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ENERGY OF AN INTERSTITIAL Li ION IN A SOLID ARGON CRYSTAL LATTICE

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ABSTRACT: A calculation was made for the energy of an interstitial Li ion in a crystal lattice of solid Ar. The method used is due to Hove and Krumhansl, in which the interaction energy is separated into serveral contributions: one of them corresponding to a semi-infinite crystal; another to a semi-infinite plane; and finally, a line of atoms. In order to describe the interaction potential between the Li ion and the Ar atoms we have used the method of Norgett and Lidiard. The contributions of each interaction potential (i.e., the semi-infinite solid, the plane and the line) to the total energy, are shown in separate tables. The use of Fourier transforms in the calculation of lattice sums is illustrated in the appendix.

A. INTRODUCTION

The energy of formation of crystal defects was first calculated by Mott and Littleton[1] many years ago. Since then the energy of formation of point defects in noble gas solids[2,3] and the energy of migration of inert gases in ionic crystals have been evaluated.[4] Also, the optical properties of substitutional impurities, such as H and Li in noble gas solids,[5] have been and are being studied. The interaction of the Li^+ ion with the inert gas atoms of the crystal is, however, a major uncertainity in all of these models, although a hypothesis on the nature of this interaction[4] has been experimentally verified.[6] For the computation of the parameters involved in our problem we have, therefore, made use of this hypothesis.

B. THE POTENTIALS

The conventional Born-Mayer form of the potential

$$b\,[1 + (Z_i/N_i) + (Z_j/N_j)]\,\exp\{(r_i + r_j - r)/\rho\} \tag{1}$$

may be used to describe the closed shell interactions between the ions i and j, a distance r apart, of an ionic lattice; Z_i and N_i are, respectively, the net charge and the number of electrons in the outermost filled shell of ion i. Because the data that would allow the deduction of the potential function for the ion-inert gas interaction is absent, we will assume true the function suggested in Ref. 4:

$$b'\exp\{(r_i + r_j - r)/\rho'\} \tag{2}$$

where b' and ρ' are independent of i and j.

For the van der Waals contribution to the energy expression, it is necessary to estimate the ion-inert gas interaction, which can be done by interpolation among the interionic interactions. The van der Waals potential is given by the usual sum of dipole-dipole and dipole-quadrupole terms:

$$-C_{ij}r^{-6} - d_{ij}r^{-8}\,. \tag{3}$$

The values of C_{ij} and d_{ij}, for the Li-Ar interaction, were obtained by the method of Ref. 4.

In contrast with the case of one noble gas atom in an alkali halide lattice, the polarization energy is important in our problem. We evaluate it by a method similar to that of Mott and Littleton.[1]

The polarization of the medium (at a large distance r from the charge Q) is

$$P = (Q/r^2)(1/4\pi)[1 - (1/K_0)]\,; \tag{4}$$

and from the definition of polarization

$$P = 4\mu_{\mathrm{Ar}}/d^3 \tag{5}$$

where

$$\mu_{\mathrm{Ar}} = \alpha_{\mathrm{Ar}} E \tag{6}$$

(μ_{Ar} is the dipole at a lattice point due to a Li^+ ion, d is the side of the cubic unitary cell, α_{Ar} is the polarizability of the Ar atom, and E is the electrical field), we obtain, using Eqs. 4, 5 and 6, the polarization energy

$$E_P = -\tfrac{1}{2} Q \sum_j (\mu_{\mathrm{Ar}}/r_j^2) = -(Q^2 d^3/32\pi)\,[1-(1/K_0)] \sum_j (1/r_j^4) \tag{7}$$

where K_0 is the dielectric constant and r_j denotes the distance of any lattice point from Q. The summations are over all the lattice points.

