# Lattice relaxation and tendency for crystallographic distortions around a hydrogen impurity in the alkali series

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The spherical solid model is applied to the calculation of lattice relaxations around a single proton impurity in Li, Na, and K. A tendency towards a crystallographic distortion in all three metals is observed, which is consistent with the transition from a bcc to a NaCl structure occurring in the stoichiometric limit of the alkali hydrides.

## I. INTRODUCTION

The alkali hydrides crystallize in a face-centered-cubic lattice while the pure alkali metals have the body-centered-cubic structure. The comparison of measured densities indicates that the distance between two metallic ions is much greater in the pure metal than in the hydride[1] as can be seen from Table I. These facts are explained by the following visualization of the hydration process, starting from the pure metal: (i) trapping of hydrogen atoms at the midpoint of each vertical bond between two alkali atoms (see Fig. 1), and (ii) expansion of these bonds (for instance, $h = BC$) and simultaneous contraction of the horizontal lengths (for instance, $l = AB$). When the perfect hydride lattice is obtained, $h$ and $l$ are both equal to the NaCl lattice parameter $a_H$. These modifications are considerable in magnitude, as shown in Table I: The dilations range from 16% in Li to 8% in K, and the contractions from 18% in Li to 24% in K.

In this paper, we report an attempt to demonstrate by means of qualitative calculations that the relaxations of the metal ions around a single H impurity in an alkali-metal host are consistent with the above picture.

We have applied here the model of lattice relaxation that we previously used for hydrogen in aluminum.[2,3] Let us first recall the basic features of that model. A proton introduced in a metal is a strong perturbation, so that methods where the displaced electron density is obtained in linear response (for instance, the lattice-static method[4]) are not applicable. The "spherical solid model"[5,6] (SSM) as applied in Refs. 2 and 3 allows one to overcome this difficulty by treating the proton potential to all orders, together with the spherical average (around the proton) of the metal ions potential. The idea of the SSM is that the difference in energy between the lattice with the proton and the perfect lattice is accurately evaluated in spherical symmetry:

TABLE I. Lattice parameters and characteristic ratios in the alkali metals and alkali hydrides.

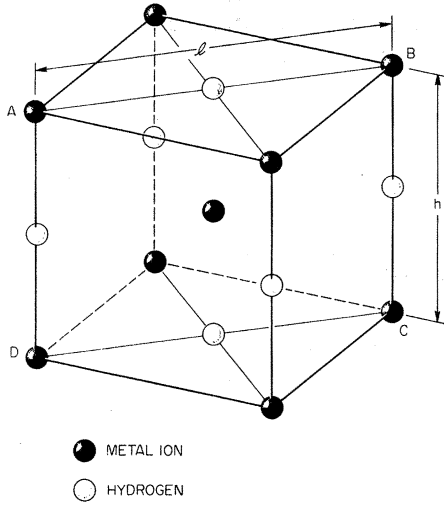| | Lattice constant (a.u.) | | Distance of two metal ions | | Distance $l$ | $a_H/h$ | $a_H/l$ |
| | Hydride: $a_H$ | Metal: $a_M$ | Hydride | Metal | Metal | | |
|---|---|---|---|---|---|---|---|
| Li | 7.72 | 6.63 | 5.46 | 5.74 | 9.38 | 1.16 | 0.82 |
| Na | 9.22 | 8.10 | 6.52 | 7.01 | 11.46 | 1.14 | 0.80 |
| K | 10.79 | 10.03 | 7.63 | 8.68 | 14.19 | 1.08 | 0.76 |

FIG. 1. Positions of the metal and H ions in the bcc structure before the lattice relaxation. The plane $ABCD$ will become a face of the cube in the NaCl hydride lattice.

$$E_1\{\vec{R}_i'\}=(E_1\{\vec{R}_i'\}-E_0\{\vec{R}_i'\})_{\text{SSM}}+E_0\{\vec{R}_i'\} \ .$$

$$(1)$$

In Eq. (1) the indexes 0 and 1 refer to the solid with and without the proton, respectively. The

vectors $\vec{R}_i'$ give the positions of the ions around the origin where the proton sits in the impurity case. Equation (1) is assumed to be valid even when the $\vec{R}_i'$ are not the positions in the perfect lattice, but the relaxed positions, provided that a high degree of symmetry is kept, as is the case for H at the octahedral site in a fcc lattice. The relaxed positions of the ions are assumed to be of the form

$$\vec{R}_i' =(1+\lambda_i)\vec{R}_i \ ,$$

$$(2)$$

(i.e., the displacements are radial) with $\lambda_i$ equal for all the atoms in the same shell around the proton. The values of the $\lambda$'s are obtained by minimizing $E_1\{\vec{R}_i'\}$ expanded up to $\lambda^2$ using second-order perturbation theory. The variation of the average ($\langle \ \rangle$ means spherical average) ionic potential due to relaxation is as follows:

$$\Delta V(r)= \sum_i \langle V(\vec{r}-\vec{R}_i-\lambda\vec{R}_i)-V(\vec{r}-\vec{R}_i)\rangle \ ,$$

$$= \sum_i \lambda_i u_i(r)+\tfrac{1}{2}\lambda_i^2 v_i(r) \ ,$$

$$(3)$$

so that, to second order in $\lambda$ (Refs. 2 and 3),

$$\Delta(E_1-E_0)_{\text{SSM}}= \sum_i \frac{Z}{R_i}(-\lambda_i+\lambda_i^2)+ \sum_i \int (n_1-n_0)(\lambda_i u_i+\tfrac{1}{2}\lambda_i^2 v_i)d\vec{r}+\tfrac{1}{2}\sum_{ij} \lambda_i\lambda_j \int (\rho_{1i}-\rho_{0i})u_j d\vec{r} \ . \quad (4)$$

