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POLARIZATION OF RARE GAS ATOMS IN THE VICINITY OF SURFACES OF ALKALI HALIDE CRYSTALS

By

Kazuko HIGASHI,*) Hiroshi TATEWAKI*)
and Takashi NAKAMURA*)

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In this short note we provide some numerical material which supplements two previous papers[1,2] by two of the present authors (H. T. and T. N.). These papers, hereafter referred to as I and II, have dealt with the interaction potential of rare gas (RG) atoms with single-crystal surfaces of alkali halides (AH). This RG-AH interaction potential has been the subject of numerous theoretical studies since Lennard-Jones and Dent's article (1928).[3] A good account of the general features and theories of the interaction potentials of the RG-AH system or other systems of similar kinds have been given in a recent review article by Hoinkes[4] or in an earlier book by Steele.[5] The study of the RG-AH potential is of particular interest in connection with experiments of physisorption and molecular beam scattering by solid surfaces.[4,5]

The most well-known and widely used method for computing the RG-AH interaction potential is the pairwise summation calculation,[3~5] where we proceed as follows. First the most important contribution to the interaction potential is calculated by summing over all two-body interaction potentials such as the 12-6 or exp-6 potentials between the RG atom and the lattice ions of the AH crystals. In the vicinity of a surface of an ionic crystal there exists a strong static electric field arising from the charges of the lattice ions. Therefore the energy lowering ΔE due to the polarization of the RG atoms by this electric field is added to the sum of the two-body potentials to obtain the RG-AH interaction potential.[3,5]

The previous papers, I and II have concerned the calculation of this polarization energy ΔE. The customarily used formula for computing ΔE is

$$-\frac{1}{2}\alpha F^2, \qquad (1)$$

where α is the polarizability (or more exactly, the dipole polarizability) of the RG atom

*) Research Institute for Catalysis, Hokkaido University, Sapporo, 060 Japan

and F is the strength of the electric field at the center of the RG atom. The formula (1) is based on the assumption that the electric field F is homogeneous over the region occupied by the RG atom. As early as 1933, Lenel[6] cast some doubt upon the use of (1) for the reason that near a surface of an ionic crystal the electric field is far from being homogeneous. In I, it has been shown that the following correction term should be added to (1) in order to take care of the field inhomogeneity:

$$-\frac{1}{12}\alpha_Q(F_{xx}^2+F_{yy}^2+F_{zz}^2+2F_{xy}^2+2F_{yz}^2+2F_{zx}^2). \qquad (2)$$

In (2), α_Q is the quadrupole polarizability of the RG atom and F_{xx}, F_{xy}, $\cdots$, etc. are the gradients of the electric field at the center of the RG atom; *i.e.*, $F_{\alpha\beta}$ is the gradient in the β-direction ($\beta=x,y,z$) of the α-component F_α ($\alpha=x,y,z$) of the electric field $\vec{F}$. Thus we write

$$\Delta E=\Delta E_1+\Delta E_2, \qquad (3)$$

where ΔE_1 and ΔE_2 are the quantities given by (1) and (2), respectively.

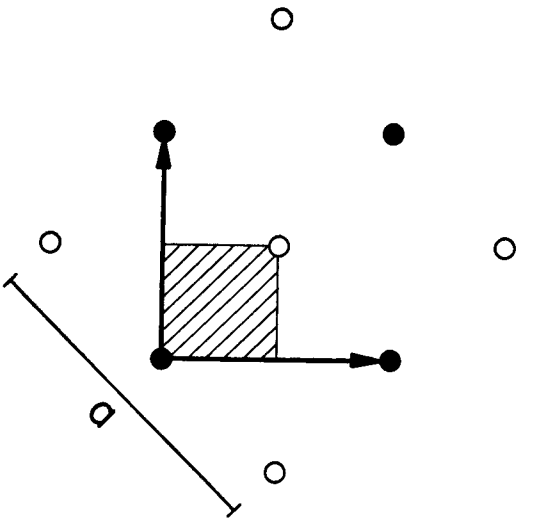

Fig. 1. Two-dimensional lattice of the (001) surface layer of a NaCl-type crystal (a, the lattice constant of the crystal).

