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Heat of solution of hydrogen in Al and Mg†

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Electron charge distribution around a proton in Al and Mg has been calculated self-consistently using the Kohn-Sham density functional formalism. The exchange-correlation potential has been treated both in the local-density approximation and including the first gradient correction. The results are used to compute the heat of solution of hydrogen in Al and Mg. Comparison has been made with earlier theoretical and experimental values.

Heat of solution of hydrogen is defined as the energy of a hydrogen atom dissolved in a metal minus the energy per hydrogen atom in a hydrogen molecule. Freidel[1] first treated this problem by solving a set of single-particle Schrödinger equations self-consistently in copper. More recently, Popovic *et al.*[2] have theoretically estimated the heat of solution in Al and Mg, using their nearly self-consistent electron densities calculated within the Hohenberg-Kohn-Sham[3] (HKS) formalism in the local-density approximation. They have obtained 0.45 and −0.05 eV as the respective heats of solution for Al and Mg, which compare favorably with the corresponding experimental results 0.65 and 0.25 eV.

The purpose of this paper is twofold: First, one would like to know how the heat of solution would change if one were to use *fully self-consistent* electron densities (obtained to a high degree of accuracy) in the local-density approximation, since the theoretical[2] heat of solution in Mg not only disagrees with experiment in magnitude but is of the wrong sign. Second, the influence of the gradient correction to exchange-correlation energy on the heat of solution has never been reported before.

We have closely followed the procedure of Popovic *et al.*[2] In calculating the nonlinear electron density around a proton, we have not considered the effect of periodic arrangements of ions (the calculation is done in the jellium approximation). Thus, our results are only meaningful for simple metals where band structure effects are negligible. The heat of solution can be written

$$\Delta H = 15.86 + \Delta H_{e\text{-}p}\ \text{eV}\,. \tag{1}$$

The first term in Eq. (1) is equal to the sum of the ionization energy of a hydrogen atom (13.6 eV) and the dissociation energy of a hydrogen molecule (2.26 eV). The second term is the change in energy of an electron and a proton in the solid as compared to that in vacuum. Following Popovic *et al.*[2] $\Delta H_{e\text{-}p}$ can be expressed as,

$$\Delta H_{e\text{-}p} = \Delta H_1 + \Delta H_2\,, \tag{2}$$

where the contribution ΔH_1 depends only on the properties of the perfect crystal. This has been evaluated by Popovic *et al.*[2] for Al and Mg in the linear-response theory using the Heine-Aberenkov form for the electron-ion pseudopotential. The term ΔH_2 depends on the nonlinear response of the electrons to the presence of a proton and is expressed

$$\Delta H_2 = \sum_{q\neq 0} S(\vec{q})W(\vec{q})\Delta n(\vec{q}) + E_{\text{corr}}\,, \tag{3}$$

where $S(\vec{q})$ is the lattice structure factor and $W(\vec{q})$ is the bare-ion pseudopotential of the host lattice. $\Delta n(\vec{q})$ is the Fourier transform of the displaced charge density $\Delta n(\vec{r}) = n(\vec{r}) - n_0$ around the proton

$$\Delta n(\vec{q}) = \int_0^\infty dr\, 4\pi r^2 \Delta n(\vec{r}) j_0(qr)\,. \tag{4}$$

The first term in Eq. (3) can be viewed as the interaction energy between the electron-screening charge around the proton and the lattice ions. Thus the magnitude and phase of the Friedel oscillations in the displaced charge density play an important role in the determination of this contribution. The second term in Eq. (3), E_{corr}, is the electron-proton correlation energy and can be calculated using Feynman-Hellman theorem

$$E_{\text{corr}} = \int_0^1 \frac{dZ}{Z} V_{\text{int}}(Z)\,, \tag{5}$$

with $V_{\text{int}}(Z)$ as the interaction energy between the electron and a fictitious point charge Ze (the value of which lies between 0 and 1),

$$V_{\mathrm{int}}(Z) = -e^2 \int d^3r \frac{Z}{r} \Delta n(Z,r), \qquad (6)$$

where $\Delta n(Z,r)$ is the displaced charge density around a heavy point impurity carrying a charge Ze and needs to be evaluated for $0 \leq Z \leq 1$ using a nonlinear response theory. Popovic *et al.*[2] have evaluated $\Delta n(Z,r)$ in a nearly self-consistent way by using the density functional formalism of Hohenberg-Kohn-Sham[3] and by treating the exchange-correlation energy in the local-density approximation. Our result differs from that of Popovic *et al.*[2] only in that we have evaluated Δn $\Delta n(Z,r)$ self-consistently to an accuracy of about 0.1% using for the exchange-correlation energy per particle the result of Vashishta and Singwi[4] in both local density and using first gradient contribution. Our result for the heat of solution in the local-density approximation differs appreciably from that of Popovic *et al.*[2] This discrepancy is due to the sensitivity of the heat of solution to the value of $\Delta n(Z,r)$ since ΔH in Eq. (1) is a result of cancellation of two large numbers. In what follows, it is emphasized that an accurate knowledge of the displaced electron density around a proton is necessary.

