Electron structure and activation energy of hydrogen in α -Zr using nonlinear response theory

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Abstract. The electron structure of hydrogen in hcp Zr is calculated by using self-consistent nonlinear screening theory. The host-ion contribution is included through the spherical solid model potential (SSMP). The resulting charge density and scattering phase shifts are used to calculate the activation energy and residual resistivity of hydrogen in α -Zr matrix. The calculated activation energy 0.285 eV is found in reasonably good agreement with experimental value 0.3 eV. The estimated residual resistivity $0.53 \mu\Omega \text{ cm/at\%}$ for Zr-H system using the scattering phase shifts agrees reasonably well with the observed value $0.27 \mu\Omega \text{ cm/at\%}$. The calculated configurational energy shows that hydrogen prefers tetrahedral(T)-sites over octahedral(O)-sites in α -Zr. The strong binding energy of electron-proton suggests that hydrogen forms zirconium hydride.

Keywords. Induced charge density; impurity potential; spherical solid model potential; self energy; residual resistivity; activation energy.

1. Introduction

Although atomic hydrogen is a simplest solute in a metal that can be thought of, a comprehensive theory of metal-hydrogen interactions has yet to be developed. The electronic structure of a proton in jellium density corresponding to Cu was first carried out in his pioneering work by Friedel (1952). Popovic *et al* (1976) extended the nonlinear screening theory to calculate the electronic structure and heat of solution of hydrogen in jellium density corresponding to Al and Mg. Since then a number of groups have published similar results (Zaremba *et al* 1977; Manninen *et al* 1977; Jena and Singwi 1978). The study of the heat of solution of hydrogen has also been made by taking lattice contribution within jellium model (Manninen and Nieminen 1979; Perrot and Rasolt 1981; Craig 1983). Attempts to study lattice relaxation effects around H impurity in simple metals have also been made. For more details of theoretical work on hydrogen in simple metals, we refer a recent review article by Gupta (1984). The treatment of H as an impurity in transition metals is much more complex than simple metals due to the presence of the metal *d*-electrons. *Ab initio* calculations such as the KKR Green's function method (Deutz *et al* 1981; Klein and Pickett 1982) and the large supercell model (Gupta 1982) require heavy computation efforts.

Pure Zr has superconducting transition temperature $T_c = 0.7^\circ\text{K}$. After implantation of small dose of hydrogen (deuterium) the value of T_c for Zr increases to 3.14 (4.65) $^\circ\text{K}$ (Stritzker and Meyer 1980). Zirconium is a getter material. It has low vapour pressure, therefore, it is used to wrap the volatile material during annealing to avoid its oxidation and evaporation. Though, zirconium forms stable zirconium

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hydride and may be a potential source for hydrogen storage, very little is known about its electronic properties. Darby *et al* (1978) treated the screening of the proton in hcp α -Zr semiempirically. They found that hydrogen prefers tetrahedral (T)-interstitial sites in α -Zr. The same conclusion has been drawn by Narang *et al* (1977) from their neutron diffraction experiment. Considering the linear screening approximation for the proton-electron interaction, Singh *et al* (1981) calculated the activation energy for interstitial H in α -Zr. The configurational energy was found minimum at octahedral (O)-sites. This shows that linear screening theory is inadequate to describe the strong electron-proton interaction. The minimum energy value of hydrogen at T-positions indicates that electron-proton interaction contributes significantly to the energy. Therefore, it is necessary to incorporate the proton screening due to Fermi gas with utmost care, for which a self-consistent calculation is required. To the best of our knowledge no one has done the full self-consistent calculation to study electronic structure of H in α -Zr and hence leading to the calculation of the configurational energy and diffusion parameters such as activation energy. Therefore, we thought it worthwhile to calculate the induced charge density of H in α -Zr by following the self-consistent procedure suggested by Manninen and Nieminen (1979), where the lattice contribution is included through the spherical solid model potential (SSMP). The phase shifts obtained while solving the Schrödinger equation has been used to calculate the residual resistivity of dilute metal-hydrogen system to test the validity of partial phase shift analysis.