We shall now look at some numerical results obtained for the Ar-NaCl system. The calculation method employed will be explained latter. The (001) surface of NaCl crystal is depicted in Fig. 1, where the array of anions (●) and cations (○) together with a two-dimensional unit cell determined by two primitive translation vectors (arrows), $\vec{a}_1$ and $\vec{a}_2$ are shown. The location of any anion in the surface atomic layer is given by

$$l_1\vec{a}_1+l_2\vec{a}_2,$$

and that of any cation by

$$\left(l_1+\frac{1}{2}\right)\vec{a}_1+\left(l_2+\frac{1}{2}\right)\vec{a}_2,$$

where l_1 and l_2 are integers. The hatched area in Fig. 1 is a quater of the unit cell. In Figs. 2 through 6 the variations of the electric field $\vec{F}$ and of the interaction energies ΔE_1 and ΔE_2 within this area are displayed. The variations in the remaining part of the unit cell are obvious because of the symmetry of the ionic array. In the following the coordinate axes are so chosen that the z-axis is perpendicular to the crystal surface and z is the distance from the surface lattice plane.

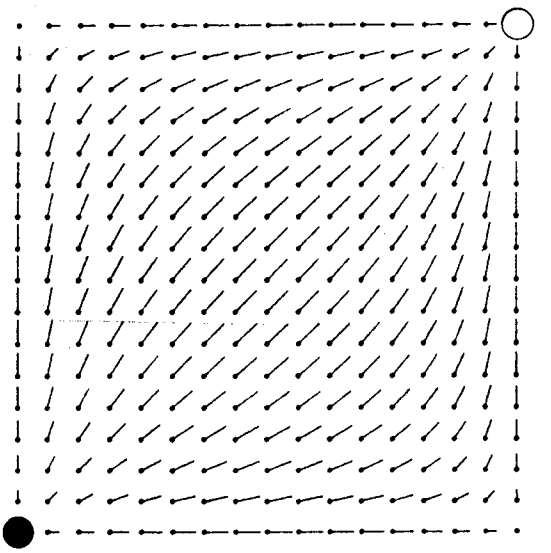

Fig. 2. Electric field (F_x, F_y) at 0.3 nm above the (001) surface plane of NaCl.

Figs. 2 through 4 clearly show the inhomogeneity of the electric field the Ar atom feels in the vicinity of the NaCl surface; *i. e.*, they demonstrate how the field changes as the atom moves parallel to the NaCl (001) surface at the distance of 0.3 nm from the surface. The dot-rod diagram, Fig. 2 illustrates the variation of the component parallel to the surface of the electric field; *i. e.*, the rods indicate the directions of the two-dimentional electric field vectors (F_x, F_y) computed at 17^2 mesh points (dots), the length of each rod being proportional to the square root of the length of the vector, $(F_x^2+F_y^2)^{\frac{1}{4}}$.*) Figs. 3 and 4 are contour maps of the z-component F_z and strength F,

*) The largest rod, found at the center of the figure, corresponds to an electric field vector of length, 2.80 V/nm. This dot-rod diagram and the contour maps in the present paper have been drawn by using Program Package ⟨PLOT79⟩ developed by H. V. McIntosh and N. H. F. Beebe.

