estimate the residual resistivity for dilute Al-H system. This model does not favour the formation of AlH, i.e., hydrogen exists in Al matrix as a free ion.

Keywords. Spherical solid model potential; induced charge density; residual resistivity; impurity potential.

1. Introduction

When hydrogen atoms diffuse in a metal, they dissociate into protons and electrons. Protons being positively charged are screened by conduction electrons. They displace the host ions from the equilibrium positions. As a result, the positive charge density in the vicinity of the proton changes.

The first linear theory of proton in Cu was proposed by Friedel (1952). It is now well established that the screening of the proton is nonlinear. Popovic *et al* (1976) have calculated the electronic structure, activation energy and heat of solution of hydrogen in simple metals using the density functional theory (Kohn and Sham 1965). Almladh and von Barth (1976), Kahn *et al* (1980) and Perrot and Rasolt (1981) have extended the study of Popovic *et al* (1976) by including the lattice contribution through a simple form of spherical solid model potential.

Jena and Singwi (1978) added the first gradient correction of exchange-correlation potential and found s-type bound state of the proton. Manninen and Nieminen (1979) added the lattice contribution in a more comprehensive way through the spherical solid model potential and calculated the heat of solution of hydrogen muonium in simple metals.

In some of the above studies, size effect is neglected. In others, both size effect and lattice contributions have been neglected. These contributions change considerably the electronic structure, effective potential and self-energy and residual resistivity of H^+ in Al by including the contribution of size effect and discrete lattice. This model does not favour the formation of AlH.

2. Theory

2.1 Size effect

The hydrogen impurity at an interstitial position displaces the host ions away from the equilibrium position. Therefore, the positive charge density decreases and the electron charge density increases in the vicinity of the impurity. As a result of the dilation, the net

charge of the proton is given as (Beal-Monod and Kohn 1968; Flynn and Stoneham 1970):

$$Z = Z_i - (\delta V/V)Z_H, \quad (1)$$

where Z_i and Z_H are the valence of impurity and host atom, respectively. In the continuum model of the lattice, the fractional charge in the host atom volume $\delta V/V$ can be calculated as has been suggested by Blatt (1957).

2.2 Spherical solid model potential

The spherical solid model potential is defined as the sum of spherical average of the host-ion potential and electrostatic potential of the positive background of jellium (Manninen and Nieminen 1979):

$$V_{ss}(r) = -(1/4\pi) \int d\Omega \sum_l w(\mathbf{r} - \mathbf{r}_l) + \int d\mathbf{r}' n_0/|\mathbf{r} - \mathbf{r}'|, \quad (2)$$

Here $d\Omega$ is the elementary solid angle. $n_0 (= 3/4\pi r_s^3)$ is the uniform charge density of the host and r_s the electron density parameter. For simplicity we consider the Ashcroft model potential for bare ion $w(r)$, i.e.

$$w(r) = (Z_H/r) \theta(r - r_c), \quad (3)$$

where r_c is the potential parameter and $\theta(r)$ the step function.

2.3 Non linear screening

Single electron eigen values ε_k and corresponding radial wave function $R_{lk}(r)$ are obtained by solving the following one particle radial equation:

$$\left[-\frac{1}{2} d^2/dr^2 + V_{\text{eff}}(r) + l(l+1)/2r^2 - \varepsilon_k \right] r R_{lk}(r) = 0. \quad (4)$$

For the continuum states $\varepsilon_k = k^2$, zero energy is taken to be the potential far from the impurity where its effect almost vanishes. Thus the effective potential field, in which the electron moves, is

$$V_{\text{eff}}(\mathbf{r}) = \Phi(\mathbf{r}) + V_{ss}(\mathbf{r}) + V_{xc}(n(\mathbf{r})). \quad (5)$$

The parametrized form of $V_{xc}(n(\mathbf{r}))$ proposed by Gunnarson and Lundquist (1976) has been adopted for the detailed calculations. Following Popovic *et al* (1976), the induced electron charge density is written as

$$\begin{aligned} \delta n_i(r) &= n(r) - n_0(r), \\ &= 1/\pi^2 \int_0^{K_F} dk k^2 \sum_{l=0}^{\infty} (2l+1) [R_{lk}^2(r) - J_l^2(kr)] + 2R_b^2(r), \end{aligned} \quad (6)$$

where k is the electron wave vector and k_F the Fermi momentum. The sum over angular momentum quantum number l in (6) converges very rapidly. This is because the

effective potential is localized so that the radial wave functions $R_{lk}(r)$ for large l will differ from the unperturbed electron Bessel functions $j_l(kr)$. s -type bound state may occur some time, therefore, the band structure charge density is also added in (6). In the present calculation the bound states with two electrons are considered. The electrostatic potential $\phi(\mathbf{r})$ is obtained by solving the Poisson equation

$$\nabla^2 \phi(\mathbf{r}) = -4\pi(Z_i \delta(\mathbf{r}) + n_0 - n(\mathbf{r})), \quad (7)$$

following the procedure of Manninen *et al* (1975) for achieving better convergency.

