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Energetics of hydrogen in aluminum

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A detailed account of the results obtained for the energetics of a proton in aluminum is reported. The central model used in the calculations is the so-called "spherical solid model" in which the part of the ionic potential which is spherically symmetric around the impurity is treated to all orders. Various additional effects, such as the contributions of the nonspherical potential and lattice relaxation are investigated. The variation of the heat of solution of H in Al with position is calculated, and the zero-point vibration energy estimated.

I. INTRODUCTION

In this paper, we report the complete results obtained for the energetics of a hydrogen impurity in metallic aluminum. First, the heat of solution for a proton located in various sites along the $(x,x,x)a$ and $(\frac{1}{2},y,y)a$ directions is given, neglecting the lattice relaxation. The new equilibrium positions of the Al ions due to relaxation are then estimated within second-order-perturbation theory applied to the system of host and impurity; the corresponding relaxation energy is computed and shown to lower the heat of solution by approximately 10%.

In Sec. II we present the main assumptions which are the basis of the spherical solid model (SSM) used here and indicate how it can be applied to the calculation of the heat of solution with spherically symmetric densities. The formulation of corrections for (i) nonspherical effects around the impurity and (ii) relaxation of the lattice is then derived. The numerical results are presented and discussed in Sec. III, where the effect of zero-point vibrations is considered and where connection with experiments is made.

II. THEORETICAL FORMULATION

The heat of solution of a hydrogen in a metallic host can be written

$$\Delta H = H_1\{\vec{R}_i\} - H_0\{\vec{R}_{i0}\} + \Delta H^{\text{zp}} + \Delta H_0 \ , \tag{1}$$

where $H_1\{\vec{R}_i\}$ is the total energy of the solid containing the impurity with the metallic ions in their relaxed positions $\vec{R}_i$ (with respect to the proton), $H_0\{\vec{R}_{i0}\}$ is the energy of the metallic host without the impurity with the ions in the positions $\vec{R}_{i0}$ of the perfect lattice, ΔH^{zp} is the energy associated with zero-point vibrations, and $\Delta H_0 = 15.86$ eV is the negative of the energy of the neutral impurity in its molecular state. Equation (1) can be transformed to

$$\Delta H = H_1\{\vec{R}_{i0}\} - H_0\{\vec{R}_{i0}\} + \Delta H_0 + \Delta H^{\text{re}} + \Delta H^{\text{zp}} \ , \tag{2}$$

$$\Delta H^{\text{re}} = H_1\{\vec{R}_i\} - H_1\{\vec{R}_{i0}\} \ , \tag{3}$$

ΔH^{re} being the relaxation energy which will be assumed to be a small part of ΔH.

A. Heat of solution within the spherical solid model

The SSM allows for an exact treatment of the spherical part of the ionic potential in the problem of an impurity in a solid, while keeping the mathematical formulation adapted to the (one-center) jellium model.[1-5] The impurity position C in the lattice is the obvious center of coordinates for the SSM where that part of the ionic potential which is spherical around C is included in the effective total potential. Apart from the proton-lattice interaction and a quantity $Z_1\epsilon^0_{ZN}$ which comes from the extra electron added by the impurity ($Z_1 = 1$ is the charge of H and ϵ^0_{ZN} is the Fermi energy of the perfect metal[6]; hereafter, Ref. 6 will be referred to as I) $H_1\{\vec{R}_{i0}\} - H_0\{\vec{R}_{i0}\}$ is entirely determined by the displaced electron charge highly localized around the proton. Consequently, a very large cancellation of the nonspherical effects occurs in the difference of Eq. (3), justifying the use of the SSM. We therefore approximate ΔH by

$$\Delta H = \Delta H^{\text{sp}} + \Delta H^{\text{ns}} + \Delta H^{\text{re}} + \Delta H^{\text{zp}} \ , \tag{4}$$

$$\Delta H^{\text{sp}} = (H_1\{\vec{R}_{i0}\} - H_0\{\vec{R}_{i0}\})_{\text{SSM}} + \Delta H_0 \ , \tag{5}$$

