Heat of solution of hydrogen in aluminum

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The interaction of a proton with an aluminum host is treated within the spherical model of a solid. Our results give for the heat of solution and activation energy of H in Al 0.593 and 0.5 eV, respectively, compared with the experimental values of 0.66 and 0.52 eV. The previously untreated nonspherical corrections are also estimated and shown to be small.

I. INTRODUCTION

The interaction of hydrogen with its metallic host has been given wide attention in many recent publications. Primarily two different regions, with distinct theoretical emphasis, have been examined. The region of high concentration of hydrogen has generally been treated via a band-structure approach[1-4] and applied to nonsimple metals like palladium which can dissolve large quantities of hydrogen. The region of low concentration has been largely treated from a proton-jellium interaction and applied to simple metals like aluminum[5-10] which can dissolve only small quantities of hydrogen. It is the second problem we wish to treat in this paper. The small amount of hydrogen dissolved in most metals does not make this problem without practical interest. For example, the formation of hydrogen gas bubbles upon solidification is just one example of the need for a microscopic treatment of hydrogen-metal interaction. From a theoretical point of view the simplicity of a proton embedded in an almost uniform electron gas makes it potentially a candidate for yet finer understanding of electron impurity interactions.

In Sec. II we introduce the general form for the heat of solution of an arbitrary impurity. We then evaluate this energy within the spherical solid model of H in an Al host. In Sec. III we estimate the yet untreated nonspherical corrections and show them to be very small.

II. HEAT OF SOLUTION WITHIN THE SPHERICAL SOLID MODEL

Consider a collection of N ions (positioned at points $\vec{R}_i$) and ZN electrons in which we embed an impurity of nuclear charge $+Z_1 e$ (at point $\vec{r}_1$) with its equal number of Z_1 electrons. The heat of solution ΔH is defined as the difference between the energy of this configuration and the one where the neutral impurity is removed to infinity. This energy ΔH can be readily written as

$$\Delta H = \Delta H_0 + \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 \tag{1}$$

with

$$\Delta H_1 = \sum_{i=1}^{ZN} \epsilon_i^1 - \epsilon_i^0 \ . \tag{1a}$$

$$\Delta H_2 = Z_1 \epsilon_{ZN}^0 \ . \tag{1b}$$

$$\Delta H_3 = \sum_{c=1}^{Z_c} \epsilon_c \ . \tag{1c}$$

$$\Delta H_4 = -\frac{e^2}{2} \int d^3r \int d^3r' \{ [n_1(\vec{r}') - n_0(\vec{r}')][n_1(\vec{r}) - n_0(\vec{r})] + [n_1(\vec{r}') - n_0(\vec{r}')][n_0(\vec{r}) - n_0] \}/|\vec{r} - \vec{r}'| \ . \tag{1d}$$

$$\Delta H_5 = E_{xc}(n_1(\vec{r})) - E_{xc}(n_0(\vec{r})) - \int d^3r [v_{xc}(n_1(\vec{r}))n_1(\vec{r}) - v_{xc}(n_0(\vec{r}))n_0(\vec{r})] \ . \tag{1e}$$

$$\Delta H_6 = Z_1 Z e^2 \sum_{i=1}^{N} \frac{1}{|\vec{r}_1 - \vec{R}_i|} - Z_1 e^2 \int \frac{d^3r n_0}{|\vec{r}_1 - \vec{r}|} \ . \tag{1f}$$

In Eqs. (1a)–(1f) $E_{xc}(n(\vec{r}))$ is the exchange and correlation functional,[11,12] v_{xc} the functional derivative $\delta E_{xc}/\delta n$, ϵ_c the binding energy of the Z_c bound states (if any), n_0 the uniform density of the ZN electrons in volume Ω_0, and $n_1(\vec{r})$ is the electron density of the $ZN + Z_1$ electrons in the presence of the impurity and N ions. It is given as the solution of the self-consistent equation[10]