An alternative simple one-parameter screened Coulomb potential function, which has been shown to provide an accurate description of a proton impurity in both electron gas and a transition metal (Sholl and Smith 1978) is

$$V_{sc}(r) = -Z(1 + \beta r/2) \exp(-\beta r)/r. \quad (8)$$

The parameter β is chosen so that $V_{sc}(r)$ satisfies the Friedel sum rule. By solving the Poisson equation we find that $V_{sc}(r)$ yields a simple analytical form of induced charge density:

$$\delta n_i(r) = (Z\beta^3/8\pi) \exp(-\beta r). \quad (9)$$

Equation (9) yields a finite value of $\delta n_i(r)$ at $r = 0$. The simple function $V_{sc}(r)$ and $\delta n_i(r)$ given by (8) and (9), respectively, can be easily used to evaluate the self-energy of the induced charge analytically. As a result, the self-energy, defined as

$$E_s = \frac{1}{2} \int V_{sc}(r) \delta n_i(r) d\mathbf{r}, \quad (10)$$

reduces to

$$E_s = -3Z^2\beta/32 \text{ a.u.} \quad (11)$$

However, the charge density corresponding to Thomas–Fermi potential comes out to be $-Z^2\beta/4 \text{ a.u.}$

3. Calculations and results

3.1 Effective charge on the proton

The effective charge on the proton in Al metal is estimated using (1). The value of $\delta V/V$ and Z are given in table 2. The proton charge is reduced by 40% by the Blatt correction (Blatt 1957).

3.2 Spherical solid model potential

The potential parameter r_c , Madelung constant α_M , octahedral coordinates and the atomic radius r_0 for Al are given in table 1. The potential $V_{ss}(r)$ is terminated at $r = 8 \text{ a.u.}$ because it becomes negligibly small for larger values of r . The calculated $V_{ss}(r)$ for Al is shown in figure 1. The number of nearest neighbours and their position with respect to

Table 1. The host parameters used in the calculations. r_0 is the atomic radius, Z_H is the valence, r_c is the Ashcroft model potential parameter and α_M is the Madelung constant for octahedral site.

Parameter	r_0 (a.u.)	Z_H	r_c (a.u.)	α_M	oct. site
	2.985	3	1.12	0.42586	$(\frac{1}{2} \frac{1}{2} \frac{1}{2})$

Figure 1. The spherical solid model potential $V_{ss}(r)$ for Al around the octahedral site. The position and number of nearest neighbours to the octahedral site are also indicated.

the octahedral site are also indicated in the figure 1. $V_{ss}(r)$ has maxima around neighbouring ion shells and minima between the two shells. The potential depends upon Z_H , r_c and the octahedral site.

3.3 Phase shifts and impurity potential

We have followed the procedure of Manninen *et al* (1975) for solving (4)–(7), self-consistently. The s -type bound states are also included. The radial part of the Schrödinger equation is solved numerically in steps of 0.05 a.u. up to a radius of $R_0 = 10$ a.u. using Fox-Goodwin VI method. The phase shifts are calculated by matching the numerical solution with asymptotic solution at R_0 . The self-consistency of the calculation is checked using the Friedel sum rule

$$Z = 2/\pi \sum_{l=0}^6 (2l+1) \delta_l(k_F). \quad (12)$$

In (12) l is an orbital quantum number and $\delta_l(k_F)$ are scattering phase shifts at the

Table 2. $\delta V/V$ is the fractional change in atomic volume, Z is the effective charge on impurity, β is potential parameter, α' and β' are potential parameters, $V_{ss}(r)$ is spherical solid model potential, n_i is net charge on impurity, E_c is the self-energy and $\Delta\rho$ is residual resistivity.

Physical quantities	Present model ($V_{ss}(r)$ is included)	Jellium model ($V_{ss}(r)$ is not included)	
$\delta V/V$	0.13	0.13	0
Z	0.61	0.61	1.0
α'		1.0222	1.1520
β'		1.2693	1.1709
β	1.6877	1.8124	2.6355
$n_i(e)$	0.43	0.41	0.57
E_c (ryd)	-0.1177	-0.1264	-0.1839
$\Delta\rho(\mu\Omega \text{ cm at.}\%)$			
expt.			—
cal.	0.2936	0.2870	0.6847

Table 3. The scattering phase shifts $\delta_l(k_F)$ for proton (H^+) in Al. $l=0, 1, 2, \dots$ represents s, p, d, ... phase shifts.