$Z$ is the valence of the host ions, $n_0$ and $n_1$ are the density profiles obtained in the SSM for the perfect and nonperfect solids, respectively,[7] and $\rho_{0i}$ and $\rho_{1i}$ are the electron densities induced in these two systems by the perturbation $u_i$. Additional details of Eq. (4) may be found in Refs. 2, 3, and 7. The energy of the perfect lattice $E_0\{R_i'\}$ [last term in Eq. (1)] is expanded to order $\lambda^2$ in standard pseudopotential theory, the structure factor being the only quantity which depends on the $\{\vec{R}_i'\}$. A pseudopotential of the smoothed Ashcroft form is used:

$$V(q)=-\frac{4\pi Z}{q^2\Omega_0} \cos(qR_c)e^{-(q/q_o)^2} \ .$$

$$(5)$$

The expansion of $\Delta E_1$ in the lattice displacements $\lambda_a$ is written as

$$\Delta E_1=- \sum_a \lambda_a S_a +\tfrac{1}{2} \sum_a \sum_b \lambda_a\lambda_b T_{ab} \ ,$$

$$(6)$$

which reaches its minimum for:

$$\sum_b T_{ab}\lambda_b =S_a \ , \quad a=1,2,\dots \ .$$

$$(7)$$

## II. RESULTS AND DISCUSSION

We carried out the calculations for the alkali metals Li, Na, and K, using the pseudopotential parameters given in Table II. These parameters were fitted in order to reproduce the bottom of the conduction band computed using the augmented plane wave (APW) band-structure method. This procedure is approximately equivalent to a fit of the phase shift for the momentum $l=0$ at the Fermi level. A good convergence of the relaxation displacements was obtained by taking into account four shells of atoms. The $\lambda$'s for the first two shells are shown in Table III. They are all positive

TABLE II. Pseudopotential parameters (a.u.) for the alkali ions.

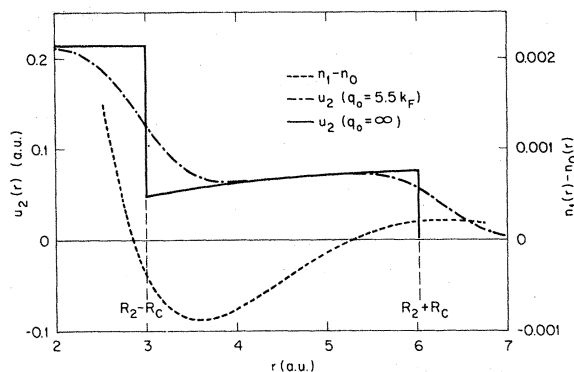|      | $R_c$  | $q_0$ |
|------|--------|-------|
| Li   | 1.658  | 2.78  |
| Na   | 1.670  | 2.33  |
| K    | 2.255  | 1.99  |



FIG. 2. Profile of the density displaced by the proton in lithium, and first-order variation of the pseudopotential $(u_2)$ for the ions in the second shell.

in the first shell, and decrease from Li to K: The bond $h$ (Fig. 1) increases when the impurity is introduced in the alkali metal, in qualitative agreement with the values of the ratio $a_H/h$ in Table I. In the second shell of atoms, the calculated $\lambda$'s are all negative, and greater in magnitude than 1%, corresponding to a contraction consistent with the values of $a_H/l$, smaller than one, shown in Table I. Clearly, the relaxations due to a single impurity indicate a tendency towards the change of crystal structure. Of particular interest is the difference in the relaxation of the second shell in the alkali series as compared with that of Al-H, treated in Refs. 2, 3, and 7 and tabulated again in Tables III and IV. Before discussing these differences, the qualitative nature of our results should be emphasized. This is particularly true for two reasons. The first one is the use of the spherical model for shells containing only two and four atoms, a situation much less favorable than in fcc metals like aluminum. Second, we have described lithium with a simple local pseudopotential which cannot simulate the strong $p$ scattering well known in that metal.