The plan of the paper is as follows: The necessary formalism is presented in § 2. The calculations and results are presented in § 3. The conclusion is given in § 4.

2. Theory

2.1 Spherical solid model potential (SSMP)

For a system of N ions, the total ionic potential is written as the sum of individual ionic potential $w(|r-r_l|)$, i.e.

$$V_H(r) = \sum_l w(|r-r_l|), \quad (1)$$

where r_l is the position vector of the l th ion. By including exact form of $V_H(r)$, the solution of Schrödinger equation becomes very cumbersome, so we include only the spherical part of $V_H(r)$ by taking its angular average (Manninen and Nieminen 1979), i.e.

$$V_{av}(r) = \frac{1}{4\pi} \int d\Omega \sum_l w_H(|r-r_l|), \quad (2)$$

where $d\Omega$ is solid angle. By including the potential due to jellium charge density $n_0 = 3/4\pi r_s^3$, where r_s is electron density parameter, the spherical solid model potential (SSMP) takes the form

$$V_{ss}(r) = \frac{1}{4\pi} \int d\Omega \sum_l w_H(|r-r_l|) + \int \frac{dr' n_0}{|r-r'|}. \quad (3)$$

2.2 Activation energy

The proton–host interaction energy in second-order perturbation theory is given by (Harrison 1966):

$$\Delta E(R_p) = \sum_l \frac{Z_p Z_H e^2}{|r_p - r_l|} + \int dr \delta n(r - r_p) \sum_l w_H(r - r_l), \quad (4)$$

where r_p is the position vector of the proton and R_p , relative position of hydrogen with respect to some interstitial site. Taking the Fourier transform of second term in (4) and then solving it, we arrive at the following result:

$$\Delta E(R_p) = \sum_l \frac{Z_p Z_H e^2}{|r_p - r_l|} - \sum_l \frac{Z_p Z_H e^2}{|r_p - r_l|} \int dq \delta n(q) w_H(q) \frac{\sin(q|r_p - r_l|)}{q|r_p - r_l|}, \quad (5)$$

where $w_H(q)$ and $\delta n(q)$ are the Fourier transform of $w_H(r)$ and $\delta n(r)$, respectively. Rearranging the various terms in (5), we finally get

$$\Delta E(R_p) = \frac{2Z_p e^2}{\pi} \sum_l \frac{1}{|r_p - r_l|} \left\{ \frac{\pi Z_H}{2} - Z_H \int dq \delta n(q) w_H(q) \frac{\sin(q|r_p - r_l|)}{q} \right\}, \quad (6)$$

where we have chosen the Ashcroft (1966) potential with core radius $r_c = 2.004$ a.u. to represent the host–ion potential $w(r)$ for simplicity of the calculation.

2.3 Nonlinear screening and screening impurity potential

For a single hydrogen impurity in a metal, the Hamiltonian may be written as (Sholl and Smith 1978):

$$H_{MH} = -\frac{1}{2} \nabla^2 + U(r) + V(r) + V_{xc}(n(r)), \quad (7)$$

where $V(r)$ is the additional Coulomb potential energy due to the impurity. $U(r)$ is the interaction potential due to metallic ions. $V_{xc}(n(r))$ is the functional derivative of a universal exchange and correlation energy functional of the electron mean density. The total charge density $n(r)$ for the complete system is now written as

$$n(r) = n_0(r) + \delta n(r). \quad (8)$$

The impurity potential

$$V(r) = \int \frac{\delta n(r') dr'}{|r - r'|}, \quad (9)$$

can be obtained by solving Poisson equation

$$\nabla^2 V(r) = -4\pi \delta n(r). \quad (10)$$

Ideally, the potential $V(r)$ and the charge density $\delta n(r)$ should be determined self-consistently so that the eigenstates of the Hamiltonian (7) produce a charge density which is identical to that obtained from (10). In the crystal the conduction band states are represented by the block function. As a result the impurity site will no longer follow the spherical symmetry of jellium model and the direct solution of second-order partial

differential equation for a single electron eigen states is no longer possible. The success has been achieved recently in the self-consistent solution for a proton in jellium by taking a part of $U(r)$ which is spherically symmetric around impurity (Manninen and Nieminen 1979; Perrot and Rasolt 1981, 1982). Very recently, the Green's function matrix method has been extended to include the band structure description of the host metal (Craig 1983).