where all the localized quantities entering the "spherical" approximation ΔH^{sp} to the heat of solution are calculated within the SSM. The spherical contribution to the heat of solution can be computed (see I) from the results of two SSM self-consistent calculations and in both of them, the spherical average of the ionic potential included in the effective potential is, in atomic units:

$$V_0^0(r) = \sum_{\vec{K}} w(K) e^{i\vec{K}\cdot\vec{\tau}} \frac{\sin Kr}{Kr} \quad , \tag{6}$$

$$w(K) = -\frac{4\pi Z}{\Omega_0 K^2}\left[D\frac{\sin KR_c}{KR_c} + (1-D)\cos KR_c\right] \times \exp[-(K/q_0)^2] \quad . \tag{7}$$

$\vec{K}$ is a reciprocal-lattice vector, $\vec{\tau}$ fixes the position of C with respect to the lattice, Ω_0 is the unit-cell volume, and Z is the valence charge of Al ($Z=3$). The individual ionic pseudopotential of the smooth Heine-Abarenkov form [Eq. (7)] is used and the parameters R_c and D are chosen to fit the binding energy of Al. The ratio of the damping parameter q_0 to the Fermi momentum k_F is $q_0/k_F = 5.5$. In the first SSM calculation, the proton is placed at the center C and the spherical density profile $n_1(r)$ is obtained. In the second calculation, where the proton is drawn out, the density $n_0(r)$ (also spherically symmetric around C) is generated. These densities satisfy the normalization condition

$$\int d\vec{r}[n_1(r) - n_0(r)] = Z_1 \quad . \tag{8}$$

By varying the position of the proton in the lattice, and keeping it as the center of spherical symmetry, a potential-energy surface for the proton in the metal can be determined.

B. Nonspherical correction to the heat of solution

The nonspherical contributions ΔH^{ns} have been first treated in I. Since we use the same formulation in the calculations of lattice relaxation (see Sec. II C and Appendix) we repeat below some of the key steps in our derivation. Now the ΔH^{ns} originates in the nonspherical part of the ionic potential

$$V_0^{\text{ns}}(\vec{r}) = \sum_{\substack{l,m \\ l\neq 0}} V_0^{lm}(r)\, Y_{lm}(\hat{r}) \quad , \tag{9}$$

which is dropped in the SSM. Our basic assumption is that ΔH^{ns} is very small, so that it can be treated as a second-order perturbation. In such an approach, it is clear that ΔH^{ns} would vanish if the polarizabilities of the two systems (the solid with the impurity and the perfect solid) were the same. These, however, differ since the density profiles $n_1(r)$ and $n_0(r)$ are very different around the center C. The main point in the calculation of ΔH^{ns} is thus a correct treatment of the relation between the polarizability and the electron density around C. Such a problem can be solved in the framework of the density functional formalism, with the kinetic and exchange energy functional

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

The derivation of ΔH^{ns} following these lines is given in I. We recall that the nonspherically induced electron density $n^{\text{ns}}(\vec{r})$ due to $V_0^{\text{ns}}(\vec{r})$ is a solution of

$$V_0^{\text{ns}}(\vec{r}) + \int d^3r' \frac{n^{\text{ns}}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \left[(3\pi^2)^{2/3} n(r)^{-1/3} - \frac{1}{3}\left[\frac{3}{\pi}\right]^{1/3} n(r)^{-2/3} - \frac{|\nabla n(r)|^2}{36 n^3(r)} + \frac{\nabla^2 n(r)}{36 n^2(r)}\right] n^{\text{ns}}(\vec{r}) - \frac{1}{36 n(r)}\nabla^2 n^{\text{ns}}(\vec{r}) + \frac{\nabla n^{\text{ns}}(\vec{r})\cdot\nabla n(r)}{36 n^2(r)} = \mu^{\text{ns}} \quad , \tag{11}$$

where $n(r)$ is either $n_1(r)$ or $n_0(r)$, depending on whether we are considering the metal-impurity system or just the metal host, respectively. Equation (11) can be transformed to a fourth-order differential equation and is solved after expanding $n^{\text{ns}}(\vec{r})$ in spherical harmonics ($l \neq 0$) (see I).