We now return to the comparison of Al and the alkali series. It must be pointed out that the relaxation of the second shell in Al is an order of magnitude smaller than in the alkalis. This is a strong difference which has to be explained on physical grounds. In Eq. (7), the right-hand-side term $S_a$ is given by the first-order terms of Eq. (4) (the ex-

pansion of the perfect lattice $E_0$ contains second-order terms only):

$$s_a = \frac{S_a}{n_a} = \frac{Z}{R_a} - \int (n_1 - n_0)u_a d\vec{r} . \tag{8}$$

The diagonal matrix elements $T_{aa}$ are always positive and much greater than the off-diagonal terms, so that

$$\lambda_a \approx n_a s_a / T_{aa} . \tag{9}$$

$n_a$ is the number of atoms in the shell at distance $R_a$ from the proton. The physical meaning of $s_a$ can be understood in the following way. Let us assume that the damping parameter $q_0$ in the pseudopotential[8] [Eq. (5)] can be considered as infinite, so that $V(q)$ is a true Ashcroft potential. The expression for $u_a$ becomes very simple:

$$u_a = \begin{cases} \dfrac{Z}{R_a} , & r < R_a - R_c \\[2ex] \dfrac{Z}{2R_a}\left[1 - \dfrac{R_c}{r}\right] , & R_a - R_c < r < R_a + R_c \\[2ex] 0 , & R_a + R_c < r . \end{cases} \tag{10}$$

TABLE III. Lattice relaxation around a H impurity in the alkali metals, in comparison with aluminum. $R_1$ and $R_2$ are the distances to the first two shells in the perfect lattice; $\lambda_1$ and $\lambda_2$ are the relative variation of these distances. Note the slight difference in the lattice constants of Tables I and III. Our calculations correspond to the parameters listed here.

|                    | Li     | Na     | K      | Al     |
|--------------------|--------|--------|--------|--------|
| $R_1$ (a.u.)       | 3.298  | 3.850  | 4.725  | 3.819  |
| $\lambda_1 \times 100$ | 6.42   | 3.28   | 1.97   | 2.41   |
| $R_2$ (a.u.)       | 4.665  | 5.445  | 6.682  | 6.615  |
| $\lambda_2 \times 100$ | $-1.51$ | $-1.65$ | $-2.07$ | $-0.25$ |

TABLE IV. Analysis of the quantities which determine the relaxation of the second shell of ions, and test of the approximation based on the charges displaced outside ($Q_2$) and inside ($q_2$) the shell of ions.

|     | $Q_2$ | $q_2$ | $\mu_2$ | $\left[\dfrac{R_2}{Z}s_2\right]$ appr. | $\left[\dfrac{R_2}{Z}s_2\right]$ exact |
|-----|--------|--------|--------|--------|--------|
| Li  | $-0.046$ | $-0.165$ | $0.341$ | $-0.074$ | $-0.065$ |
| Na  | $-0.042$ | $-0.220$ | $0.297$ | $-0.075$ | $-0.076$ |
| K   | $-0.070$ | $-0.252$ | $0.325$ | $-0.111$ | $-0.122$ |
| Al  | $-0.011$ | $-0.046$ | $0.163$ | $-0.015$ | $-0.013$ |

Restricting to the second shell, the variations of $1/r$ are small compared to the dimensions of the ion, so that we can replace $u_a$, in the second region, by its volume average. Finally, $s_a$ for the second shell can be written as

$$s_2 = \frac{Z}{R_2}(Q_2 + \tfrac{1}{2}\mu_2 q_2) . \tag{11}$$

$s_2$ depends on two charges, $Q_2$ and $q_2$:

$$Q_2 = \int_{R_2+R_c}^{\infty} (n_1-n_0)4\pi r^2 dr + \tfrac{1}{2}q_2 , \tag{12}$$

$$q_2 = \int_{R_2-R_c}^{R_2+R_c} (n_1-n_0)4\pi r^2 dr . \tag{13}$$

$Q_2$ can be roughly interpreted as the charge displaced by the proton outside a sphere of radius $R_2$; $q_2$ is the charge displaced within the spherical shell where the ions are located. In Eq. (11) $q_2$ is weighted by a factor $\mu_2$ which characterizes the dimensions of the ion core:

$$\mu_2 = \frac{1}{(1/x)+(x/3)} , \quad x = \frac{R_c}{R_2} . \tag{14}$$

The density $n_1-n_0$ for lithium together with the potential $u_2$ are shown in Fig. 2. In Table IV are listed the values of $Q_2$, $q_2$, $\mu_2$ and $s_2$; all charges

are negative, so that the ions in that shell are pushed away from the proton, in all materials. The comparison between the last two rows shows that the approximation of Eq. (11) is adequate. It is clear that the small value of $\lambda_2$ in Al is a consequence of the size of $Q_2$ and $q_2$: These charges are much smaller in Al than in the alkalis because the screening by the valence electrons is stronger in the former material. We conclude that in addition to different crystal structure an important feature which differentiates the lattice relaxations for Al hydrides and the alkalis, with the latter tending to large crystallographic distortions, is the lower valence density generally found in monovalent metals.

## ACKNOWLEDGMENTS

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[8]The damping function $\exp[-(q/q_0)^2]$, which may be introduced without theoretical difficulty because the behavior of the form factor at large $q$ is not accurately known, gives the practical advantage of making lattice sums rapidly convergent. We use the value $q_0 = 5.5k_F$.