Using the procedure outlined in our earlier publication,[5] we have calculated $n(r)$ for $Z = 0.25$, 0.5, 0.75, and 1 for $r_s = 2.07$(Al) and $r_s = 2.64$(Mg) in local-density approximation and using the first gradient correction to exchange-correlation energy. All our charge densities are self-consistent to an accuracy of about 0.1%. Since the charge density for $Z = 1$ corresponds to a proton in a jellium and determines the interaction energy of the screening electron with the lattice ions, we have compared the local density result with that of the gradient correction for Mg in Fig. 1. The results for Al are similar. The Friedel oscillations are exhibited on a magnified scale since these are important in the calculation of the electron-ion interaction energy. Note that there is a noticeable change in the phase of the oscillations and that the magnitude of the Friedel oscillations using first-gradient expansion is bigger than the corresponding local-density result, which in turn is a reflection of a larger pile up of electrons on the proton site.

In calculating the contribution to the heat of solution in Eq. (1), we have taken for ΔH_1 (which depends upon the properties of perfect crystal) the values of Popovic *et al.*[2] for Al and Mg. The nonlinear contribution to the heat of solution ΔH_2 in Eq. (3) is evaluated as follows. For the computation of the electron-proton correlation energy, Eq. (5) is used with $\Delta n(Z,r)$ computed for $Z = 0.25$, 0.5, 0.75, and 1.0. Our results in the local-density approximation and including the gradient correction are listed in Table I for both Al and Mg. It is appropriate to compare our local-density result with that of Popovic *et al.*[2] who used "approximately self-consistent" charge densities. In

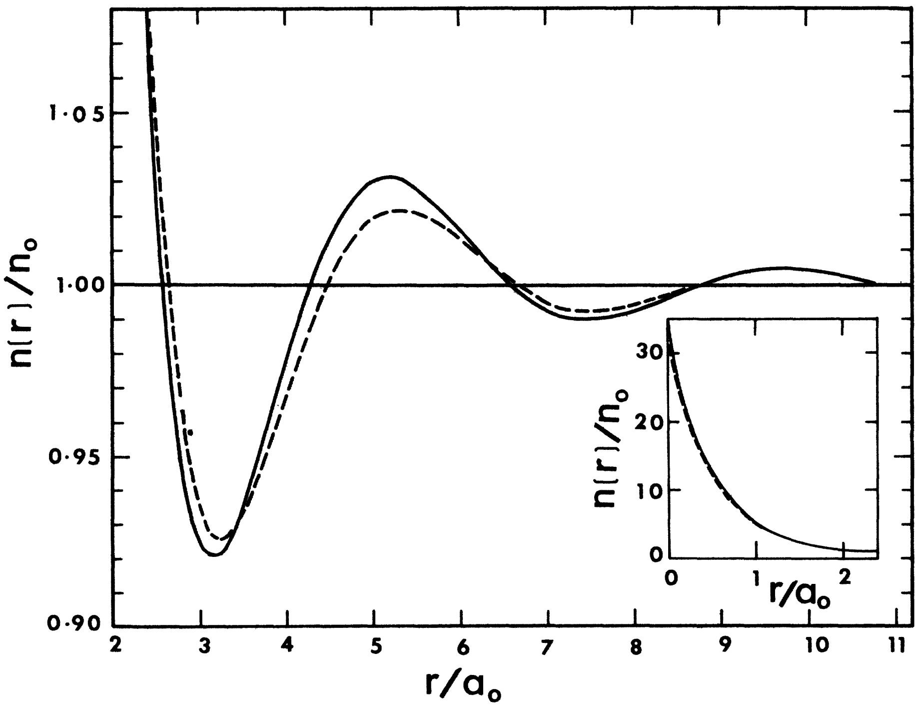

FIG. 1. Electron-charge density distribution around a proton in Mg. The dashed curve corresponds to local-density approxmation while the solid curve is obtained by including first-gradient correction to exchange-correlation energy. The indent exhibits the charge distribution around a proton for $r < 3a_0$.

TABLE I. Heat of solution ΔH of hydrogen in Al and Mg.

		Al	Mg
ΔH_1 (eV) [a]		-4.00	-3.62
in local density approximation	E_{corr} (eV)	-14.40	-13.44
	ΔH_2(eV)	-11.22	-11.97
	ΔH_{theor}(eV)	$+0.64$	$+0.26$
	ΔH_{expt} (eV)	$+0.65$ [b]	$+0.25$ [c]
with gradient correction	E_{corr}(eV)	-14.22	-13.37
	ΔH_2(eV)	-11.06	-11.83
	ΔH_{theor} (eV)	$+0.80$	$+0.41$
	ΔH_{expt}(eV)	$+0.65$ [b]	$+0.25$ [c]

[a] Reference 2.