C. Correction for lattice relaxation

The equilibrium positions of the ions in the lattice are modified in the presence of the impurity. The displacements

$$\vec{\delta}_l = \vec{R}_l - \vec{R}_{l0} \tag{12}$$

are such that they minimize the energy ΔH^{re} given by Eq. (3). We assume that a high degree of spherical symmetry is kept in the relaxation, so that we write ΔH^{re} in the following form:

$$\Delta H^{\text{re}} = (H_1\{\vec{R}_l\} - H_1\{\vec{R}_{l0}\})_{\text{SSM}} - (H_0\{\vec{R}_l\} - H_0\{\vec{R}_{l0}\})_{\text{SSM}} + H_0\{\vec{R}_l\} - H_0\{\vec{R}_{l0}\} \tag{13}$$

by formally adding and subtracting the quantity $H_0\{\vec{R}_l\} - H_0\{\vec{R}_{l0}\}$ and again calculating the difference relative to the perfect and nonperfect solids in the SSM.[7,8] As the $\vec{\delta}_i$'s are most likely small quantities, ΔH^{re} can be expanded to second order. The $\vec{\delta}_i$'s, for consistency with the SSM, are assumed to be radial

$$\vec{\delta}_i = \lambda_i \vec{R}_{i0} \tag{14}$$

with the same λ_i, for all the ions in a given shell around the impurity.

The variation of the spherical component of the ionic potential induced by relaxation is

$$\delta V_0^0(r) = (4\pi)^{-1} \int d\hat{r} \left(\sum_i w(\vec{r} - \vec{R}_i) - w(\vec{r} - \vec{R}_{i0}) \right) , \tag{15}$$

$w(\vec{r})$ being the individual pseudopotential equivalent to Eq. (7) in direct space. Expanding Eq. (15) up to λ^2 gives

$$\delta V_0^0(r) = \sum_i [\lambda_i u_i(r) + \tfrac{1}{2}\lambda_i^2 v_i(r)] \ . \tag{16}$$

Restricting for simplicity to the case $D = 0$ [Eq. (7)], we find the following expressions of u_i and v_i:

$$\begin{aligned} u_i(r) &= \frac{Z}{2rR_i} \left(\tfrac{1}{2} f_i(r) + \frac{1}{q_0\sqrt{\pi}} g_i(r) \right) , \\ v_i(r) &= \frac{-Z}{2rR_i} \left[f_i(r) + \frac{2}{q_0\sqrt{\pi}} \left(1 + \frac{q_0^2 R_i^2}{4} \right) g_i(r) \right] , \end{aligned} \tag{17}$$

with

$$\begin{aligned} f_i(r) = {} & (r - R_c)\,\mathrm{erf}(x_2) + (r + R_c)\,\mathrm{erf}(y_2) \\ & + \left(r\frac{R_i - r}{|R_i - r|} + R_c \right) \mathrm{erf}(x_1) \\ & + \left(r\frac{R_i - r}{|R_i - r|} - R_c \right) \mathrm{erf}(y_1) , \end{aligned}$$

$$g_i(r) = \exp(-x_2^2) - \exp(-x_1^2) + \exp(-y_2^2) - \exp(-y_1^2) ,$$

$$x_1 = q_0(|r - R_i| - R_c)/2; \quad y_1 = q_0(|r - R_i| + R_c)/2 ,$$

$$x_2 = q_0(r + R_i - R_c)/2; \quad y_2 = q_0(r + R_i + R_c)/2 .$$

Evaluating the SSM contribution $\Delta H_{\mathrm{SSM}}^{\mathrm{re}}$ in Eq. (13) to order λ^2, we find

$$\begin{aligned} \Delta H_{\mathrm{SSM}}^{\mathrm{re}} = {} & \sum_i \int [n_1(r) - n_0(r)][\lambda_i u_i(r) + \tfrac{1}{2}\lambda_i^2 v_i(r)]\, d\vec{r} \\ & + \tfrac{1}{2} \sum_i \sum_j \lambda_i \lambda_j \int [\rho_{1i}(r) - \rho_{0i}(r)] u_j(r)\, d\vec{r} + \sum_i \frac{ZZ_1}{R_i}(-\lambda_i + \lambda_i^2) \ . \end{aligned} \tag{18}$$

