

Activation energy of hydrogen in Lu

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Abstract. The impurity induced charge density is calculated in jellium by solving the Schrödinger equation self-consistently following the procedure of Manninen and Nieminen and using Kohn–Sham density functional formalism. The host-ion contribution is included through the spherical solid model potential (SSMP). The calculated activation energy 0.27 eV is found in good agreement with experimental value 0.28 ± 0.02 eV. The estimated residual resistivity $1.02 \mu\Omega \text{ cm/at\%}$ for Lu–H system using the resulting phase shifts agrees reasonably well with the observed value $1.75 \pm 0.10 \mu\Omega \text{ cm/at\%}$. The calculated configurational energy shows that hydrogen prefers tetrahedral(T)-sites over octahedral(O)-sites in Lu matrix. This has been confirmed by Bonnet experimentally. A very shallow value of *s*-type bound state of energy -0.00316 Ryd predicts that there is no formation of lutetium hydride solution and H^+ exists as a free ion in Lu matrix.

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

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1. Introduction

The neutron scattering analysis [1] for LuH predicts that hydrogen occupies the tetrahedral interstices of the Lu lattice in α -phase. The lutetium–hydrogen solid solution shows unusual stability [2]. The stability of the α -phase is because of an unusual short-range pairing order of the hydrogen as shown by diffuse-elastic-neutron scattering (DENS) studies [3]. Although, atomic hydrogen is the simplest solute in a metal that can be thought of, a first principle theory of Lu–H interaction has yet to be developed. The standard method for calculating pairwise interaction in simple metals is based on pseudopotential theory [4–6]. The first self-consistent calculations of the non-linear screening of a proton have been made by Popovic *et al* [7] and Almladh *et al* [8]. Since then a number of groups have published similar results [9–11]. The electronic structure of hydrogen in lutetium using Hohenberg–Kohn–Sham [12, 13] density formalism have been calculated [14] earlier, where the contribution of host-ions was neglected altogether. In this paper, we have made an attempt to calculate the electronic structure of hydrogen following the approach of Manninen and Nieminen [15]. The electron–ion interactions have been included through spherical solid model potential (SSMP) [15]. The induced charge density so obtained is further used to calculate the activation energy of hydrogen in lutetium matrix. The resulting phase shifts

obtained while solving the Schrödinger equation have been used to estimate the residual resistivity of lutetium-hydrogen system.

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

2. Theory for nonlinear screening and screening impurity potential

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

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

For the continuum states $\epsilon_k = k^2/2$, 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

$$V_{\text{eff}}(r) = -\frac{Z}{r} + V(r) + V_{\text{ss}}(r) + V_{\text{xc}}(n(r)) - V_{\text{xc}}(n_0(r)), \quad (2)$$

for a spherically symmetric potential field. $V_{\text{xc}}(n(r))$ is the functional derivative of a universal exchange and correlation energy functional of the electron mean density. $n_0(r)$ is the charge density of jellium corresponding to host-matrix. $n(r)$ is the sum of jellium charge density and the charge density arises due to host ions and impurity. The impurity potential

$$V(r) = \int \frac{\delta n(r') dr'}{|r-r'|} \quad (3)$$

can be obtained by solving Poisson equation

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

Ideally, the potential $V(r)$ and the induced charge density $\delta n(r)$ should be determined self-consistently so that the eigenstates $R_{lk}(r)$ produce a charge density which is identical to that obtained from (4). In the crystal, the conduction band states are represented by the Bloch 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 eigenstates is no longer possible. The success has been achieved in the self-consistent solution for a proton in jellium by taking a part of ionic potential that is $V_{\text{ss}}(r)$ which is spherically symmetric around impurity [15–17]. Very recently, the Green's function matrix method has been extended to include the band structure description of the host metal [18].