[b] W. Eichenauer, Z. Metallkd. 59, 613 (1968).

[c] Z. D. Popovic and G. R. Piercy (unpublished, quoted in Ref. 2).

Al, our result for the correlation energy (−14.40 eV) is 0.2 eV more negative than theirs (−14.20 eV), while in Mg our result of E_{corr} is 0.10 eV more positive than theirs. Although this discrepancy amounts to less than 2% correction, it is a large factor compared to the experimental heat of solution (0.65 eV for Al and 0.25 eV for Mg. Similarly, our result for the electron-ion interaction term, ΔH_2 in Eq. (3) (listed in Table I) also differs from that of Popovic *et al.*[2] This is because of the fact that the amplitudes of the Friedel oscillation in our fully self-consistent calculation are somewhat larger than those in the calculation of Popovic *et al.*[2] Combining the contributions ΔH_1 and ΔH_2, we obtain the heats of solution of hydrogen in Al and Mg in the local density approximation to be 0.64 and 0.26 eV, respectively. These compare well with experimental values of 0.65 and 0.25 eV for Al and Mg, respectively. The corresponding values of Popovic *et al.*[2] for Al and Mg are 0.45 and −0.05 eV.

The discrepancy between the present values for the heats of solution and those of Popovic *et al.*[2] could be due to two reasons: (a) Our calculation of the electron density is fully self-consistent, whereas that of Popovic *et al.* is approximately self-consistent. (b) We have used for the exchange-correlation energy the form given by Vashista and Singwi,[4] while Popovic *et al.* have used the values given by Hedin and Lundqvist.[6] Recently, Zaremba *et al.*[7] have also done a fully self-consistent calculation using the Hedin-Lundquist values. The difference of 0.28 and 0.08 eV in E_{corr} for Al and Mg, respectively, between the values of Zaremba *et al.* and Popovic *et al.* has to be due to the use of approximate self-consistent charge densities in the latter calculation. The corresponding difference of 0.09 and 0.17 eV between our calculation and that of Zaremba *et al.* should be attributed to the use of different forms of exchange-correlation potential. In order to assess the accuracy in our calculated numbers for the heat of solution, we have repeated the computation by taking charge densities of the last two successive interations (ninth and tenth iteration in our case). We find that our results are accurate to only the first place of decimal. The striking agreement between theory and experiment should be treated with caution in the light of what follows. One element of uncertainty is in the choice of the electron-ion pseudopotential that enters into the calculation of both ΔH_1 and ΔH_2. We have used the same Heine-Aberenkov-type model potentials for Al and Mg as Popovic *et al.*[2] did.

Calculations of the two contributions to ΔH_2 were also carried out for Al and Mg using the gradient correction to the exchange-correlation potential. Results are quoted in Table I. The electron-proton correlation energies for both Al and Mg are found to be slightly more positive than the corresponding local-density result. The electron-ion interaction energies are also slightly different. Our calculated heats of solution using gradient expansion are 0.80 and 0.41 eV for Al and Mg, respectively. Thus it is seen that the gradient correction worsens the agreement with experiment. While the first-gradient correction is known to overestimate the effect, the inclusion of higher gradients in the expansion of the exchange-correlation energy is not expected to improve the agreement between theory and experiment substantially.

From this we draw the following conclusions: (a) The heat of solution of hydrogen depends quite sensitively on the nature of the nonlinear electron distribution around the proton. In order to assess the success of a given model, it is necessary to demand a high accuracy in the electron-charge density and the form of exchange-correlation potential for a homogeneous electron gas. Jellium approximation with local density formulation of the HKS theory gives a reasonable description of the heat of solution of hydrogen in simple metals. (b) While the inclusion of the gradient correction in the exchange-correlation energy destroys the remarkably good agreement between theory and experiment, heat of solution of hydrogen in a simple metal can still be understood, at least semiquantitatively, from first principle calculations.

No calculation of the heat of solution is yet available in which the effect of the periodic arrangement of ions on the electron-screening cloud has been taken into account. Undoubtedly, both the contributions to ΔH_2 will be modified. One can take this effect into account in an approximate way in a spherical solid model where the effects of ions lying at a fixed distance from the proton is angular averaged. However, such a calculation would still be considered semiquantitative, since the accuracy of a spherical solid model has not been adequately established. A convincing way of carrying out a quantitative calculation of the heat of solution is to treat dilute hydrogen in a metal as forming a superlattice (with proton at the center surrounded by enough host ions so that hydrogen-hydrogen interactions could be neglected) and the self-consistency imposed through the HKS[3] procedure. Obviously, this is an enormous task, but the availability of high-speed computers provides room for optimism.

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