

Electronic structure and activation energy of hydrogen in NEG alloy using nonlinear response theory

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Abstract. Electronic structure of hydrogen in NEG alloy [$Zr_{0.70}V_{0.246}Fe_{0.054}$] is calculated by using nonlinear response theory [Kohn and Sham, *Phys. Rev.* **A140**, 1133 (1965)]. The configurational energy is calculated by assuming the ideal hcp structure for NEG alloy. The calculated configurational energy predicts that hydrogen prefers octahedral (O)-site in NEG alloy. *s*-Type shallow bound state of energy -1.580×10^{-5} Ryd. suggests that hydrogen does not form NEG hydride and it stays as a free ion in NEG alloy. This conclusion confirms the prediction of Tripathi *et al.*

Keywords. Electronic structure; activation energy; residual resistivity; self energy.

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1. Introduction

The alloys of Zr, V, Fe, Al, etc. have the property of pumping residual gases, if they are heated to a specified temperature in vacuum. These are widely used in accelerators and industries for achieving ultrahigh vacuum. Out of commercially available strips of these materials, Zr, V, Fe alloy has the advantage of having a much lower operating and regeneration temperature as compared to the earlier Zr–Al alloy.

Atomic hydrogen is the simplest solute in a solid that can be thought of. The electronic structure and activation energy of single hydrogen in free electron-like metals and transition metals have been extensively studied in the past by a number of authors [1–3]. Norskov and coworkers [1] have studied the electronic structure of hydrogen in a number of free electron-like metals using the effective medium theory. Williams *et al* [2] in a classic paper have studied the formation of transition metal-hydride phases using augmented-spherical-wave (ASW) method. The Green function method is used by Puska *et al* [3] to calculate the activation energy of hydrogen in a number of transition metals. Many of the alloys of Ti, Zr, Hf react with hydrogen to give ternary hydrides and some of these have attracted interest as storage media. The best known is the intermetallic compound TiFe, which takes up nearly two atoms of hydrogen. TiCo, which is structurally similar to TiFe, also forms a ternary hydride $TiCoH_x$. In the Ti–Ni system, TiNi forms a ternary of the

approximate composition $\text{TiNiH}_{1.4}$. It is more stable than the hydride of TiCo. Zirconium alloys are of interest historically in providing one of the first examples of a ternary hydride [4,5]. For more details of transition metal ternary hydrides, the review article by Switendick [6] is referred.

In order to use zirconium alloys efficiently, it is necessary to understand their gettering action. In this report, we have studied the electronic structure of hydrogen in jellium of non-evaporable getter of Zr, V and Fe alloy using density functional formalism [7]. The resulting electronic structure and phase shifts are used to calculate the configurational energy and residual resistivity of H in NEG material, respectively. An alternative form of one-parameter impurity potential [8] is used to calculate the self-energy of hydrogen.

2. Theory

2.1 Nonlinear screening and impurity potential

Following Popovic *et al* [9], the induced charge density due to impurity in a jellium is given by

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

where k is the electron wave vector and k_F is the Fermi momentum. s -Type bound state occurs sometimes; therefore, the bound state charge density is also added in (1). $R_b(r)$ represents the radial wave function of the bound state. $n(r)$ and $n_0(r)$ are the charge density of an electron with and without impurity in jellium, respectively.

The electron eigenvalue ε_k and corresponding radial wave function $R_{lk}(r)$ are obtained by solving the following radial part of Schrödinger equation

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

For 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

$$V_{\text{eff}}(r) = -\frac{Z}{r} + V(r) + V_{xc}(n(r)) - V_{xc}(n_0(r)), \quad (3)$$

Z is the effective charge of the impurity ion. The parameterized form of $V_{xc}(n(r))$ proposed by Gunnarson and Lundquist [10] has been adopted for the detailed calculation.