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

where

$$V_{\text{eff}}(\vec{r}) = v_1(\vec{r}) + V_0(\vec{r})$$
$$+ e^2 \int d^3r' \frac{n_1(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{xc}(n_1(\vec{r})) \quad (3)$$

with $v_1(\vec{r}) = -Z_1 e^2/|\vec{r} - \vec{r}_1|$, $V_0(\vec{r})$ the ionic potential, and

$$n_1(\vec{r}) = \sum_{i=1}^{ZN+Z_1} \psi_i^{1*}(\vec{r})\psi_i^1(\vec{r}) \quad . \quad (4)$$

The density $n_0(\vec{r})$ is similarly given by

$$n_0(\vec{r}) = \sum_{i=1}^{ZN} \psi_i^{0*}(\vec{r})\psi_i^0(\vec{r}) \quad , \quad (5)$$

where $\psi_i^0(\vec{r})$ and ϵ_i^0 satisfy the same Eq. (2) without $v_1(\vec{r})$ and with $n_1(\vec{r})$ replaced by $n_0(\vec{r})$. The term ΔH_0 is the negative of the energy of the neutral impurity (or equivalent atom) in its molecular state. For example, in the case of a proton which combines to form a hydrogen molecule $\Delta H_0 = 15.86$ eV, and includes the ionization energy of the H atom (1 Ry) and the additional dissociation energy of the molecule (2.28 eV per atom). The last term ΔH_6 is the Madelung energy of the impurity at position $\vec{r}_1$ which can be easily calculated for any arbitrary configuration of ions.

We therefore turn next to Eqs. (1a)–(1e) with a brief discussion. Let us first assume that Eqs. (2)–(4) have been solved exactly for $n_0(\vec{r})$, $n_1(\vec{r})$, ϵ_i^0, and ϵ_i^1 and consequently for ΔH. The density $n_0(\vec{r})$ and $n_1(\vec{r})$ differ from each other (to any relevant extent) in a localized region (of volume Ω_1) around the impurity and from charge neutrality $\int_{\Omega_1} d^3r [n_1(\vec{r}) - n_0(\vec{r})] \approx Z_1$. The terms in Eq. (1)

which depend explicitly on the density (i.e., ΔH_4 and ΔH_5) can therefore be evaluated within such a finite volume. The other two terms ΔH_1 and ΔH_3 are also a consequence of the change introduced by the local environment at the impurity. On the other hand ΔH_2, which is the eigenvalue of Eq. (2) for the highest occupied state, is clearly *not* a *locally* determined quantity; we will therefore treat this contribution separately.

Before we proceed to the treatment of ΔH within the spherical model it is instructive to reduce Eq. (1) to the well-known linear response form[6] where ΔH is calculated only to second order in $V_0(\vec{r}) + v_1(\vec{r})$. We write $n_1(\vec{r}) = \Delta n_1(\vec{r}) + n_0(\vec{r})$ and $n_0(\vec{r})$ $= \Delta n_0(\vec{r}) + n_0$ [recall $\int d^3r \Delta n_1(\vec{r}) = Z_1$ and $\int d^3r \Delta n_0(\vec{r}) = 0$]. We need to know $\Delta n_1(\vec{r})$ only to linear order in $V_0(\vec{r})$ and $v_1(\vec{r})$, and in momentum space these are given by the well-known linear-response forms,[6] i.e.,

$$\Delta n_0(\vec{q}) = -\frac{\pi_0(\vec{q})}{\epsilon(\vec{q})} V_0(\vec{q})$$

and

$$\Delta n_1(\vec{q}) = -\frac{\pi_0(\vec{q})}{\epsilon(\vec{q})} v_1(\vec{q}) \quad (6)$$

with $\pi_0(q)$ the noninteracting Lindhard static[13] response function and $\epsilon(q)$ the full static dielectric function[6]

$$\epsilon(q) = 1 + [(4\pi e^2/q^2) + G_{xc}(q)]\pi_0(q) \quad .$$

The function $G_{xc}(q)$ is the momentum representation for the linear expansion of $v_{xc}(n(\vec{r}))$, i.e.,

$$v_{xc}(n(\vec{r})) \approx v_{xc}(n_0) + \int d^3r' G_{xc}(n_0, \vec{r} - \vec{r}')\Delta n(\vec{r}') \quad . \quad (7)$$