C. LATTICE SUMS

The lattice sums for potentials of the type given by Eqs. 2 and 3 are already known[2] for f.c.c. crystals. Here, we use a method (due to Hove and Krumhansl[7]) different from the customary ones[2] to obtain the contribution–resulting from the potentials in formulas 2 and 3 –for all the lattice points. This method gives the contributions of the diverse crystal planes interacting with an impurity atom. This information can be used to obtain some surface parameters in terms of the bulk properties of the crystal, and it is also valuable even if the point at which the interaction energy is to be evaluated, is not in the lattice. The computation of such sums, however, has been thoroughly done only for the Coulomb potential, important when estimating the relaxation energy of crystal defects.[8]

To find the interaction energy of the Li^+ ion with the atoms of the crystal, we first break the total energy into two parts:

$$A = 2B + C \tag{8}$$

where B and C are, respectively, the contributions of a semi-infinite crystal, whose (100) face is a unit distance away from the lattice point in question, and that from the (100) plane containing the lattice point. C is further broken up into

$$C = 2D + F \tag{9}$$

where D and F are, respectively, the contributions from the semi-infinite plane a unit distance away, and from the (1,0) line containing the lattice point.

For a face-centered cubic crystal with basis

$$[000;\ \frac{a}{2}\ \frac{a}{2}\ 0;\ \frac{a}{2}\ 0\ \frac{a}{2};\ 0\ \frac{a}{2}\ \frac{a}{2}],$$

the type A interaction is given by the potential $\phi_A(r)$:

$$\begin{aligned} \phi_A(r) = 2 \sum_{\ell_3=0}^{\infty} \Big\{ \sum_{\substack{m_1 m_2 \\ \text{even}}} [\exp(2\pi i (m_1 x_1 + m_2 x_2))] \times \\ \times [E_{\mu,\ell_3}(0) + E_{\mu,\ell_3}(\tfrac{1}{2})] + \sum_{\substack{m_1 m_2 \\ \text{odd}}} [\exp(2\pi i (m_1 x_1 + m_2 x_2))] \times \\ \times [E_{\mu,\ell_3}(0) - E_{\mu,\ell_3}(\tfrac{1}{2})] \Big\} \end{aligned} \tag{10}$$

where the interaction energy:

$$\begin{aligned} E_{\mu,\ell_3}(x_3^5) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\xi_1\, d\xi_2\, \epsilon \{ a [\xi_1^2 + \xi_2^2 + (z + \ell_3 + x_3^5)^2]^{\frac{1}{2}} \} \times \\ \times \exp[-2\pi i (m_1 \xi_1 + m_2 \xi_2)] \end{aligned} \tag{11}$$

(μ stands for the pair of integers m_1, m_2) is the double Fourier transform; while E_{m,ℓ_3} is a single Fourier transform of an individual interaction energy. They were obtained from the Foster and Campell tables.[9] m_1, m_2 are components of a general reciprocal vector, ℓ_3 is one of the components of the position vector of the unit cell, x_3^5 is one of the components of the position vector of an atom within the unit cell, while $z = -x_3$ denotes the normal -distance of a particle from a surface under it.

The interaction of type D for the same lattice is:

$$\phi_D = 2 \sum_{\ell_3=0}^{\infty} \sum_{\substack{m \\ \text{even}}} \exp(2\pi m x_1)(E_m \ell_3(0) + E_m \ell_3(\tfrac{1}{2})); \tag{12}$$

and the contribution of type F is

$$\phi_F = 2 \sum_{s=1}^{\infty} (\tfrac{1}{2} as)^{-n} \tag{13}$$

where n takes the values 4, 6 and 8. Using Eq. 2 we get

$$\phi'_F = 2 \sum_{s=1}^{\infty} b' \exp\{(r_i + r_j - \tfrac{1}{2} sa)/\rho'\}. \tag{14}$$

D. COMMENTS

Because the radius and polarizability of the Li^+ ion are very small when compared with those of other ions, the interaction energy found here for the Born-Mayer and van der Waals potentials, is about an order of magnitude less than that for other ions; whereas, the polarization energy we computed is close to the value, using an approximate calculation done by Jost.[10]

The double Fourier transforms for four different interaction potentials -when the Li^+ ion interacts with a semi-infinite solid- are given in Table 2. The single Fourier transforms for the same potentials, when the Li^+ ion interacts with a plane and with a line of atoms, are given, respectively, in Tables 3 and 4. In Table 5 the contribution to the total energy of each interaction potential is shown for the semi-infinite solid, the plane and line cases.