In order to find self-consistent potential $V(r)$, Popovic *et al* [7] considered the case of electron gas. The induced electron charge density due to impurity in jellium is written as

$$\begin{aligned} \delta n(r) &= n(r) - n_0(r) \\ &= \frac{1}{\pi^2} \int_0^{k_F} dk k^2 \sum_l (2l+1) [R_{lk}^2(r) - j_l^2(kr)] + 2R_b^2(r), \end{aligned} \quad (5)$$

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where k is the electron wave vector and k_F is the Fermi momentum. s -type bound state sometimes occur; therefore the bound state charge density is also added in (5). Equations (1) and (2) are solved self-consistently. For starting the iteration, the following host-impurity screened Coulomb potential was considered by Popovic *et al* [7]:

$$V_{sc}(r) = -\frac{Z}{r} \exp(-\alpha r^\beta). \quad (6)$$

With parameter β fixed, the parameter α was determined so that the Friedel sum rule

$$Z = \frac{2}{\pi} \sum_l (2l+1) \delta_l(k_F) \quad (7)$$

is satisfied with high accuracy. $\delta_l(k_F)$ is the phase shift at Fermi sphere corresponding to angular momentum quantum number l . By varying β , this iterative procedure was repeated until both the initial potential $V_{sc}(r)$ and self-consistent potential $V_{eff}(r)$ satisfy the Friedel sum rule simultaneously.

After including $V_{ss}(r)$, it is always not possible to find out the proper values of α and β which may satisfy the Friedel sum rule for both $V_{sc}(r)$ and $V_{eff}(r)$ simultaneously. Therefore, Manninen *et al* [11] suggested that the impurity potential $V(r)$ may be obtained by rewriting the Poisson equation as

$$\nabla^2 V - k_{TF}^2 V = -4\pi\delta n(r) - k_{TF}^2 V. \quad (8)$$

By solving (8), we get

$$V(r) = \frac{1}{4\pi} \int dr \frac{\exp(-k_{TF}|r-r'|)}{|r-r'|} \{4\pi\delta n(r') + k_{TF}^2 V(r')\}, \quad (9)$$

k_{TF} is Thomas–Fermi (TF) screening parameter $(4K_F/\pi)^{1/2}$. The TF potential may be chosen as the initial potential $V_{eff}^{(0)}(r)$ for solving (1) and (2) self-consistently. By solving (1) and (2) numerically, we get a new potential $V_{eff}^{(1)}$, which can be inserted again into (1). This procedure has to be continued until the potential $V_{eff}^{(1)}$ does not change in successive iterations. In this procedure, the Coulombic tail, if persists, gets truncated due to exponential term. The self-consistency is achieved within 0.01% in the charge density. Equation (9) leads to a convergence after 10 iterations when starting from TF potential. In the present calculation, the initial potential is taken in the form [19]

$$V_{sc}(r) = -\frac{Z}{r} \left(1 + \frac{\beta r}{2}\right) \exp(-\beta r) \quad (10)$$

instead of TF potential, because, it provides an accurate description of a proton impurity in both electron gas and transition metal [19]. The parameter β is determined self-consistently.

3. Calculations and results

3.1 Spherical solid model potential (SSMP) $V_{ss}(r)$

Spherical solid model potential $V_{ss}(r)$ is calculated following the procedure of Manninen and Nieminen [15]. The Ashcroft [20] potential with core radius

