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Nonlinear, Self-Consistent Theory of Proton Screening in Metals Applied to Hydrogen in Al and Mg†

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The density-functional formalism has been used to treat self-consistently the nonlinear screening of a proton in an electron gas. The results have been used to calculate activation energies for diffusion of hydrogen in Al and Mg. The theory is in good agreement with experimental results which are only available for Al. Hydrogen-vacancy trapping has also been investigated and was found to be a distinct possibility in the case of Al.

Apart from notable exceptions such as Pd and Ta, the solubility of H_2 in most metals is very low; for instance Al and Mg near their melting points dissolve about 1 atomic ppm[1] and 700 atomic ppm,[2] respectively, of H_2 at atmospheric pressure. In spite of this, the behavior of a proton and the surrounding electronic structure in simple metals such as these are of considerable interest since the proton is the simplest impurity, being a point ion with no complicating core-electron structure. The hydrogen molecule dissociates upon dissolving and because of the small solubilities, the screened protons may be regarded as independent impurities. We present here calculations for Al and Mg of the energy of the metal for various positions of the proton. Self-consistent, nonlinear theory has been used to treat the screening of the proton, and the lattice was taken into account using first-order perturbation theory. The results indicate that the proton at the octahedral site in Al, rather than the tetrahedral site, gives a lower energy but that the proton at a vacant site leads to a much lower energy than either of these, implying a strong tendency for proton-vacancy trapping. In the case of Mg the octahedral and tetrahedral sites had indistinguishable energies but binding to a vacancy was not indicated. The activation energies for proton diffusion were estimated and the result for Al is in good agreement with experiment, which suggests that the method is reliable.

Since the pioneering work of Friedel[3] on the screening of a proton in the electron gas and the hydrogen heat of solution for Cu, little theoretical work on the properties of hydrogen in metals has been presented. Subsequent work has been limited in scope by the use of the Thomas-Fermi method or linear-response theory.

The electron-proton interaction potential is simply the Coulomb interaction $-e^2/r$. However the price paid for this simplicity is severe since there are many indications that this is a strong interaction, with the electrons responding in a very nonlinear manner to the presence of the proton. For instance the positron, much less massive, is a weaker perturbation of the electrons in metals because of its recoil; but in spite of this the positron annihilation rate in metals, which is proportional to the electron density at the position of the positron, is substantially larger than first-order perturbation theory indicates (×1.5 for Al, ×5 for Na[4]). Furthermore, nonlinear-response calculations[5] of the electron density around a positron and a heavy point ion with charge $-e$ both indicate that linear-response theory is grossly in error. This implies that unlike a pseudoion, the proton scatters electrons very strongly and its effect cannot be estimated adequately by using low-order perturbation theory.

The calculations reported here have been performed in two stages: First of all the displaced electron density $\Delta n(\vec{r})$ around a proton in "jellium" of the appropriate mean electron density n_0 has been calculated; then the effect of the ions has been estimated to first order in perturbation theory using a local pseudopotential for the electron-ion interaction.

The calculation of $\Delta n(\vec{r})$ is based on the density-functional formalism of Hohenberg and Kohn[6] and Kohn and Sham.[7] A local, single-particle potential, $V_{\text{eff}}(\vec{r})$, is used to generate a set of single-particle wave functions $\psi_i(\vec{r})$ from the Schrödinger equation,

$$[-(\hbar^2/2m)\nabla^2 + V_{\text{eff}}(\vec{r})]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}). \qquad (1)$$

The exact ground-state density is given in principle by

$$n(\vec{r}) = \sum_{\epsilon_i<\mu} |\psi_i(\vec{r})|^2, \qquad (2)$$

where μ is the electron chemical potential. In practice approximations are involved because of an incomplete knowledge of the form of V_{eff}. The approximate procedure for dealing with exchange and correlation proposed by Kohn and Sham[7] has been adopted with V_{eff} given by

$$V_{\text{eff}}(\vec{r}) = -\frac{e^2}{r} + e^2\int d^3r' \frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \mu_{\text{xc}}(n(\vec{r})). \qquad (3)$$