In order to find improved potential, Popovic *et al* (1976) considered the case of electron gas. This is equivalent to put $U(r) = 0$ in (7). Following Popovic *et al* (1976), the induced electron charge density is written as

$$\begin{aligned}\delta n(r) &= n(r) - n_0(r) \\ &= \frac{1}{\pi^2} \int_0^{k_F} dk k^2 \sum_l (2l+1) [R_{lk}^2(r) - j_l^2(kr)] + 2R_b^2(r),\end{aligned}\quad (11)$$

where k is the electron wave vector, and k_F is the Fermi momentum. $j_l(kr)$ are spherical Bessel functions. s-Type bound state sometimes occur; therefore, the bound state charge density $R_b^2(r)$ is also added in (11).

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

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) + \frac{l(l+1)}{2r^2} - \varepsilon_k \right] r R_{lk}(r) = 0. \quad (12)$$

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

$$V_{\text{eff}}(r) = -\frac{Z}{r} + V(r) + V_{\text{ss}}(r) + V_{\text{xc}}(n(r)) - V_{\text{xc}}(n_0(r)), \quad (13)$$

for a spherically symmetric potential field. V_{xc} is the functional derivative of a universal exchange and correlation-energy functional $E_{\text{xc}}(n(r))$ of particle density $n(r)$. Equations (12) and (13) are solved self-consistently.

After including $V_{\text{ss}}(r)$ in (13) it is always not possible to find out convergent solution of (12) with the procedure of Popovic *et al* (1976). Therefore, Manninen *et al* (1975) suggested that the impurity potential $V(r)$ may be obtained by rewriting the Poisson equation as:

$$\nabla^2 V(r) - k_{\text{TF}}^2 V(r) = -4\pi\delta n(r) - k_{\text{TF}}^2 V(r). \quad (14)$$

By solving (14), we get

$$V(r) = \frac{1}{4\pi} \int dr' \frac{\exp(-k_{\text{TF}}|r-r'|)}{|r-r'|} \{4\pi\delta n(r') + k_{\text{TF}}^2 V(r')\}, \quad (15)$$

k_{TF} is Thomas-Fermi(TF) screening parameter $(4k_F/\pi)^{1/2}$. The TF potential may be chosen as the initial potential. In the present calculation, the initial potential is taken of the form

$$V_{\text{eff}}^{(0)}(r) = -\frac{Z}{r} \left(1 + \frac{\beta r}{2} \right) \exp(-\beta r), \quad (16)$$

instead of TF potential, because, it provides an accurate description of a proton impurity in both electron gas and transition metal (Sholl and Smith 1978). The parameter β is determined self-consistently, so that the Friedel sum rule

$$Z = \frac{2}{\pi} \sum_l (2l+1) \delta_l(k_F), \quad (17)$$

is satisfied with high accuracy. $\delta_l(k_F)$ is the phase shift at Fermi sphere corresponding to angular momentum quantum number l . By solving (12) and (13) numerically, we get a new potential $V_{\text{eff}}^{(1)}(r)$, which can be inserted again into (12). This procedure has to be repeated until the potential $V_{\text{eff}}^{(1)}(r)$ and $V_{\text{eff}}(r)$ satisfy the Friedel sum rule simultaneously. In this procedure, the Coulomb tail if persists, gets truncated due to exponential term. The self-consistency is achieved within 2% in the charge density. Equation (12) leads to a convergence after 10 iterations when starting from $V_{\text{eff}}^{(0)}(r)$. Iterative procedure was repeated until both the initial potential $V_{\text{sc}}(r)$ and self-consistent potential $V_{\text{eff}}(r)$ satisfied the Friedel sum rule simultaneously.