The potential

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

can be obtained by solving the Poisson equation

Nonlinear response theory

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

For a spherical potential field, (2) and (3) are solved self-consistently following the procedure of Popovic *et al* [9]. To start with the impurity screened potential

$$V_{ir}(r) = -\frac{Z}{r} \exp(-\alpha r^\beta), \quad (5)$$

is taken in place of $V_{\text{eff}}(r)$. With parameter β fixed, the parameter α was determined so that the Friedel sum rule

$$Z = \frac{2}{\pi} \sum_l (2l+1) \delta_l(k_F), \quad (6)$$

is satisfied with high accuracy. The radial equation is solved numerically in the steps of 0.05 a.u. up to the radius $R_0 = 10$ a.u. The resulting wave functions are used to generate $\delta n(r)$, which in turn, generate $V_{\text{eff}}(r)$. By varying β this iterative procedure is repeated until both the trial potential $V_{ir}(r)$ and the self-consistent potential $V_{\text{eff}}(r)$ satisfy the Friedel sum rule simultaneously. The first seven phase shifts $\delta_l(k_F)$ have been used to satisfy (6) as their magnitude becomes too small beyond $l = 6$. The radial wave function $R_b(r)$ and the corresponding bound state energy ε_b are determined by matching the numerical solution to the asymptotic solution given by

$$rR_b(r) \sim \exp[-k_0 r], \quad (7)$$

where $k_0 = (-2\varepsilon_b)^{1/2}$, at $r = R_0$, the distance at which the potential is set equal to zero, where it becomes negligibly small.

An alternative 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 [8] is

$$V_{sc}(r) = -\frac{Z}{r} \left(1 + \frac{\beta r}{2}\right) \exp(-\beta r), \quad (8)$$

$V_{sc}(r)$ via Poisson's equation yield a simple analytical form of induced charge density:

$$\delta n(r) = \frac{Z\beta^3}{8\pi} \exp(-\beta r). \quad (9)$$

Obviously $\delta n(r)$ is finite at the origin. The value of $\delta n(r)$ at origin has been used to calculate β . The value of β so obtained is found to be 2.2681 a.u. The impurity potential $\delta v_i(r) = V_{sc}(r)$ and $\delta n(r)$ given by (8) and (9), respectively, lead to evaluate the self-energy of the proton analytically. As a result the self-energy, which is defined as

$$E_{sc} = \frac{1}{2} \int \delta v_i(r) \delta n(r) dr, \quad (10)$$

reduces to

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

However the self-energy for Thomas–Fermi potential comes out to be $-Z^2\beta/4$ a.u.

3. Calculation and results

The calculation of various properties of H in NEG alloy is done in virtual crystal approximation. The effective valence Z_{alloy} of virtual NEG alloy, $Z_{\text{r}1-x-y}\text{V}_x\text{Fe}_y$, is taken to be the average of the valencies of constituents, i.e.,

$$Z_{\text{alloy}} = [1 - x - y]Z_{\text{Zr}} + xZ_{\text{V}} + yZ_{\text{Fe}}. \quad (12)$$

The valence Z of Zr, V and Fe are taken to be 4, 5 and 3, respectively. Similarly, the atomic radius of virtual lattice r_0^{alloy} is obtained from the expression

$$r_0^{\text{alloy}} = [1 - x - y]r_0^{\text{Zr}} + xr_0^{\text{V}} + yr_0^{\text{Fe}}, \quad (13)$$

by using the room temperature values of atomic radii 3.346 a.u., 2.817 a.u. and 2.665 a.u. for Zr, V and Fe, respectively.

3.1 Impurity potential

The self-consistent effective potential given by (3) is shown in figure 1. The magnitude of the potential decreases rapidly and becomes negligible beyond Wigner–Seitz radius. In the inset, the potential is plotted on a magnified scale beyond $r = 3$ a.u. to show the Friedel oscillations clearly. The calculated $V_{tr}(r)$ is also shown in figure 1 for comparison. The parameters α and β of trial potential are found to be 1.1750 a.u. and 1.1592 a.u., respectively. The two potentials are almost equal up to $r = 6.0$ a.u. They can be separated, if we plot them on a magnified scale. At large distances $V_{tr}(r)$ decreases exponentially, while $V_{\text{eff}}(r)$ exhibits Friedel oscillations of small magnitude. One-parameter impurity potential $V_{sc}(r)$ is also plotted in figure 1 for comparison.