δ_l	Present model	Jellium model	
0	0.682792	0.641037	1.086077
1	0.129128	0.080010	0.121071
2	0.026103	0.012006	0.019446
3	0.006210	0.001979	0.003203
4	0.001475	0.000247	0.000372
5	0.000621	0.000075	0.000015
6	0.000391	0.000012	-0.000133

Fermi-energy E_F . The first seven phase shifts $\delta_l(k_F)$ have been used to satisfy (12) as their values become too small for $l > 6$. The induced electron density $\delta n_i(r)$ is calculated by using the first seven partial radial waves obtained by varying k from $0 \rightarrow k_F$. The phase shifts so calculated are given in table 3. The s and p phase shifts are found to be dominating. We have also calculated the induced charge density in jellium following the procedure of Popovic *et al* (1976) without including the size effect and then by including it. The phase shifts calculated without $V_{ss}(r)$ converge fast. It is found that the size effect reduces the magnitude of the phase shifts considerably. Therefore, we conclude that both $V_{ss}(r)$ and size effect change the scattering of impurity at Fermi surface.

The impurity potential so calculated are shown in figure 2. The potentials are strongly attractive in the vicinity of the impurity and exhibit Friedel oscillations at large distances. A comparison of $\delta V_i(r)$ calculated by including size effect with that calculated by including both size effect and $V_{ss}(r)$ show that the lattice contribution enhances the attractive nature of $\delta V_i(r)$.

3.4 Electronic charge density and charge transfer

The calculated impurity induced charge density $\delta n_i(r)$ in Al is shown in figure 3. There is pile up of charge on the impurity site. It decreases rapidly as we move away from the

Figure 2. The proton induced self-consistent potential $\delta V_i(r)$ in Al. The solid line represents $\delta V_i(r)$ by including both $V_{ss}(r)$ and size effect. Dash and dash-dot lines represent $\delta V_i(r)$ with size effect and without size effect, respectively, in jellium model (Popovic *et al* 1976).

centre and becomes oscillatory at large r . As compared to $\delta n_i(r)$ in jellium model (Popovic *et al* 1976) we found that the lattice contribution and size effect both reduce the magnitude of $\delta n_i(r)$.

An s -type very shallow bound state of energy -0.7450×10^{-8} ryd. is also found in our calculations. This suggests that there is no formation of AlH, i.e. the protons exist at interstitial sites in Al matrix as free ions. The impurity induced self-energy is calculated using (11). The calculated E_s for proton in Al is found to be -0.1177 ryd. The electron charge density $\delta n_i(r)$ is integrated in the hydrogen core (1 a.u.) to give Z_{core} , which comes out to be 0.18e. This gives the net charge on the proton $n_s = Z - Z_{\text{core}} = 0.43e$. Comparing with the $n_s = 0.41e$ in jellium model we found that the lattice effect reduces the net charge on proton due to enhanced scattering.

3.5 Residual resistivity

The residual resistivity $\Delta\rho$ for Al-H is estimated using the expression for liquid crystals (Blatt 1957)

$$\Delta\rho = \frac{2.732}{k_F Z_H} \sum_0^6 (l+1) \sin^2(\delta_l - \delta_{l+1}), \quad (13)$$

using the phase shifts given in table 3. The value of residual resistivity is found to be $0.2936 \mu\Omega \text{ cm/at.}\%$. The corresponding value in jellium is found to be $0.2870 \mu\Omega$

Figure 3. The ratio of proton induced charge density and electron charge density $\delta n_1(r)/n_0$. The rest of the description is the same as that of figure 2.

cm/at.%. Thus the lattice contribution enhances the residual resistivity by 2%. On the other hand, the size effect reduces the residual resistivity by 58%. Thus both the size effect and lattice contribution are required to give the correct description of residual resistivity of dilute metal-hydrogen system.

4. Conclusion

In this paper induced charge density is calculated by including the size effect and lattice contribution. The lattice contribution is included through spherical solid model. The Fermi surface is assumed to be essentially spherical. The discrete lattice and the relaxation effects are found to be essential to describe properly the effective charge, charge transfer and self-energy of the hydrogen impurity. A very shallow bound state of energy -0.7450×10^{-8} ryd. obtained using the present model suggests that there is no aluminium-hydride formation, i.e. proton exists at interstitial sites in Al matrix as free ions.

Acknowledgements

The authors wish to thank Prof. G K Mehta and Dr D K Avasthi for helpful discussions and suggestions. The authors are grateful to Prof. V C Sahni and Dr J K Sharma for encouraging us to carry out this work. The numerical calculations have been carried out with the PC/AT 386 purchased out of DST grant.

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