The first term is the first-order perturbation of ΔH, linear in δV_0^0; $n_1(r)$ and $n_0(r)$ are the density profiles of the unrelaxed systems, metal host with and without the proton, respectively. The second sum is the second-order perturbation: $\rho_{1i}(r)$ and $\rho_{0i}(r)$ are the electron densities induced by $u_i(r)$ in the two systems. They are solutions of Eq. (11) for a spherical external perturbation $\delta V_0^0(r)$ (see Appendix). Finally, the last sum in Eq. (18) gives the change in electrostatic interaction between the proton and the lattice.

The second contribution $\Delta H_0^{\mathrm{re}} = H_0\{\vec{R}_i\} - H_0\{\vec{R}_{i0}\}$ is estimated in standard second-order pseudopotential theory of simple metals. ΔH_0^{re} comes from the variation of the structure factor

$$S(\vec{q}) = \frac{1}{N} \sum_i e^{i\vec{q}\cdot\vec{R}_i} \tag{19}$$

in the band-structure and electrostatic contributions to the binding energy of the metal without the impurity

$$\Delta H_0^{\mathrm{re}} = \lim_{\eta \to \infty} \tfrac{1}{2} N \Omega_0 \sum_q{}' \Delta[S^*(\vec{q}) S(\vec{q})] F(q) , \tag{20}$$

$$F(q) = -w^2(q) \frac{\pi_0(q)}{\epsilon(q)} + \frac{4\pi Z^2}{\Omega_0^2} \frac{\exp(-q^2/4\eta)}{q^2} . \tag{21}$$

$\pi_0(q)$ is the irreducible polarizability of the noninteracting electron gas and $\epsilon(q)$ the dielectric constant of the interacting electron gas. The variation of the structure-dependent term is

$$N^2 \Delta[S^*(\vec{q}) S(\vec{q})] = \sum_i \sum_j [i\vec{q}\cdot\vec{\delta}_{ij} - \tfrac{1}{2}(\vec{q}\cdot\vec{\delta}_{ij})^2] \exp(i\vec{q}\cdot\vec{R}_{ij0}) \ . \tag{22}$$

The terms linear in $\vec{\delta}_{ij} = \vec{\delta}_i - \vec{\delta}_j$ vanish after summation, so that

$$N^2 \Delta[S^*(\vec{q}) S(\vec{q})] = -\tfrac{1}{2} \sum_i \sum_j q^2 \delta_{ij}^2 \cos^2\theta \sum_{lm} 4\pi i^l j_l(qR_{ij0})\, Y_{lm}(\hat{\theta})\, Y_{lm}(\hat{\delta}_{ij} \cdot \hat{R}_{ij0}) , \tag{23}$$

with θ as the angle between $\vec{q}$ and $\vec{\delta}_{ij}$. Due to the behavior when $q \to 0$, namely, $F(q) = O(q^0)$ and $\Delta[S^*(q)S(q)] = O(q^2)$, the term $q = 0$ which is absent in Eq. (20) does not contribute to ΔH_0^{re}, so that the discrete sum can be replaced by an integration on $\vec{q}$:

$$\Delta H_0^{\mathrm{re}} = \lim_{\eta\to\infty} -\frac{\Omega_0^2}{16\pi^2} \sum_i \sum_j \delta_{ij}^2 \int_0^\infty q^4\, dq\, [\tfrac{2}{3} j_0(qR_{ij0}) - \tfrac{4}{3} P_2(\hat{\delta}_{ij}\cdot\hat{R}_{ij}) j_2(qR_{ij0})] F(q) \quad . \tag{24}$$