3.2 Electronic structure and self-energy of hydrogen

The induced charge density $\delta n(r)$ calculated using (1) in NEG alloy is shown in figure 2. There is a pile up of charge on the impurity site. It decreases rapidly by increasing r and becomes oscillatory beyond $r = 3$ a.u. The charge density obtained using (9) is also shown in figure 2. It is almost equal to the $\delta n(r)$ obtained self-consistently. Beyond $r = 2$ a.u. the two charge densities can be separated by plotting them on a magnified scale. From (9) it is clear that $\delta n(r)$ obtained by one-parameter impurity potential decreases exponentially and does not exhibit the Friedel oscillations at large distances.

The attractive potential of the proton affects those metal wave functions which have a finite density at the H site and leads to the so called metal hydrogen bonding band below the metal d -band. Further it can pull below the Fermi energy E_{F} some metal states which are located above E_{F} in the pure metal. The amount of binding energy by which the attractive effective potential of an impurity brings down the impurity in lower state is called the self-trapped energy or self-energy of an impurity. The value of self-energy E_{self} using (11) comes out to be -0.425 ryd.

We have also calculated the electron charge within the core of hydrogen by integrating $\delta n(r)$ from 0 to core radius (1 a.u.). It is found to be $0.44e$. This gives the net charge on the proton $n_s = Z - Z_{\text{core}} = 0.56e$.

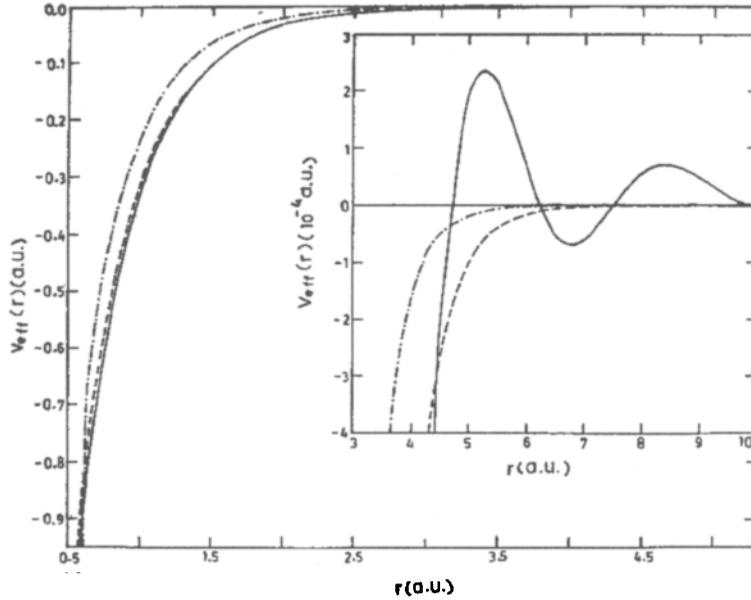


Figure 1. Self-consistent potential $V_{\text{eff}}(r)$ (solid line), trial potential $V_{\text{tr}}(r)$ (dashed line) and one-parameter potential $V_{\text{sc}}(r)$ (dash-dot line) for hydrogen in jellium density corresponding to NEG alloy ($r_s = 1.9804$ a.u.).