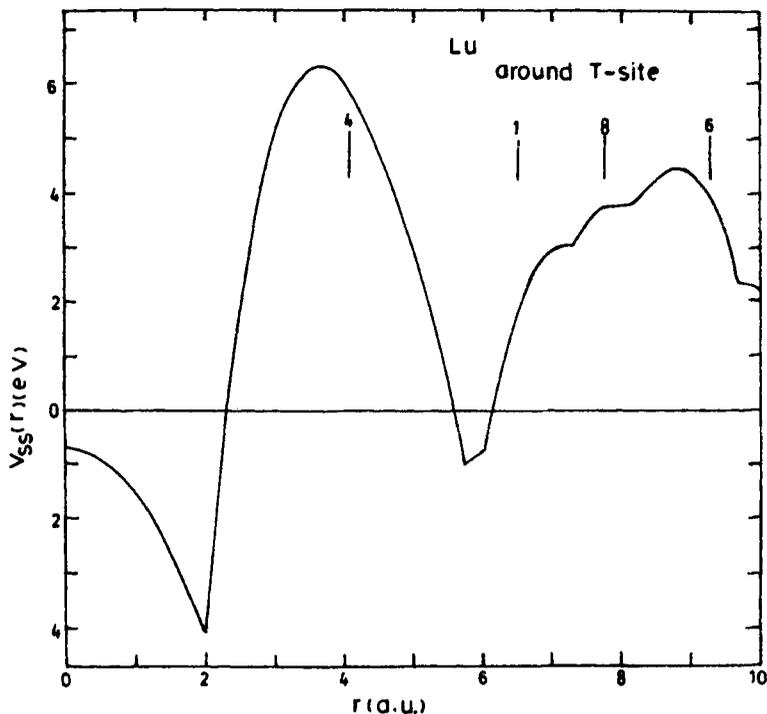


Figure 1. The spherical solid model potential (SSMP) $V_{ss}(r)$ for α -Lu around tetrahedral (T) site. The position and number of nearest neighbours to tetrahedral site are also indicated.

Table 1. The scattering phase shifts $\delta_l(E_F)$ for proton in α -Lu. $l = 0, 1, 2, \dots$ are s, p, d, \dots phase shifts

δ_l	Putting $V_{ss}(r) = 0$	Including $V_{ss}(r)$
0	1.231149	1.256097
1	0.087173	0.100300
2	0.011145	0.007663
3	0.001653	0.000479
4	0.000302	-0.001200
5	0.000411	-0.001032
6	0.000276	-0.000428

$r_c = 2.004$ a.u. is chosen to represent the host-ion potential for simplicity of the calculation. The atomic radius r_0 and c/a ratio for Lu are taken to be 3.629 and 1.586 a.u., respectively. The effective charge of the proton and bare host-ion are taken to be 1e and 3e, respectively. The calculated $V_{ss}(r)$ around tetrahedral site (T) is given in figure 1. The number of nearest neighbour and their positions with respect to T-site are indicated. It is found that Lu is more densely packed around T-site than O-site. $V_{ss}(r)$ has the maxima around the nearest neighbour sites and minima between the two sites.

It does not exhibit periodicity of the lattice, therefore, it can be regarded just as a correction term of $V_{\text{eff}}(r)$ for discrete nature of the lattice. The relative magnitude of $V_{\text{ss}}(r)$ also depends upon Z_{H} and r_{c} , because it is shifted upward by a constant amount $3r_0^2/2r_s^3$, which is obtained by taking $q \rightarrow 0$ limit of first part of $V_{\text{ss}}(r)$ given by (6) in the paper of Manninen and Nieminen [15].

3.2 Phase shifts and impurity potential

The calculation of induced charge density and impurity potential is done using the method of Popovic *et al* [7] without including $V_{\text{ss}}(r)$. The parametrized form of $V_{\text{xc}}(n(r))$ proposed by Gunnarson and Lundquist [21] has been taken for the detailed calculation. The values of potential parameters (6) α and β are found to be 1.0739 and 1.2321 a.u., respectively. The resulting phase shifts are given in table 1. The above mentioned procedure (Popovic *et al* [7]) does not converge sometimes, therefore, the calculation of induced charge density by including $V_{\text{ss}}(r)$ is done following the procedure of Manninen and Nieminen [15]. 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 tetrahedral site by putting $\delta n(r) = n_{\text{p}}(r)$, $Z = Z_{\text{p}}$,