Using the symmetry in $\vec{\mathrm{R}}_{i0}$ and $\vec{\mathrm{R}}_{j0}$ and the cubic properties of the lattice, a sum like

$$S = \sum_i \sum_j \delta_{ij}^2 P_2(\hat{\delta}_{ij}\cdot\hat{R}_{ij0}) F(qR_{ij0})$$

is equivalent, for any function F, to

$$S = \sum_i \sum_j \lambda_i\lambda_j \left(-3\frac{(\vec{\mathrm{R}}_i\cdot\vec{\mathrm{R}}_{ij0})(\vec{\mathrm{R}}_j\cdot\vec{\mathrm{R}}_{ij0})}{R_{ij0}^2} + (\vec{\mathrm{R}}_{i0}\cdot\vec{\mathrm{R}}_{j0}) \right) F(qR_{ij0}) \quad .$$

Calculating the integrals which depend on the parameter η in Eq. (24) and properly taking the limit $\eta\to\infty$ leads finally to

$$\begin{aligned}\Delta H_0^{\mathrm{re}} = & -\tfrac{1}{2} Z^2 \sum_{ij}{}' [\lambda_i^2 R_{i0}^2 - \lambda_i\lambda_j(\vec{\mathrm{R}}_{i0}\cdot\vec{\mathrm{R}}_{j0})] I(R_{ij0}) \\ & + \tfrac{1}{2} Z^2 \sum_{ij}{}' \lambda_i\lambda_j \left(-3\frac{(\vec{\mathrm{R}}_{i0}\cdot\vec{\mathrm{R}}_{ij0})(\vec{\mathrm{R}}_{j0}\cdot\vec{\mathrm{R}}_{ij0})}{R_{ij0}^2} + (\vec{\mathrm{R}}_{i0}\cdot\vec{\mathrm{R}}_{j0}) \right) J(R_{ij0}) \quad , \end{aligned} \tag{25}$$

with

$$I(R_{ij0}) = -\tfrac{8}{3} \int_0^\infty dq\; j_0(qR_{ij0}) \cos^2 qR_c \exp[-2(q/q_0)^2] \frac{\pi_0(q)}{\epsilon(q)} \quad ,$$

$$J(R_{ij0}) = -\tfrac{8}{3} \int_0^\infty dq\; j_2(qR_{ij0}) \cos^2 qR_c \exp[-2(q/q_0)^2] \frac{\pi_0(q)}{\epsilon(q)} + R_{ij0}^{-3} \quad .$$

The pseudopotential defined by Eq. (7) with $D=0$ has been used. The functions $I(R_{ij0})$ and $J(R_{ij0})$ decrease to zero for large R_{ij0}. The total relaxation energy $\Delta H^{\mathrm{re}} = \Delta H_{\mathrm{SSM}}^{\mathrm{re}} + \Delta H_0^{\mathrm{re}}$ can be written as[9]

$$\Delta H^{\mathrm{re}} = \sum_a \lambda_a S_a + \frac{1}{2} \sum_a \sum_b \lambda_a \lambda_b T_{ab} \quad , \tag{26}$$

where index a (or b) corresponds now to a particular star of vectors $\vec{\mathrm{R}}_{i0}$ stable under the cubic group. The minimization of ΔH^{re} with respect to the λ's gives the linear system

$$\sum_b T_{ab}\lambda_b + S_a = 0, \quad a = 1, 2, \ldots \quad , \tag{27}$$

the dimension of which is the number of stars taken into account. With the λ's solutions of Eq. (27)

$$\Delta H^{\mathrm{re}} = \sum_a \lambda_a S_a \quad . \tag{28}$$

Equations (18) and (25) can be easily modified for the case of a proton in a vacancy; we shall not give the corresponding expressions here.