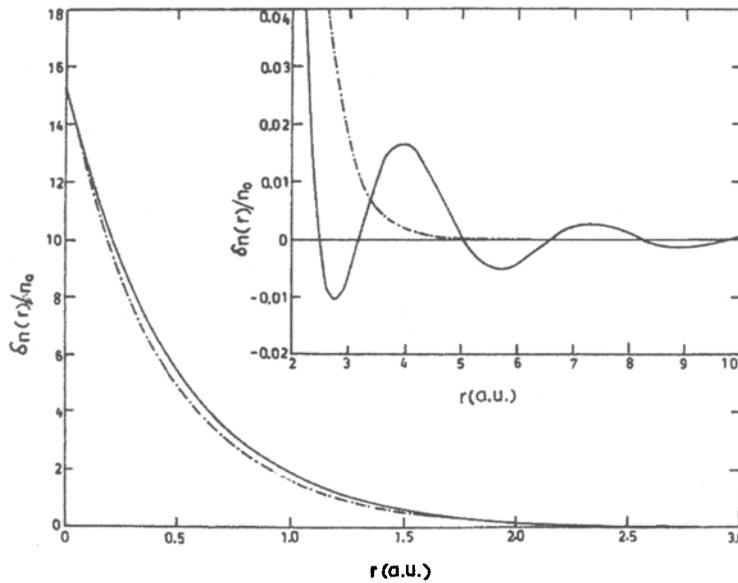


Figure 2. The ratio of nonlinear charge density of hydrogen and jellium density $\delta n(r)/n_0$ (solid line) in jellium density corresponding to NEG alloy ($r_s = 1.9804$ a.u.). The $\delta n(r)/n_0$ obtained from (9) is shown by dash-dot line.

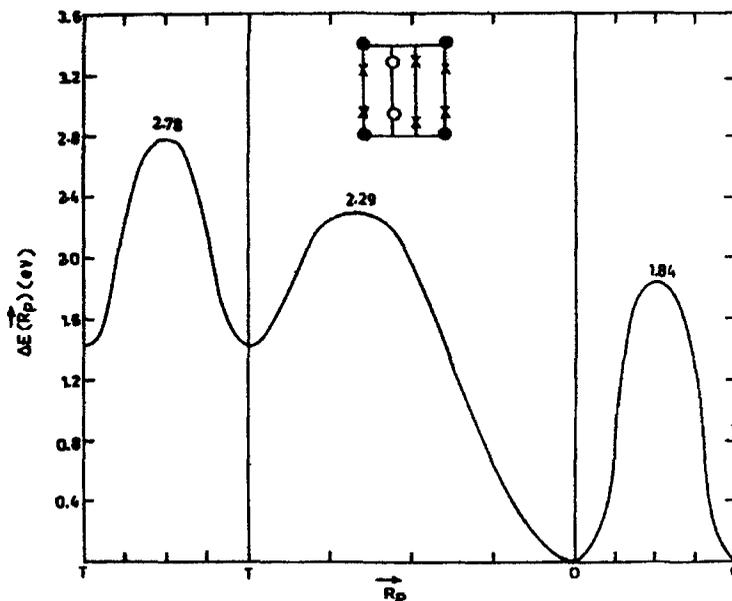


Figure 3. The configurational energy $\Delta E(R_p)$ of hydrogen in NEG alloy, where R_p represents position of hydrogen with respect to some interstitial site. Inset: $O \rightarrow$ octahedral positions; $X \rightarrow$ tetrahedral positions; $\bullet \rightarrow$ host ions.

3.3 Configurational energy

The calculation of configurational energy of H is done in virtual crystal approximation of NEG system. The hcp structure with ideal axial ratio $c/a = 1.633$ is considered. The non-linear charge density $\delta n(r)$ combined with second-order perturbation theory [11] is used to calculate the configurational energy. The Ashcroft [12] model potential with core radius $r_c = 2.004$ a.u. is taken to represent the host-ion potential for simplicity of the calculation. The calculated configurational energy 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 midpoint of both $T-T$, $O-O$ paths. Along $O-T$ path it is found maximum at about 66% distance. The octahedral position is found to be most favourable position for hydrogen impurity as configurational energy is minimum at O -site. The migration energy along $O-O$, $O-T$ and $T-T$ paths are found to be 1.84 eV, 2.29 eV and 2.78 eV, respectively. The activation energy E_{ac} is defined as the minimum height of the barrier to be crossed by hydrogen for its migration. The theoretical value of activation energy $E_{ac} = 1.84$ eV is found somewhat higher than the corresponding experimental [13] value 1.55 eV at 600 K, because theoretical value of activation energy is calculated using the formula derived at $T = 0$ and using the atomic radii of constituent metals of NEG alloy at room temperature. Apart from this, some important contributions which will be discussed in §4, have been ignored in the present calculation. The experimental [14] values of activation energy of hydrogen in constituent metals α -Fe, V and Zr are 0.105 eV, 0.045 eV and 0.61 eV at 600 K, 300 K and 600 K, respectively. The value of E_{ac} is an important parameter to deduce the diffusion coefficient $D = D_0 \exp(-E_{ac}/K_B T)$, where K_B is Boltzmann