Return to Eqs. (2) and (3) and expand

$$V_{\text{eff}}(\vec{r}) = \bar{V} + \Delta V(\vec{r}) \quad , \quad (8)$$

where

$$\bar{V} = \frac{1}{\Omega_0}\left[\int_{\Omega_0} d^3r\left(V_0(\vec{r}) + e^2 \int \frac{d^3r' n_0}{|\vec{r} - \vec{r}'|}\right)\right] + v_{xc}(n_0) \quad (9)$$

and

$$\Delta V(\vec{r}) = v_1(\vec{r}) + V_0(\vec{r}) + \int d^3r'\left[\left(\frac{e^2}{|\vec{r} - \vec{r}'|} + G_{xc}(n_0, \vec{r} - \vec{r}')\right)[\Delta n_0(\vec{r}') + \Delta n_1(\vec{r}')]\right.$$

$$+ \frac{1}{2}\left(\int d^3r'' K_{xc}(n_0, \vec{r} - \vec{r}', \vec{r} - \vec{r}'', \vec{r}' - \vec{r}'')[\Delta n_0(\vec{r}') + \Delta n_1(\vec{r}')]\right.$$

$$\left.\left. \times [\Delta n_0(\vec{r}'') + \Delta n_1(\vec{r}'')]\right)\right] \quad , \quad (10)$$

where in $V_0(\vec{r})$ the uniform part has been separated and included in Eq. (9).

Using Eqs. (1)−(10), the relation

$$\int d^3r'' K_{xc}(n_0, \vec{r} - \vec{r}', \vec{r} - \vec{r}'', \vec{r}' - \vec{r}'')$$

$$= \frac{\partial}{\partial n_0} G_{xc}(n_0, \vec{r} - \vec{r}')$$

and taking a careful account of the extra electrons introduced by the impurity through $\Delta n_1(\vec{r})$ in Eq. (10) the following expression for ΔH in linear response can be derived:

$$\Delta H_1 + \Delta H_4 + \Delta H_5$$

$$= -\frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \frac{\pi_0(q)}{\epsilon(q)} \{ [v_1(q)]^2 + 2v_1(q)V_0(q) \}$$

$$\tag{11}$$

and

$$\Delta H_2 = Z_1 \left[\frac{\hbar^2 k_F^2}{2m} + \bar{V} \right]$$

$$+ \frac{Z_1}{\Omega_0} \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \left| \frac{V_0(q)}{\epsilon(q)} \right|^2$$

$$\times \left[\frac{\partial G_{xc}(q)\pi_0^2(q)}{\partial n_0} - \frac{\partial \pi_0(q)}{\partial n_0} \right] , \tag{12}$$

and in linear response the potential $v_1(\vec{r})$ cannot support any bound states so $\Delta H_3 = 0$. Now if the potential of a single ion is $w(\vec{r})$ then $V_0(\vec{r})$ $= \sum_{i=1}^{N} w(\vec{r} - \vec{R}_i)$ and $V_0(\vec{q}) = w(\vec{q})S(\vec{q})$ with $S(\vec{q}) = \sum_{i=1}^{N} e^{i\vec{q}\cdot\vec{R}_i}$. Combining Eqs. (11) and (12) yields the well-known form for ΔH in linear response.[6] We again make the observation that, unlike Eq. (11), ΔH_2 depends on the whole collection of ions and not on the local behavior around the impurity.