3. Calculations and results

3.1 Spherical solid model potential (SSMP)

The atomic radius r_0 and c/a ratio for α -Zr are taken as 3.345 a.u. and 1.595, respectively. The proton and bare host-ion charge are taken as 1e and 4e, respectively. The summation in (3) is carried out up to 26th shell. The calculated SSMP around octahedral (O) and tetrahedral (T)-sites are shown in figure 1. The number of nearest neighbours (nn) and their positions with respect to O(T)-site are also included there. The nn positions around O(T)-site indicate that α -Zr ions are more densely packed around T-site. The maxima in $V_{\text{ss}}(r)$ occur around the nearest neighbour sites and minima occur between the two-sites. It does not show exact periodicity of the lattice, therefore, it can be regarded just a correction term to $V_{\text{eff}}(r)$ due to the discrete nature of lattice. The relative magnitude of potential also depends upon Z_{H} and r_c , because it is shifted by constant amount $3r_c^2/2r_s^3$, which is obtained by taking $q \rightarrow 0$ limit of first part of $V_{\text{ss}}(r)$ in (3).

3.2 Phase shifts and impurity potential

The calculation of induced charge density and impurity potential is done by solving (12) and (13) following the procedure of Manninen and Nieminen (1979). The parametrized form of $V_{\text{xc}}(n(r))$ proposed by Gunnarson and Lundquist (1976) has been taken for detailed calculations. In the first step, the calculation is done for the perfect crystal by putting $n(r) = n_{\text{H}}(r)$, $Z = 0$ and $\delta n(r) = n_{\text{H}}(r) - n_0$. The self-consistently calculated $V_{\text{H}}(r)$ and $\delta n_{\text{H}}(r)$ are obtained. In the second step, the calculation is repeated with impurity at interstitial site by putting $n(r) = n_{\text{p}}(r)$, $Z = Z_{\text{p}}$, $\delta n(r) = n_{\text{p}}(r) - n_0$ and self-consistently calculated $V_{\text{p}}(r)$ and $\delta n_{\text{p}}(r)$ are obtained. In both the cases, the Friedel sum rule (17) is satisfied. The difference

$$\delta v_i(r) = V_{\text{p}}(r) - V_{\text{H}}(r), \quad (18)$$

and

$$\delta n_i(r) = \delta n_{\text{p}}(r) - \delta n_{\text{H}}(r), \quad (19)$$

Figure 1. The spherical solid model potential (SSMP) $V_{ss}(r)$ for α -Zr around octahedral-site and tetrahedral(T)-site. The position and number of nearest neighbours to octahedral (tetrahedral)-site are also indicated.

gives the impurity interaction potential and the impurity induced charge density, respectively.

The impurity induced charge density $\delta n_i(r)$ calculated using (19) in α -Zr is shown in figure 2 by solid lines. There is pile up of charge on the impurity site. It decreases rapidly by increasing r and becomes oscillatory beyond $r=3.0$ a.u. It is found that the linear screening theory grossly underestimates the induced charge density (shown by dashed lines) by a factor of 6.5 at $r=0$. This indicates the importance of nonlinear screening theory while calculating the induced charge density of hydrogen in metals.

Figure 2. The ratio of proton induced charge density and electron charge density $\delta n_i(r)/n_0$. The solid and dashed lines represent $\delta n(r)/n_0$ obtained using nonlinear and linear screening theory, respectively. The results in the inset are given on magnified scale..

3.3 Self-energy of proton

By solving Poisson equation by using the analytical form $V_{\text{eff}}^{(0)}(r)$ given by (16), one can obtain the charge density

$$\delta n_i(r) = \frac{Z\beta^3}{8\pi} \exp(-\beta r). \quad (20)$$

At $r = 0$, (20) reduces to:

$$\delta n_i(0) = \frac{Z\beta^3}{8\pi}. \quad (21)$$

By putting the value of $\delta n_i(0)$ in (21), one can get the value of the parameter β . The value of β so obtained is 2.2925 a.u. Substituting the value of $\delta n_i(r)$ from (20) and $\delta V_i(r) = V_{\text{eff}}^{(0)}(r)$ in the following expression

$$E_{\text{sc}} = \frac{1}{2} \int \delta V_i(r) \delta n(r) dr, \quad (22)$$

we get the impurity self-energy

$$E_{\text{sc}} = -\frac{3}{32} Z^2 \beta \text{ a.u.} \quad (23)$$

The self-energy of proton in zirconium matrix is found to be -0.430 ryd. We have also calculated the electron charge within the core of hydrogen by integrating $\delta n_i(r)$ from 0 to core radius (1 a.u.). It is found to be 0.46 e. This gives the net charge on the proton $n_s = Z - Z_{\text{core}} = 0.54$ e. The corresponding value of n_s at T-site is found to be 0.51 e.