Table 1. The scattering phase shifts $\delta_l(k_F)$ for proton in NEG at Fermi surface. $l = 0, 1, 2, \dots$ corresponds to s, p, d, \dots orbitals.

| l | $\delta_l(k_F)$ |
|-----|-----------------|
| 0 | 1.009507 |
| 1 | 0.135868 |
| 2 | 0.022980 |
| 3 | 0.004242 |
| 4 | 0.000792 |
| 5 | 0.000147 |
| 6 | 0.000026 |

constant and prefactor D_0 is independent of temperature. The value of $D_0 = 0.35 \times 10^6$ cm²/s is estimated from the experimental data given in [13]. At $T = 600$ K, the theoretical and experimental values of diffusion coefficient D are found to be 1.225×10^{-10} cm²/s and 3.344×10^{-8} cm²/s. The theoretical value of D is lower by 2 orders of magnitudes than its experimental value, as the activation energy from which D is calculated, is higher than the experimental value because of the reasons discussed above. The value of D for pure Zr at 600 K is found to be 1.150×10^{-8} cm²/s, which is one third of the experimental value of NEG system. This suggests that hydrogen absorption in NEG system at 600 K is 3 times more than the hydrogen absorption in pure Zr. This is because the diffusion coefficient of hydrogen in constituent metals α -Fe and V is of the order of 10^{-4} [14]. Therefore, these metals when they form an alloy with Zr, enhance the capacity of absorption of hydrogen in NEG alloy.

3.4 Phase shifts and residual resistivity

The phase shifts, obtained while solving the Schrödinger equation using partial phase shifts analysis are given in table 1. The s and p phase shifts are found dominating. The residual resistivity $\Delta\rho$ is estimated using the expression

$$\Delta\rho = \frac{2.732}{k_F Z_H} \sum_{l=0}^{\infty} (l+1) \sin^2(\delta_l - \delta_{l+1}), \quad (14)$$

for the liquid phase [15] by taking first seven phase shifts for dilute NEG-H system, because the value of $\delta_l(k_F)$ are found too small beyond $l = 6$. In (14) the Fermi momentum k_F is taken in atomic units. The valence of virtual host metal ion Z_H is taken equal to 4.1920 for NEG matrix. Our calculated value of $\Delta\rho$ is found to be $0.41 \mu\Omega$ cm.at%. The experimental value of $\Delta\rho$ for NEG material is not available in the literature. However, to have a rough idea of residual resistivity of getter materials, we quote the experimental [16] value $\Delta\rho = 0.27 \mu\Omega$ cm/at% for ZrH_{1.54} composition. The resistivity of Zr (high purity) at 4.2 °K is $0.213 \mu\Omega$ cm.

4. Conclusion

The electronic structure, migration energy, self-energy, charge transfer and residual resistivity of H in NEG alloy are calculated using a simple nonlinear response theory, where

the Fermi surface is taken spherical. The calculated configurational energy predicts that H prefers octahedral sites in NEG system. A very shallow *s*-type bound state of energy -1.580×10^{-5} ryd. suggests that there is a weak binding of proton and electron and that hydrogen does not form NEG-H compound. The same conclusion has been drawn by Tripathi *et al* [17] experimentally. The present results can further be improved by including relaxation and size effects in general and by taking proper account of *d* electrons, in particular, which have been neglected in the the present calculation altogether. In this respect the present study is only a step ahead in the process of understanding the getter material ZrVFe. The electronic structure $\Delta n(r)$ near impurity site is found to be very sensitive to small changes in the overall potential. Therefore, it is expected that a more rigorous treatment incorporating the band structure of the host metal would yield additional important structure in $\Delta n(r)$ - and better results of activation energy and diffusion coefficient. A careful contribution of *d* electrons using KKR–Green function method [18,19] may also provide better results. However, this will involve heavy computational efforts.

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