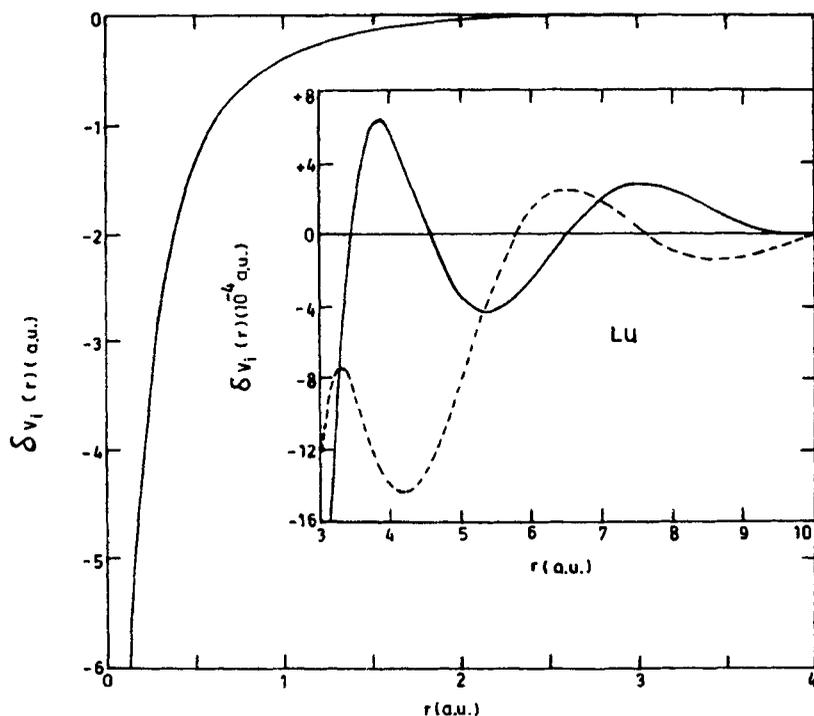


Figure 2. The proton induced self-consistent potential $\delta v_l(r)$ in α -Lu. The solid and dashed lines represent the results obtained by including $V_{\text{ss}}(r)$ and without including $V_{\text{ss}}(r)$, respectively, in jellium of α -Lu corresponding to electron density $n_0 = 3/4 \pi r_s^3$ and $r_s = 2.5166$ a.u. The two potentials overlap each other in the first graph.

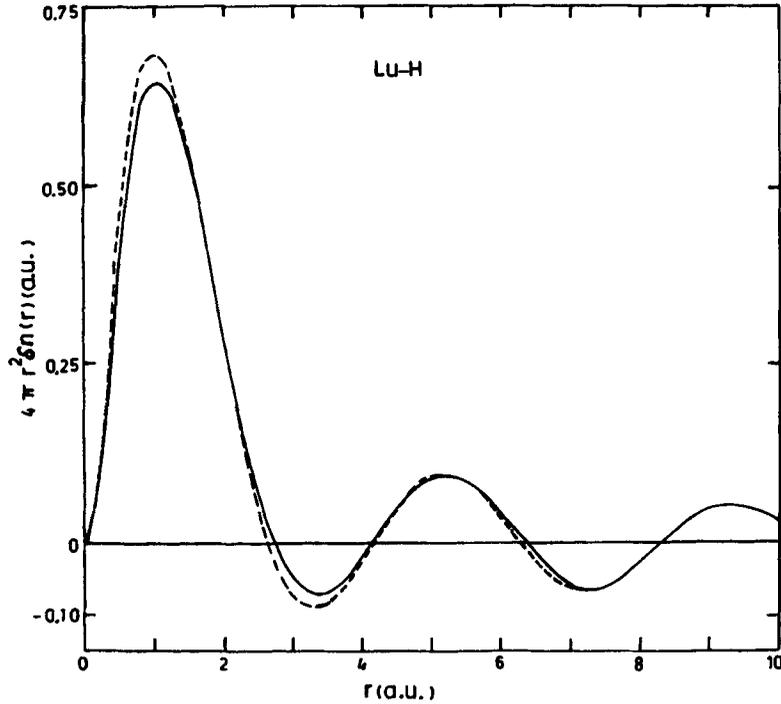


Figure 3. The proton induced charge density $4\pi r^2 \delta n_i(r)$ around tetrahedral site of α -Lu. The rest of the description is same as that of figure 2.