The first two terms of Eq. (3) constitute the electrostatic Hartree potential. The last term accounts for exchange and correlation by approximating the electron gas locally by a uniform gas of mean density $n(\vec{r})$, where $\mu_{\text{xc}}(n_0)$ is the exchange-correlation part of the chemical potential for the uniform interacting electron gas of mean density n_0. This approximation, valid for slowly varying densities, will be poor near the proton. However, in this region V_{eff} will be dominated by the Hartree potential $\sim -e^2/r$. In the actual calculations the parametrized form of the results of Singwi *et al.*[8] proposed by Hedin and Lundquist[9] was used for $\mu_{\text{xc}}(n_0)$.

The effective potential is a function of the density and so Eqs. (1)-(3) must be solved self-consistently. Approximate self-consistency was achieved by taking a trial potential, $-e^2\exp(-\alpha \times r^\beta)/r$, and choosing the constants α and β so that the correct amount of charge was displaced by the trial potential and also so that the density generated from that potential yielded, through Eq. (3), a potential which again displaced the correct amount of charge. The Schrödinger equation (1) was solved numerically by integrating the radial wave equation for seven partial waves and the displaced charge was calculated from the Friedel sum rule.[3]

The displaced density around a proton in "jellium" of density corresponding to Al is illustrated in Fig. 1. So far as we are aware this is the first time that realistic results of this type have been presented. For comparison, $\Delta n(\vec{r})$ calculated to first order in the electron-proton interaction by using the dielectric function of Singwi *et al.*[8] is also shown. Two points are noteworthy. Linear-response theory grossly underestimates the pileup of electrons near to the proton. This is not surprising in view of the results of earlier calculations of the electron density around a positron. Furthermore, linear-response theory predicts zero-phase Friedel charge-density oscillations of the form $\cos(2k_{\text{F}}r)/r^3$; the proper treatment of the strong potential near the proton leads to a roughly 90° shift in phase of the oscillations. The interaction of the electron screening cloud with the surrounding ions depends critically on

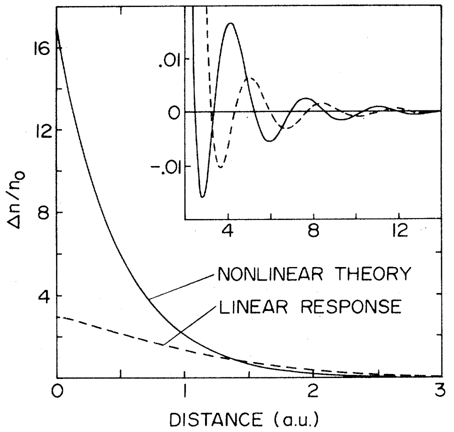

FIG. 1. Displaced electron density, $\Delta n(\vec{r})$, divided by mean density, n_0, plotted against r for a proton in an electron gas of mean density corresponding to Al ($r_s = 2.06$ a.u.). The full line was calculated by using nonlinear-response theory, the broken line, by using linear-response theory.

the phase of the oscillations in $\Delta n(\vec{r})$. The electron pileup near the proton and the shift in phase of the oscillations are very similar for Mg.

To first order in the bare electron-ion pseudopotential, $w(\vec{r})$, the portion of the total energy which depends on the relative positions of the proton at $\vec{\rho}_{\mathrm{H}}$ and the ions at $\vec{R}_n$ is

$$E(\vec{\rho}_{\mathrm{H}}) = \sum_n \frac{Ze^2}{|\vec{\rho}_{\mathrm{H}} - \vec{R}_n|} + \sum_n \int d^3r\, \Delta n(\vec{r} - \vec{\rho}_{\mathrm{H}}) w(\vec{r} - \vec{R}_n). \quad (4)$$