Finally, although the interaction potentials between ions of the families of Li and Ar have been previously considered,[4] no calculation similar to the one here presented has yet appeared.

APPENDIX

The double Fourier transform for the Born-Mayer potential is obtained here.

Let

$$\phi = b' \exp\{(r_i + r_j - r)/\rho'\} \tag{1}$$

where r_i and r_j are, respectively, the radius of the Li^+ ion and that of the Ar atom. The energy E_{BM}, corresponding to this potential interaction, will be

$$E_{BM} = \sum_K b' \exp\{(r_i + r_j - r_K)/\rho'\}, \tag{2}$$

TABLE 1

Numerical values of the constants employed in these calculations.

a (Å)	3.76
r_i (Ar) (Å)	1.57
r_j (Li^+) (Å)	.6
b' (ev)	0.159
ρ' (Å)	0.339
k_0	1.67
C_{ij} (erg cm^{-6})	7.5×10^{-60}
d_{ij} (erg cm^{-8})	7×10^{-76}
Z	.5
d (Å)	5.3
α (ev)	.0775

TABLE 2

Double Fourier transform $E_{\mu,0}$ of the individual interaction energy $\mathcal{E} = \lambda / r^n (n = 4, 6, 8)$ for the Born-Mayer potential.

n	$E_{000}(0)$	$E_{\mu,0}(0)$
4	$\alpha \pi Z^{-2}$	$\alpha 2\pi^2 (m_1^2 + m_2^2)^{1/2} Z^{-1} k_1 \left| 2\pi Z (m_1^2 + m_2^2)^{1/2} \right|$
6	$C_{ij}\, a^{-6} \frac{1}{2} \pi Z$	$C_{ij}\, a^{-6} \pi^3 Z^{-2} (m_1^2 + m_2^2) k_2 \left| 2\pi Z (m_1^2 + m_2^2)^{1/2} \right|$
8	$d_{ij}\, a^{-8} \frac{1}{3} \pi Z$	$d_{ij}\, a^{-8} \frac{\pi^4}{3} Z^{-3} (m_1^2 + m_2^2)^{3/2} k_3 \left| 2\pi Z (m_1^2 + m_2^2)^{1/2} \right|$
$B-M$		$\dfrac{a \left| 1 + 2\pi Z (m_1^2 + m_2^2 + (\frac{a}{2\pi\rho})^2 \right|^{1/2} \times \exp(-2\pi Z (m_1^2 + m_2^2 + (\frac{a}{2\pi\rho})^2)^{1/2}}{(2\pi)^2 \rho' (m_1^2 + m_2^2 + (\frac{a}{2\pi\rho})^2)^{3/2}}$

TABLE 3

Interaction energy ϕ of a plane of atoms (located at $x_3 = 0$ and extending from $x_3 = 0$ to infinity) with an atom at the point: $x_1 = x_2 = 0$, $z = -x_3$, assuming the individual interaction energy with a Born-Mayer potential.

n	$E_{00}(0)$	$E_{m0}(0)$
4	$\alpha \frac{\pi}{2} Z^{-3}$	$\alpha\pi \left\lvert 1 + 2\pi m Z \right\rvert Z^{-3} \cos(2\pi m x_1) \exp(-2\pi m Z)$
6	$\frac{3C_{ij}\, a^{-6} Z^{-5}}{4}$	$C_{ij}\, a^{-6}\, 2\pi^3 m^{5/2} Z^{-5/2} k_{5/2}(2\pi m Z) \cos(2\pi m x_1)$
8	$\frac{15 d_{ij}\, a^{-8} Z^{-7}}{24}$	$d_{ij}\, a^{-8} \frac{2}{3} \pi^4 m^{7/2} Z^{-7/2} k_{7/2}(2\pi m Z) \cos(2\pi m x_1)$
B-M		$\dfrac{2b \exp(\frac{r_i + r_j}{\rho'})\; 2Z\, k_1 (2\pi Z (m^2 + (\frac{a}{2\pi\rho'})^2)^{\frac{1}{2}})}{\pi\rho/a\,(m^2 + (\frac{a}{2\pi\rho'})^2)^{\frac{1}{2}}}$

TABLE 4

Interaction potential between one atom and a line of atoms. (Assuming, $\mathcal{E} = \lambda / r^{n}$ and a Born-Mayer potential).