$\delta n(r) = n_p(r) - n_0$ and self-consistently calculated $V_p(r)$ and $\delta n_p(r)$ are obtained. In both the cases, the Friedel sum rule (7) is satisfied. The difference

$$\delta v_i(r) = V_p(r) - V_H(r), \quad (11)$$

and

$$\delta n_i(r) = \delta n_p(r) - \delta n_H(r) \quad (12)$$

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

The phase shifts obtained by using $\delta v_i(r)$ are given in table 1. The *s* and *p* phase shifts are found dominating. The magnitude of *s* phase shift increases by 5% by including $V_{ss}(r)$. This shows that $V_{ss}(r)$ contributes considerably to the impurity scattering at Fermi surface in lutetium matrix. The SSMP is included in the self-consistent calculation only up to $r = 9$ a.u. because of convergency reasons [15]. The impurity potentials obtained by including $V_{ss}(r)$ and by putting off $V_{ss}(r)$ are shown in figure 2 by solid and dashed lines, respectively. The two potentials overlap each other. They can be separated from each other by plotting them on magnified scale. The impurity potential is strongly attractive in the vicinity of the impurity. It exhibits Friedel [22] oscillations at large distance. The lattice contribution enhances the magnitude of impurity interaction near the center of the proton. This is very much clear from figure 3, where we have plotted the impurity induced charge distribution $4\pi r^2 \delta n(r)$ vs r . The introduction of

$V_{ss}(r)$ shifts the charge distribution away from the proton center and reduces the pile-up of the charge by about 10% in the vicinity of the proton.

3.3 Self-energy of proton

The value of $\delta v_i(r)$ obtained from (11) is fitted by least square method into the analytical form given by (10). The value of β so obtained is 1.7189 a.u. By solving Poisson equation using the analytical form given by (10) for δv_p , one can obtain the charge density

$$\delta n_i(r) = \frac{Z\beta^3}{8\pi} \exp(-\beta r). \quad (13)$$

This $\delta n_i(r)$ leads to the following impurity self-energy

$$\begin{aligned} E_{sc} &= \frac{1}{2} \int \delta v_i(r) \delta n(r) dr \\ &= -\frac{3}{32} Z^2 \beta \text{ a.u.} \end{aligned} \quad (14)$$

The self-energy of proton in lutetium matrix is found to be -0.322 Ryd.

3.4 Activation energy

The configurational energy is calculated by using $\delta n(r)$ and the analytical expression obtained in second order perturbation theory [4]. The configurational energy so calculated along O–O (octahedral), O–T (tetrahedral) and T–T directions in the (1120) plane is shown in figure 4. 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 40% distance of T–O path. The tetrahedral position is the most favourable position for hydrogen impurity to stay. The same conclusion has been drawn by neutron scattering analysis for $\text{LuH}_{0.19}$ in α phase [1]. Because T–T barrier height is about 95% of T–O barrier and O–O barrier height is less than 50% of T–T barrier height, therefore, probable path for proton diffusion in α -Lu matrix may be off-symmetry paths and not the O–O–T and O–T–T paths. The minimum barrier height by which an impurity can cross is called the activation energy. It is found to be 0.27 eV. The experimental [23] value of activation diffusion energy (E_{ac}) is 0.28 ± 0.02 eV. Here it is to be noted that good agreement of calculated activation energy with experimental value is obtained by taking ionicity of hydrogen as 1. This suggests that the proton exists in ionic state in α -Lu. The diffusion coefficient is proportional to Boltzmann factor $\exp(-E_{ac}/k_B T)$, where k_B is Boltzmann constant.