The first term is the proton-ion interaction energy, while the second takes account of the interaction between the ions and the electron screening cloud. Following the work of Ho[10] and Popovic, Carbotte, and Piercy[11] on the vacancy formation energy, a local pseudopotential of the Heine-Abarenkov form was taken for $w(\vec{r})$. The depth of the potential in the core and the core radius were chosen to give the observed equilibrium lattice constant and the binding energy. In Eq. (4), the positions of the ions surrounding the proton were taken to be the unrelaxed lattice points. The added complication of calculating the relaxations of the surrounding ion positions was deemed unnecessary in view of the small relaxation-energy contribution (about 3%) to the vacancy formation calculated previously[11,12] for these metals by using lattice-statics techniques.

The energy $E(\vec{\rho}_{\mathrm{H}})$ has been calculated by using Eq. (4) for various positions of the proton.[13] In the case of Al, the energy has been calculated for $\vec{\rho}_{\mathrm{H}}$ lying on a straight line joining the octahedral and tetrahedral positions. The energy barrier for the octahedral-tetrahedral jump was found to be 0.41 eV in good agreement with the most recent measurements of the activation energy for diffusion: 0.52 eV[14] and 0.47 eV.[15] The energy at the octahedral site was slightly lower than that at the tetrahedral site by 0.14 eV suggesting that hydrogen in Al favors the octahedral interstitial site. The energy when the proton resides in a vacancy, i.e., acting as a substitutional impurity, was also calculated and it was found to be 1.23 eV lower than the energy at the octahedral site. In the case of Mg there are two possibilities for diffusion. For the first one, when the proton jumps directly from one to a neighboring octahedral site (in the direction of the c axis), an activation energy of 0.34 eV was obtained. For the second possibility, when the proton jumps first to the tetrahedral site, a lower activation energy, 0.28 eV, was obtained. Unfortunately there are no experimental results to compare with for Mg. However, such low activation energies would indicate fast diffusion, which may account for some unsuccessful attempts to quench hydrogen in high-purity Mg.[16]

Hitherto, hydrogen in Al has generally been regarded to be an interstitial impurity. The results presented above imply that 1.23 eV of energy will be liberated if an interstitial proton in Al can locate and occupy an existing vacancy, the proton being then relatively immobile. Furthermore, the heat of solution for substitutional hydrogen would be less than that for interstitial hydrogen by the amount $1.23 - 0.66$ eV $= 0.57$ eV, where the value 0.66 eV[17] has been taken for the vacancy formation energy. Inevitably there are uncertainties in the calculations and these are difficult to assess quantitatively; nevertheless this result should be regarded as a strong indication of the presence of some substitutional hydrogen in Al.

The trapping of positively charged impurity particles by vacancies in metals is not a new phenomenon. It is well established[18] that positrons are trapped at vacancies in many metals (the positron-vacancy binding energy for Al is about twice that for Mg; theoretical estimates[19] are about 2 eV and 0.9 eV, respectively). Positron trapping in metals is not restricted to vacancies; trapping at dislocations and voids has also been reported. In fact any region of substantially lower-than-average ion density would appear to trap positrons. The results above suggest that a proton in Al also prefers to reside far from the ions. Although a direct parallel cannot be drawn between the proton and the positron because of the latter's small mass and large zero-point energy in consequence, a careful investigation would seem to be indicated of the possibility of hydrogen being trapped at vacancies in those metals in which positrons are strongly trapped by vacancies, e.g., Al, Ni, Zn, Cu, Ag, and Au. In addition to positron-vacancy trapping, the trapping of He by vacancies in Ni has also been reported.[20]

There has recently been some interest in the behavior of positively charged μ mesons in solids. The muon with a mass of about 200 electron masses has been assumed to reside at interstitial positions in metals and through its mode of decay information on the local hyperfine field is obtained.[21] The muon should diffuse more rapidly than the proton but the energy for different positions should be very similar. Consequently, the possibility that the positively charged muons are trapped at vacancies in metals should be investigated; the metallurgical state of the samples could be very important.

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