The lowest-order form of Eqs. (11) and (12) would be adequate for evaluating ΔH if the potentials of the impurity and the ions were weak. Our interest here is, however, in a proton impurity where such an approximation is known not to apply.[5,14] We therefore return to Eqs. (2)−(4) and make the following approximation. We center our coordinates at the proton site $(\vec{r}_1)$ and approximate the ionic potential $V_0(\vec{r})$ around the proton by only its spherical component (angular momentum quantum numbers $l = 0$ and $m = 0$) $V_0^{l=0,m=0}(r)$, i.e., the spherical solid model.[15] Equation (2) reduces now to a one-dimensional radial equation for the radial wave functions $R_{l,k}(r)$. In atomic units (a.u.) it is

$$\left[-\frac{1}{2} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{l(l+1)}{2r^2} + V_{\text{eff}}^{0,0}(r) \right] R_{l,k}(r)$$

$$= \epsilon_k R_{l,k}(r) \tag{13}$$

and

$$\Delta n_1(r) = \frac{1}{\pi^2} \int_0^{k_F} dk\, k^2 \sum_{l=0}^{\infty} (2l+1)\{ [R_{l,k}(r)]^2 - j_l^2(kr) \}$$

$$+ \sum_{c=1}^{l_c} [R_c(r)]^2 . \tag{14}$$

where $R_c(r)$ is the radial wave function for the bound states (if any). Finally the asymptotic form of $R_{l,k}(r)$ outside the volume Ω_1 is given by

$$R_{l,k}(r) = \cos[\delta_l(k)] j_l(kr) - \sin[\delta_l(k)] n_l(kr) . \tag{15}$$

where δ_l are the phase shifts and j_l and n_l the spherical Bessel and Neuman functions.

For the aluminum host the full ionic potential $w(r)$ is replaced by a pseudopotential of the smooth Heine-Abarenkov form[16]

$$w(q) = -\frac{4\pi Ze^2}{q^2} \left[\frac{D \sin qR_c}{qR_c} + (1 - D) \cos qR_c \right] e^{-(q/q_0)^2}$$

$$\tag{16}$$

with $Z = 3$. The core R_c was chosen equal to $R_c = 1.09$ (a.u.), the well depth D was set equal to 0 and the damping parameter is $q_0 = 5.5 k_F$.[17] The spherical component of $V_0(\vec{r})$ is given by

$$V_0^{0,0}(r) = \int \frac{d^3q}{(2\pi)^3} \frac{\sin qr}{qr} w(q) e^{i\vec{q}\cdot\vec{r}} |S(\vec{q}) . \tag{17}$$

[In Eq. (17) we remove the $\vec{q} = 0$ component.] The exchange and correlation potential $v_{xc}(\vec{r})$ is calculated in the local density approximation[11]

$$v_{xc}(\vec{r}) \approx \frac{d}{dn} [n(\vec{r})\epsilon_{xc}(n(\vec{r}))]$$

by the Wigner interpolation formula. The spherical radial functions and corresponding densities $n_1(r)$ and $n_0(r)$ are calculated by solving Eq. (13) to self-consistency[17,18] with and without the proton potential $[v_1(r)$ in Eq. (3)], respectively. With these two densities the contributions of ΔH_4 and ΔH_5 are numerically integrated. The term ΔH_1 is given, in this spherical model, in terms of the phase shifts.[19] In a.u. it is

$$\Delta H_1 = -\frac{2}{\pi} \int_0^{k_F} dk\, k \sum_{l=0}^{\infty} (2l+1)[\delta_l^1(k) - \delta_l^0(k)] . \tag{18}$$

where $\delta_l^1(k)$ and $\delta_l^0(k)$ are the phase shifts of Eq. (15) with and without a proton present, respectively. Before we turn to the contribution of ΔH_2 we list in Table I the various contributions to ΔH within the spherical solid model. Four positions of the proton in an Al lattice (of density $r_s = 2.067$ a.u.) are treated. Three interstitials at the octahedral ($\vec{r}_1 = \frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a$)

TABLE I. The different contributions to the heat of solution of a proton in an Al host. For a proton at $(\frac{3}{8}a,\frac{3}{8}a,\frac{3}{8}a)$ the nonspherical contributions were neglected and the heat of solution ΔH is that of the spherical solid model only.