III. RESULTS AND DISCUSSION

The heat of solution ΔH^{sp} has been calculated within the SSM model in locations along the $(x,x,x)a$ and $(\frac{1}{2},y,y)a$. The results are shown in Table I. The definition of the various contributions $\Delta H_1, \ldots, \Delta H_6$ to ΔH^{sp} are given in I, and for completeness are redefined on Table I. ΔH^{sp} was not calculated for a proton very close to an Al ion because the use of a rigid pseudopotential may be suspect in that case. ΔH^{sp} as a function of the position of H in the lattice is shown in Fig. 1. Note that points $(\frac{1}{2},\frac{1}{2},\frac{1}{2})a$ and $(\frac{1}{2},0,0)a$ are equivalent as are points $(\frac{1}{2},\frac{3}{8},\frac{3}{8})a$ and $(\frac{1}{2},\frac{1}{8},\frac{1}{8})a$. The results of Table I have been obtained with the pseudopotential parameters $R_c = 1.09$ a.u. and $D=0$. With different parameters (which also fit the binding energy of pure Al) $R_c = 1.23$ a.u. and $D = 0.398$, we have found $\Delta H^{\mathrm{sp}} = 0.657$ eV for the substitutional impurity, and $\Delta H^{\mathrm{sp}} = 0.563$ eV for the proton in the octahedral site $(\frac{1}{2},\frac{1}{2},\frac{1}{2})a$. Our results for the heat of solution are therefore not extremely sensitive to the pseudopotential parameters.

The most favorable calculated position for H in Al is in the octahedral site. Experimental evidence is for location in the tetrahedral position $(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$ for temperatures above 35 K. But at lower temperatures, (~ 5 K) a tendency towards octahedral-site occupancy has been found, in agreement with results for other fcc metals.[10] The calculated energy surface shows a barrier in both the directions investigated, the lowest one being in the (x,x,x) direction; it corresponds to an activation energy of 0.53 eV.

From the curves of Fig. 1, we can very roughly estimate a frequency for the vibrations of H in the octahedral site. We find $\omega = 0.0035$ a.u., so that an order of magnitude of the zero-point contribution to

TABLE I. The different contributions to the heat of solution of H in Al as obtained in the spherical solid model. The various ΔH represent the difference in the energy of the perfect lattice and the one containing the H impurity. These contributions are ΔH_1 is the change in the eigenvalues of the Kohn-Sham equations, ΔH_2 is the chemcial potential, ΔH_3 is the binding of the Z_c bound states (if any), ΔH_4 is the change in the electrostatic energy of the electronic charge density, ΔH_5 is the change in the exchange and correlation energy, and ΔH_6 is the change in the Madelung energy. The mathematical forms for all these terms are written down in I.

Position of H	ΔH_1 (eV)	ΔH_2 (eV)	ΔH_3 (eV)	ΔH_4 (eV)	ΔH_5 (eV)	ΔH_6 (eV)	ΔH^{sp} (eV)
(0,0,0)	−3.991	7.526	0.000	27.780	2.495	−48.999	0.671
$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	−11.927	7.526	−0.134	−5.265	3.361	−8.570	0.851
$(\frac{5}{16},\frac{5}{16},\frac{5}{16})a$	−11.661	7.526	−0.092	−5.713	3.377	−8.218	1.079
$(\frac{3}{8},\frac{3}{8},\frac{3}{8})a$	−10.716	7.526	−0.004	−6.024	3.361	−8.912	1.091
$(\frac{7}{16},\frac{7}{16},\frac{7}{16})a$	−9.909	7.526	0.000	−5.193	3.217	−10.698	0.803
$(\frac{1}{2},\frac{1}{2},\frac{1}{2})a$	−9.507	7.526	0.000	−4.812	3.156	−11.646	0.577
$(\frac{1}{2},\frac{3}{8},\frac{3}{8})a$	−10.186	7.526	0.000	−6.330	3.317	−9.171	1.016
$(\frac{1}{2},\frac{1}{4},\frac{1}{4})a$	−11.422	7.526	−0.058	−7.212	3.484	−6.225	1.953

the heat of solution is $\Delta H^{zp}=\frac{3}{2}\hbar\omega\sim 0.147$ eV. In I we gave the results for the nonspherical corrections ΔH^{ns}. They were found to be very small for the three positions $(0,0,0)$, $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ for which the calculation was carried out. In the octahedral site for instance, we obtained $\Delta H^{ns}=0.016$ eV. We concluded that the nonspherical corrections are not a major effect and the calculation was not repeated for the new positions presented here.