3.5 Residual resistivity

To test the reliability of our calculated phase shifts, the residual resistivity $\Delta\rho$ is estimated using the following expression for liquid phase of solid [24]:

$$\Delta\rho = \frac{2.732}{k_F Z_H} = \sum_{l=0}^{\infty} (l+1) \sin^2(\delta_l - \delta_{l+1}), \quad (15)$$

where k_F is in atomic units and $Z_H = 3$ for lutetium matrix. $\Delta\rho$ for dilute Lu–H system is calculated using the first seven phase shifts as the values of δ_l become too small for $l > 6$. The calculated value of $\Delta\rho$ obtained from jellium value of phase shifts is $1.00 \mu\Omega$

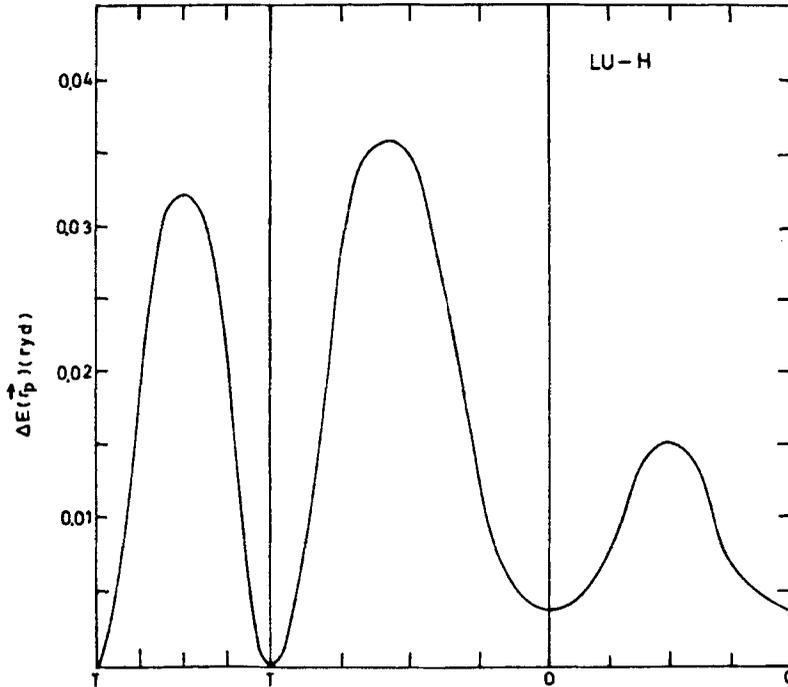


Figure 4. The configurational energy $\Delta E(r_p)$ of proton in α -Lu obtained by including $V_{ss}(r)$. r_p represents the position of proton with respect to O(T) site. Inset: O \rightarrow octahedral positions; X \rightarrow tetrahedral positions; O \rightarrow host ions.

cm/at%. The corresponding result for $\Delta\rho$ by including $V_{ss}(r)$, i.e., $1.02 \mu\Omega$ cm/at% is 2% higher. This value of $\Delta\rho$ agrees reasonably well with experimental values $(1.25 \pm 0.05) \mu\Omega$ cm/at% and $(1.70 \pm 0.10) \mu\Omega$ cm/at% reported by Daou and Bonnet [25] at 500°C and 25°C , respectively.

4. Conclusion

The induced charge density and impurity potential are calculated by including the effect of discrete lattice. Only the spherically symmetric part of the lattice potential is included. The Fermi surface is assumed essentially spherical and conduction electron wave functions are taken free particle-like. It is found that the SSMP changes the impurity scattering at Fermi surface significantly. The calculated configuration energy confirms the experimental [1] fact that hydrogen prefers T-sites over O-sites in Lu matrix. A very shallow *s*-type bound state of energy -0.00316 Ryd suggests that there is weak binding between proton and electron and that hydrogen does not form lutetium hydride solution and exists as a free ion in Lu matrix. The present calculations can be further improved by including crystal effects like relaxation effects, size effects in general and by taking proper account of *d* and *f* electrons in particular. In this respect, the present study is a step ahead in the process of understanding the Lu-H interactions. A careful calculations of KKR-Green

function method [26] may provide better results. However, this will involve heavy computational effects.

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