Position (r_1)	ΔH_1 eV	ΔH_2 eV	ΔH_3 eV	ΔH_4 eV	ΔH_5 eV	ΔH_6 eV	ΔH^{ns} eV	ΔH eV
$(0,0,0)$	-3.991	7.526	0.000	27.780	2.495	-48.999	-0.017	0.654
$(\frac{1}{4}a,\frac{1}{4}a,\frac{1}{4}a)$	-11.927	7.526	-0.134	-5.265	3.361	-8.570	0.024	0.875
$(\frac{3}{8}a,\frac{3}{8}a,\frac{3}{8}a)$	-10.716	7.526	-0.004	-6.024	3.361	-8.912		1.091
$(\frac{1}{2}a,\frac{1}{2}a,\frac{1}{2}a)$	-9.507	7.526	0.000	-4.812	3.156	-11.646	0.016	0.593

and tetrahedral $(\bar{r}_1 = \frac{1}{4}a,\frac{1}{4}a,\frac{1}{4}a)$ sites and midpoint between them $(\bar{r}_1 = \frac{3}{8}a,\frac{3}{8}a,\frac{3}{8}a)$ and one substitutional site. The two densities $n_0(r)$ and $n_1(r)$ for three of these positions are displayed in Figs. 1 and 2. For the substitutional site note that ΔH corresponds to the energy of a proton within a lattice site already vacant.

A similar study was recently carried out by Popovic et al.[6] for both interstitial and substitutional H in Al and Mg. For the case of an interstitial H one major improvement in our calculation is the treatment of the spherical component of the Al host to all orders. Our results (Table I) show an increase (0.282 eV) in the heat of solution between the tetrahedral and octahedral sites. The low-order treatment of the Al potential yields a difference of 0.13 eV,[6] while the treatment of Manninen and Nieminen[10] within the spherical model yields a much larger number of 0.75 eV. For a substitutional site the differences are much greater since Popovic et al.[6] use the same screening density for both interstitial and substitutional sites. Previous calculations[7,20] and the results of Figs. 1 and 2 demonstrate, however, that the depletion charge at

a substitutional site must be taken into account. The spherical solid model automatically accounts for such a charge depletion. Our results (Table I) indicate a preference for an interstitial site by 0.061 eV, contrary to a preference of 1.23 eV for a substitutional site suggested by Ref. 6. Again, a recent treatment[10] within a similar spherical model yields a much larger preference for an interstitial site of 0.57 eV. In Table I we also report the heat of solution for a proton positioned midway between the octahedral and tetrahedral sites from which we estimate the activation energy as ≈ 0.5 eV. This is in agreement with most recent experimental values of 0.47 (Ref. 21) or 0.52 eV.[22]

To finally calculate the heat of solution within this spherical model we must add the contribution of ΔH_2. A comparison of $n_0(r)$ (for the host Al without the proton) and $n_1(r)$ (with the proton) displayed in Figs. 1 and 2 show that both densities are in close agreement beyond $r = 7$ a.u. Therefore, according to Eqs. (1a), (1d), and (1e), to localize the treatment of ΔH_1, ΔH_4, and ΔH_5 within this spherical model is reasonable. The same treatment cannot be applied to ΔH_2 where the full crystallographic ef-
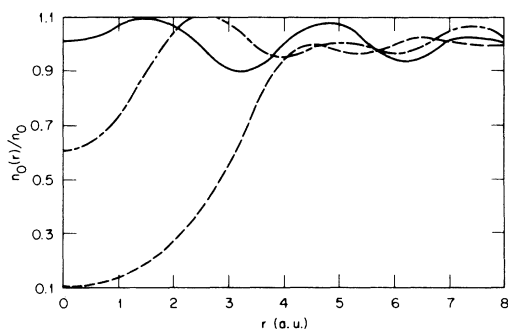

FIG. 1. The density $n_0(r)$ within the spherical solid model. $---$, $-\cdot-\cdot$, $\underline{\quad\quad}$ are the plots of $n_0(r)$ for the coordinate system set at the vacancy, octahedral, and tetrahedral sites, respectively.
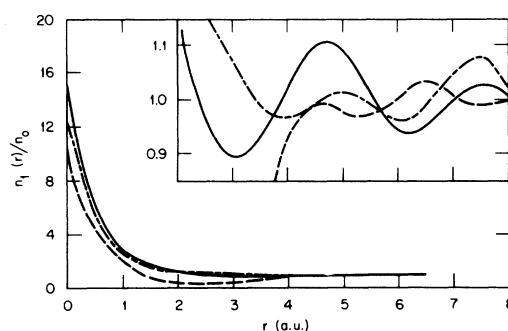