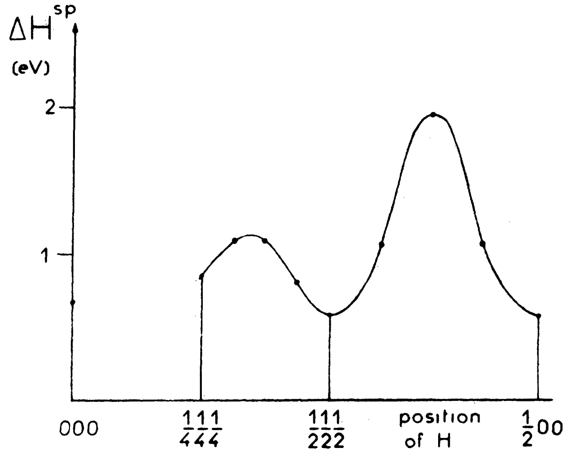

FIG. 1. Variation of the heat of solution ΔH^{sp} ("spherical" part) of H in Al, with the position of H (arbitrary units) in the fcc latttice.

We next turn to the results for the lattice relaxation contribution. In Table II, we show the relaxation displacements [λ_i is defined in Eq. (14)] for the proton in the octahedral site and in a vacancy. The vectors on each shell are measured, in both cases, with respect to the proton. The λ of the first shell is about 2 to 3% in magnitude. For the interstitial, the Al ions are pushed back and for the vacancy, they are pulled closer to the proton position. The relaxation effects seem to extend farther in the case of the vacancy, for which the relaxation energy is much larger (−0.155 eV) than for the interstitial (−0.060 eV).[11]

In Table III, we give additional results for H in the octahedral site showing the sensitivity of our results to variation in our model. The first row shows that the contribution from the modified spherical densities due to displacement of the ions is not very large (0.002 eV). ΔH^{re} is not very sensitive to the details of the pseudopotential, as shown by the second row, where the results correspond to 5% change on the core radius R_c. Finally, the most interesting comparison is that with the calculation where the densities n_0 and n_1 of the SSM are replaced by $\bar{n}$ (uniform) and n_1 by the linear approximation

$$n_1=\bar{n}+\sum_{\vec{q}}{}'\frac{\pi_0(q)}{\epsilon(q)}\frac{4\pi Z_1}{\Omega_0 q^2}\frac{\sin qr}{qr} ,$$

respectively. In that case, the displacement of the first shell is strongly overestimated and so is the relaxation energy. These relaxation effects, clearly can-

TABLE II. Lattice relaxation effects for H in Al. The two series of results refer to H in the octahedral position and in a vacancy, respectively. In each case, the convergence may be appreciated by comparison of two calculations, one with three and one with five shells.

Shell	100	111	210	221	300	ΔH^{re} (eV)
$\lambda_i \times 10^2$	2.24	−0.24	0.25	⋯	⋯	−0.059
$\lambda_i \times 10^2$	2.24	−0.25	0.26	0.01	0.06	−0.060

Shell	110	200	211	220	310	ΔH^{re} (eV)
$\lambda_i \times 10^2$	−2.30	−0.30	−0.18	⋯	⋯	−0.138
$\lambda_i \times 10^2$	−2.55	−0.35	−0.20	−0.41	−0.05	−0.155

not be approached in a realistic way within the lattice statics method, but must take into account the correct zero-order density profile of the system containing the impurity. Adding the various contributions [Eq. (4)] to ΔH we find $\Delta H \approx 0.68$ eV as compared to the experimental values 0.47 (Ref. 12) or 0.52 eV.[13] A rather large uncertainty comes from our crude estimate of ΔH^{zp} and from our second-order treatment of the chemical potential (see Ref. 23 of I). The zero-point contribution cannot be estimated from our potential curve when the proton is in a vacancy, and we, therefore, cannot give the total ΔH in that case. It seems that a good part of the excess of ΔH^{sp} is canceled by a larger ΔH^{re}, so that the difference between the heats of solution at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is probably rather small.