3.4 Activation energy

The calculated configuration energy using (6) along O–O(octahedral), O–T(tetrahedral) and T–T directions in the $(11\bar{2}0)$ plane is shown in figure 3. The configurational energy is found maximum exactly at mid point of both T–T and O–O paths. Along T–O path, it is found maximum at about 33% distance of T–O path. The configurational energy is found minimum at T-site, therefore, the tetrahedral site in α -Zr is considered the most favourable position for the proton to stay. The same conclusion has been drawn by Narang *et al* (1977) from their neutron diffraction experiment. O–T barrier height is about 3 times and T–T barrier height is about 4 times than the O–O barrier height, therefore, the probable path for proton diffusion in α -Zr matrix may be off-symmetry paths and not the O–O–T and O–T–T paths. The minimum barrier height to which an impurity can cross is called the activation energy. It is found to be 0.285 eV. The experimental (Narang *et al* 1977) value of activation diffusion energy (E_{ac}) is 0.30 eV. The good agreement of calculated and experimental value of E_{ac} shows that the screening around proton is nonlinear. The linear response theory grossly overesti-

Figure 3. The configurational energy $\Delta E(R_p)$ of proton in α -Zr. The solid and dashed lines represent the configurational energy obtained using nonlinear and linear screening theory, respectively. Inset: $\circ \rightarrow$ octahedral positions; $\times \rightarrow$ tetrahedral positions; $\bullet \rightarrow$ host ions.

mates the activation energy, which is found to be 4.73 eV. This shows that nonlinear theory is very essential for understanding the scattering around hydrogen impurity in α -Zr.

3.5 Phase shifts and residual resistivity

The phase shifts are obtained while solving the Schrödinger equation (12) self-consistently using partial phase shifts analysis. The s and p phase shifts are found dominating. To test the validity of our calculated phase shifts ($\delta_l(k_F)$) at Fermi surface, the residual resistivity $\Delta\rho$ is estimated using the expression for liquid phase of solid (Blatt 1957). $\Delta\rho$ is calculated using the first seven values of $\delta_l(k_F)$, because the phase shifts beyond $l > 6$ are found too small. Our calculated value of $\Delta\rho$ is found to be $0.53 \mu\Omega \text{ cm/at\%}$. The experimental value of residual resistivity for $\text{ZrH}_{1.54}$ is available in the literature (Bickel and Berlincourt 1970). The derived value of $\Delta\rho$ for dilute zirconium hydride solution comes out to be $0.27 \mu\Omega \text{ cm/at\%}$. The resistivity of Zr (high purity) at 4.2°K is $0.213 \mu\Omega \text{ cm}$.

4. Conclusion

The induced charge density and impurity potential of proton are calculated by including the explicit form of host-ion potential. The Fermi surface is assumed to be spherical and conduction electron wave function is taken as free particle like. The calculated activation energy confirms the experimental (Narang *et al* 1977) fact that hydrogen prefers T-sites in α -Zr matrix. s-Type bound state energy -0.00484 ryd (-0.067 eV) suggests that there is strong binding of proton and electron. Therefore, hydrogen forms zirconium hydride (Müller *et al* 1968) and does not exist as a free H^+ in Zr matrix. The present calculation may be improved by including crystal effects like relaxation effects, size effect in general and by taking proper account of *d* electrons in particular. A careful calculation of *d* electrons of KKR-Green function method (Deutz *et al* 1981; Klein and Pickett 1982) may provide better results. However, this will involve heavy computational efforts.

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