FIG. 2. The density $n_1(r)$ within the spherical solid model. $---$, $-\cdot-\cdot$, $\underline{\quad\quad}$ are the plots of $n_1(r)$ for the proton placed in a vacancy, octahedral, and tetrahedral sites, respectively.

fects must be included. The constant term $\bar{V}$ contribution to ΔH_2 and the kinetic energy $\hbar^2 k_F^2/2m$ are trivial to calculate. Higher-order contributions to ϵ_N^0 can be calculated either by a full band-structure calculation of the Fermi energy of Al [Eq. (2)] or a second-order perturbation treatment [Eq. (12)]. The last term in Eq. (12) gives a contribution of -0.049 Ry (-0.667 eV), so that $\Delta H_2 = 0.553$ Ry (7.526 eV).[23] The heat of solution is given by the value of ΔH for a proton at the octahedral site and from Table I is 0.593 eV, in good agreement with the experimental value of 0.66 eV.

Clearly the greatest uncertainty in our results depends upon the spherical treatment of the Al potential. The nonspherical corrections, however, are very difficult to calculate and have been totally ignored in all previous calculations of heat of solution.[6,7] We turn to an estimate of these corrections for H in Al in the following section.

III. NONSPHERICAL CORRECTIONS TO THE HEAT OF SOLUTION

In the previous section we treated ΔH_1, ΔH_4, and ΔH_5 within the spherical model by replacing the crystal potential $V_0(\bar{r})$ by $V_0^{0,0}(r)$ within some large volume Ω_1. In this section we treat the nonspherical terms $V_0^{ns}(\bar{r})$ [in $V_0(\bar{r})$] as a linear-order correction to $V_0^{0,0}(r)$. Our task is to solve for the nonspherical addition to the spherical electron densities $n_0(r)$ and $n_1(r)$ to linear order in $V_0^{ns}(\bar{r})$. From the Feynman-Hellman theorem the nonspherical contributions to the heat of solution is then given by

$$\Delta H^{ns} = \frac{1}{2} \int d^3r V_0^{ns}(\bar{r})[n_1^{ns}(\bar{r}) - n_0^{ns}(\bar{r})] , \quad (19)$$

where $n_0^{ns}(\bar{r})$ and $n_1^{ns}(\bar{r})$ are the linear-order nonspherical additions to $n_0(r)$ and $n_1(r)$, respectively. Expand next $V_0^{ns}(\bar{r})$ and $n^{ns}(\bar{r})$ in terms of the spherical harmonics; i.e.,

$$V_0^{ns}(\bar{r}) = \sum_{\substack{l,m \\ l \neq 0}} V_0^{l,m}(r) Y_{l,m}(\theta, \phi)$$

and

$$n^{ns}(\bar{r}) = \sum_{\substack{l,m \\ l \neq 0}} n^{l,m}(r) Y_{l,m}(\theta, \phi) . \quad (20)$$

Equation (19) can now be written as

$$\Delta H^{ns} = \frac{1}{2} \sum_{l \neq 0}^{\infty} \sum_{m=-l}^{l} \int dr r^2 V_0^{l,m}(r)[n_1^{l,m}(r) - n_0^{l,m}(r)] . \quad (21)$$