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APPENDIX

The term in Eq. (18) which is most difficult to treat in a consistent fashion is

$$\Delta H_{ij}^{\mathrm{sc}} = \lambda_i \lambda_j \int [\rho_{1i}(r) - \rho_{0i}(r)] u_j(r)\, d\vec{r} \ . \qquad \text{(A1)}$$

TABLE III. Test of various effects in the lattice relaxation of H in Al (octahedral site). First row: no second-order effects [$\rho_{1i} = \rho_{0i} = 0$ in Eq. (18)]. Second row: variation of the pseudopotential $R_c = 1.14$, $D = 0$ instead of $R_c = 1.09$, $D = 0$. Third row: density profile $n_1(q) - n_0(q)$ obtained by linear screening of the proton, $n_1(q) - n_0(q) = [\pi_0(q)/\epsilon(q)] 4\pi Z_1 / q^2 \Omega_0$.

Shell	100	111	210	221	300	ΔH^{re} (eV)
$\lambda_i \times 10^2$	2.16	−0.26	0.24	−0.01	0.01	−0.057
$\lambda_i \times 10^2$	2.11	−0.20	0.23	−0.00	0.01	−0.062
$\lambda_i \times 10^2$	3.52	0.03	0.34	0.03	0.08	−0.168

We therefore thought it useful to present just the key relations in its treatment. The densities $\lambda_i \rho_{1i}(r)$ and $\lambda_j \rho_{0i}(r)$ correspond to the response of the electron gas (in the SSM), with and without the proton, respectively, when the aluminum ions are displaced by δ_i from the perfect lattice positions. A systematic treatment of Eq. (A1) requires, therefore, the polarizabilities of the electron gas with and without the impurity. We choose to define these by constructing the screened potential

$$V_s(\vec{r}) = V(\vec{r}) + \int \frac{d\vec{r}'\, n(\vec{r}')}{|\vec{r}-\vec{r}'|} \quad . \tag{A2}$$

In Eq. (A2), $V(\vec{r})$ includes the potential of the Al host with or without the impurity potential and the electron density $n(\vec{r})$ corresponds to these two $V(\vec{r})$. We now allow for small displacements δ_i of the ions and write a similar expansion for the spherical part of $V_s(\vec{r})$ (to first order in λ_i) as in Eq. (16), i.e.,

$$\delta V_s^0(r) = \sum_i \lambda_i v_s^i(r) \quad . \tag{A3}$$

[Note again that $\delta V_s^0(r)$ contains both the displacement of the ions as well as the corresponding electron response.] We choose to define our polarization functions as

$$v_s^i(r) = \int dr'\, r'^2 L(r,r')\, \delta\rho_0^i(r') \quad , \tag{A4}$$

where

$$\delta\rho_0^i(r) = -\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\frac{u_i(r)}{4\pi} \right) \quad , \tag{A5}$$

with $u_i(r)$ as given in Eq. (17). Equation (A1) can now be written as

$$\Delta H_{ij}^{\text{sc}} = 4\pi\lambda_i\lambda_j \int dr\, r^2 \int dr'\, r'^2 \{ [L_1(r,r') - L_0(r,r')]\, \delta\rho_0^i(r')\, \delta\rho_0^j(r) \} \quad . \tag{A6}$$

Finally, using Eqs. (A2)–(A4) in Eq. (11) yields the set of Eqs. (29)–(31) in I (with $l=0$). Setting $n(r)=n_1(r)$ or $n_0(r)$ [in Eq. (29) of I], we solve numerically for the polarizability $L_1(r,r')$ or $L_0(r,r')$, respectively, and use these in Eq. (A6) by performing the numerical integration over r and r'.

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