ϕ_n'	ϕ_{B-M}'
$2\lambda (d)^{-n} \sum^{\infty} (\frac{\ell}{2})^{-n} \ell = 1$	$2b' \sum^{\infty} \exp(\frac{r_i + r_j - \frac{d}{2}}{\rho'}) \ell = 1$

TABLE 5

Different contributions to the total energy: the subscript denotes the type of interaction potential and the superscript indicates the semi-infinite solid (3), the plane (2), and the line (1) cases. All the energies are negative except for the Born-Mayer type.

ϕ_4^1	ϕ_4^2	ϕ_4^3	ϕ_4
.374	2.06	3.07	5.509
ϕ_6^1	ϕ_6^2	ϕ_6^3	ϕ_6
0.324	.159	.189	.3804
ϕ_8^1	ϕ_8^2	ϕ_8^3	ϕ_8
.00374	.038	.042	.0831
ϕ_{B-M}^1	ϕ_{B-M}^2	ϕ_{B-M}^3	ϕ_{B-M}
.056	.104	.544	.704

and we can write for the exp in Eq. 2, using the notation of Ref. 6,

$$\exp\,[-\alpha(\beta'^2 - p^2)^{1/2}]$$

with

$$\alpha = a/2\pi\rho, \qquad \beta' = 2\pi(\xi^2 + z^2)^{1/2}.$$

To replace the sum by two integrals, the first one being

$$I_1 = 2\pi\,\alpha(\xi_2^2 + z^2)^{1/2}\, K_1\,[\delta(\xi_2^2 + z^2)^{1/2}]\;[\pi(m_1^2 + \alpha^2)^{1/2}]^{-1} \tag{3}$$

where

$$\delta = 2\pi(m_1^2 + \alpha^2)^{1/2}$$

we do as follows:

Let

$$\xi^2 = -q^2/4\pi^2$$

then

$$I_1 = 2\pi\,\alpha\,[z^2 - (q^2/4\pi^2)]^{1/2}\, K_1\,[(\delta/2\pi)(z'^2 - q^2)^{1/2}] \times$$
$$\times\;[\pi(m_1^2 + \alpha^2)^{1/2}]^{-1} \tag{4}$$

where $z' = 2\pi z$ and K_1 is a Bessel function of the second kind with an imaginary argument.

Integrating I_1, we obtain:

$$\begin{aligned} I_2 &= \alpha(m_1^2 + \alpha^2)^{1/2}\,[\pi(m_1^2 + \alpha^2)^{1/2}]^{-1} \times \\ &\quad\times\,[1 + 2\pi(z + \ell_3 + x_3)\,(m_1^2 + m_2^2 + \alpha^2)^{1/2}] \times \\ &\quad\times\,\exp\,[-2\pi(z + \ell_3 + x_3)\,(m_1^2 + m_2^2 + \alpha^2)^{1/2}] \times \\ &\quad\times\,[z\,(m_1^2 + m_2^2 + \alpha^2)^{3/2}]^{-1} \end{aligned} \tag{5}$$

where we have replaced z by $(z + \ell_3 + x_3)$.

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RESUMEN

Se calcula la energía de un ión intersticial de Li en una red cristalina de Ar sólido. El método consistió en dividir el cristal en varias regiones y se calculó entonces la interacción de un ión con un sólido semi-infinito, con un plano semi-infinito y con una línea de átomos. Para describir el potencial debido a la interacción de un ión de Li^+ con uno de Ar, hemos usado el método de Norgett and Lidiard. Las diferentes contribuciones a la energía se presentan en tablas y en un apendice se ilustra para uno de los potenciales de interacción el uso de las transformadas de Fourier para el cálculo de sumas de la red.