The treatment of $n^{ns}(\bar{r})$ was first presented in Refs. 17 and 24 for a vacancy formation energy. For completeness we present the key relations below. We write first the ground-state-energy functional as[11]

$$E[n] = \int d^3r V_{ext}(\bar{r})n(\bar{r})$$
$$+ \frac{1}{2} \int d^3r \int d^3r' \frac{n(\bar{r})n(\bar{r}')}{|\bar{r} - \bar{r}'|} + G[n] \quad (22)$$

with $V_{ext}(\bar{r})$ set equal to $V_0(\bar{r})$ or $V_0(\bar{r}) + v_1(\bar{r})$ and $n(\bar{r})$ set accordingly to $n_0(\bar{r})$ or $n_1(\bar{r})$ [$v_1(\bar{r})$ is spherically symmetrical]. $G[n(\bar{r})]$ is a universal functional representing the kinetic, exchange, and correlation energies. Finally the density $n(\bar{r})$ is given by

$$\delta E[n]/\delta n = \mu . \quad (23)$$

The densites $n_0(r)$ and $n_1(r)$ are the exact spherical solutions for Eqs. (22) and (23) for the spherical component of $V_{ext}(\bar{r})$. To get $n^{ns}(\bar{r})$ expand Eq. (23) to linear order, i.e.,

$$V_{ext}^{ns}(\bar{r}) + \int d^3r' \frac{n^{ns}(\bar{r}')}{|\bar{r} - \bar{r}'|} + \frac{\partial^2 G}{\partial n^2}[n(\bar{r})]n^{ns}(\bar{r}) = \mu^{ns} . \quad (24)$$

[Clearly $V_{ext}^{ns}(\bar{r}) = V_0^{ns}(\bar{r})$.]

To evaluate Eq. (24) we must choose an approximate form for $G[n(\bar{r})]$ and for the present calculation we take[24]

$$G[n(\bar{r})] \approx \frac{3}{10}(3\pi^2)^{2/3} \int d^3r n^{5/3}(\bar{r}) + \frac{1}{72} \int d^3r \frac{|\nabla n(\bar{r})|^2}{n(\bar{r})} - \frac{3}{4}\left[\frac{3}{\pi}\right]^{1/3} \int d^3r n^{4/3}(\bar{r}) . \quad (25)$$

then Eq. (24) reduces to[24]

$$V_0^{ns}(\bar{r}) + \int d^3r' \frac{n^{ns}(\bar{r}')}{|\bar{r} - \bar{r}'|} + \left[(3\pi^2)^{2/3}n(r)^{-1/3} - \frac{1}{3}\left[\frac{3}{\pi}\right]^{1/3} n(r)^{-2/3} - \frac{|\nabla n(r)|^2}{36n^3(r)} + \frac{\nabla^2 n(r)}{36n^2(r)}\right]n^{ns}(\bar{r})$$

$$- \frac{1}{36n(r)}\nabla^2 n^{ns}(\bar{r}) + \frac{\nabla n^{ns}(\bar{r}) \cdot \nabla n(r)}{36n^2(r)} = \mu^{ns} . \quad (26)$$

[Again recall that $n(r)$ is spherical and equal to either $n_0(r)$ or $n_1(r)$.]

To solve Eq. (26) we choose to calculate the electrostatic potential $v^{ns}(\bar{r})$ rather than the density $n^{ns}(\bar{r})$;

i.e.,

$$v^{ns}(\vec{r}) = V_0^{ns}(\vec{r}) + \int d^3r' \frac{n^{ns}(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad . \tag{27}$$

We write the angular momentum components of $v^{ns}(\vec{r})$ in terms of response functions $L_l(r,r')$,[24] i.e.,

$$v^{l,m}(r) = \int dr' r'^2 L_l(r,r') \rho_0^{l,m}(r') \quad , \tag{28}$$

where $\rho_0(\vec{r})$ is the density corresponding to the ionic potential $V_0(\vec{r})$;

$$V_0(\vec{r}) = \int d^3r' \rho_0(\vec{r}')/|\vec{r} - \vec{r}'| \quad .$$

After a considerable amount of algebra we get the following set of equations for $L_l(r,r')$:

$$L_l''''(r,r') + L_l'''(r,r')\left[\frac{4}{r} - \frac{n'(r)}{n(r)}\right] + L_l''(r,r')\left[T(r) - \frac{2l(l+1)}{r^2} - \frac{2n'(r)}{rn(r)}\right]$$

$$+ L_l'(r,r')\left[\frac{2}{r}T(r) - \frac{n'(r)}{n(r)}\left(-\frac{2}{r^2} - \frac{l(l+1)}{r^2}\right)\right] + L_l(r,r')\left[\frac{2}{k_h}n(r) + T(r)\left(-\frac{l(l+1)}{r^2}\right) - \frac{2l(l+1)}{r^4}\right]$$

$$+ \frac{[l(l+1)]^2}{r^4} - \frac{2l(l+1)}{r^3}\frac{n'(r)}{n(r)}\right] = 0 \quad . \tag{29}$$

where

$$T(r) = \left[\frac{n'(r)}{n(r)}\right]^2 - \frac{2n'(r)}{rn(r)} - \frac{n''(r)}{n(r)} + \frac{2k_l}{3k_h}n^{1/3}(r) - \frac{4}{3k_h}n^{2/3}(r); \quad k_l = 2^{5/3}\pi^{-4/3}3^{-2/3}r_s; \tag{30}$$

$$k_h = 2^{11/3}3^{-11/3}\pi^{-4/3}r_s; \quad r_s = (3/4\pi n_{bulk})^{1/3} \quad .$$

In Eqs. (29) and (30) the density has been scaled by the bulk density and the length by the Thomas-Fermi screening length and we note that the sign in the second term of Eq. (30) is in error in Ref. 24. The boundary conditions are found by demanding that $L_l(r,r')$ and its derivatives are continuous; they are

$$\lim_{\epsilon \to 0} L_l'(r' + \epsilon, r') - L_l'(r' - \epsilon, r') = -1/r'^2 \quad .$$

$$\lim_{\epsilon \to 0} L_l''(r' + \epsilon, r') - L_l''(r' - \epsilon, r') = +2/r'^3 \quad . \tag{31}$$

$$\lim_{\epsilon \to 0} L_l'''(r' + \epsilon, r') - L_l'''(r' - \epsilon, r')$$
$$= -[6 + l(l+1)]/r'^4 \quad .$$

To write the form of ΔH^{ns} in Eq. (21) in terms of $L_l(r,r')$ is not difficult and we get

$$\Delta H^{ns} = \frac{1}{2}\sum_{l \neq 0}^{\infty}\sum_{m=-l}^{l}\int drr^2\int dr' r'^2 \rho_0^{l,m}(r)[\rho_0^{l,m}(r')]^*$$
$$\times [L_l^1(r,r') - L_l^0(r,r')] \quad . \tag{32}$$

The response functions L_l^0 and L_l^1 are solved numerically for a fine grid of r and r' by setting $n(r)$ in Eqs. (29) and (30) equal to $n_0(r)$ and $n_1(r)$, respectively, for the appropriate densities at the tetrahedral, octahedral, and substitutional sites (Figs. 1 and 2).

The expression for the nonspherical components $\rho_0^{l,m}(r)$ can also be derived and is given as

$$\rho_0^{l,m}(r) = i^l\sum_{\vec{Q}}Q^2 w(Q)e^{i\vec{Q}\cdot\vec{r}}Y_{l,m}^*(\hat{Q})j_l(Qr) \quad , \tag{33}$$

where $\vec{Q}$ is the reciprocal-lattice vector, $\hat{Q}$ a unit vector along $\vec{Q}$, and the sum over $\vec{Q}$ is performed numerically for a grid of r.

With both $\rho_0^{l,m}(r)$ and $L_l(r,r')$ tabulated, the integrals over r and r' in Eq. (32) are performed and the sum over l and m is carried out up to $l = 14$. Our results are listed in Table I and surprisingly these contributions to the heat of solution of H in Al are very small. In addition, we can conclude with some confidence that these corrections are likely to be small in other metal hydrides such as Mg, Na, etc. For theoretical studies of impurities at low concentration these are important and useful conclusions. They imply that further refinements can be achieved without overdue concern for these very hard-to-treat nonspherical terms. For example, the replacement of the crystal pseudopotential by the full ionic potential, the treatment of lattice relaxation, and the zero-point energy, all within the spherical solid, are currently being investigated.

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