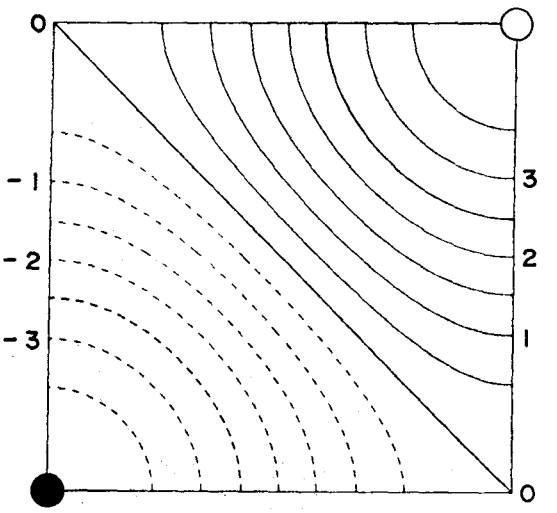

Fig. 3. Contour map of the electric field F_z at 0.3 nm above the (001) surface plane of NaCl. The values are in units of V/nm.

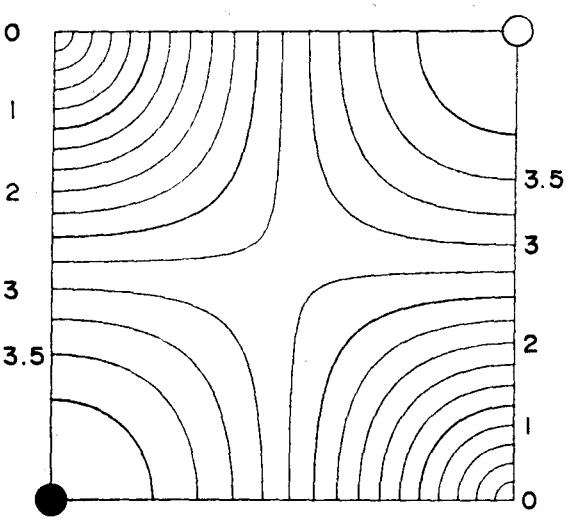

Fig. 4. Contour map of the electric field F at 0.3 nm above the (001) surface plane of NaCl. The values are in units of V/nm. House and Jaycock have given a very similar contour map in their article, ref. 7.

respectively, of the electric field. House and Jaycock[7] have pointed out that some authors used F_z^2 for $F^2=F_x^2+F_y^2+F_z^2$ in (1), which would lead to errors*) in calculating

*) See also p. I452 of II.

the polarization energy. The difference between F_2 and F is clearly shown in Figs. 3 and 4; among other things, F_2 vanishes along one of the diagonals of the square in Fig. 3.

As mentioned earlier, we are interested in how the electric field fluctuates in an area comparable to the size of the Ar atom. In Fig. 7 the size of the Ar atom is compared with the size of the square region considered in Figs. 2 though 4 (*i. e.*, the hatched region of Fig. 1). In drawing Fig. 7 the lattice constant a of NaCl and the radius of Ar have been taken to be 0.563 nm[8] and 0.192 nm (half of the nearest neighbor distance in Ar crystal[8]), respectively.

In Figs. 5 and 6, contour maps of the dipole polarization energy ΔE_1 and the quadrupole polarization energy ΔE_2 are given. The numerical values of the polarizabilities used here are:[2] $\alpha=1.63\ \text{A}^3$ and $\alpha_Q=1.957\ \text{A}^5$. These maps illustrates the conclusion of I and II that ΔE_2 is by no means negligible as compared with ΔE_1. Notice that ΔE_1 vanishes at two corners of the square (called Site C in II) but ΔE_2 does not.

In the pairwise summation calculation of the RG-AH interaction potential, we are faced with the evaluation of lattice sums of the form,

$$U(\vec{r}) = \sum_p C_p|\vec{r}-\vec{r}_p|^{-n} \qquad (4)$$

as a function of the coordinates $\vec{r}=(x,y,z)$. In (4), C_p is a constant, $\vec{r}_p$ is the coordinates of the p-th lattice site, n is a positive integer, and the summation is over all the lattice sites of a semi-infinite crystal. Hove and Krumhansl[9] have pointed out that the evaluation of (4) by a direct summation over the lattice sites is often very inconvenient if

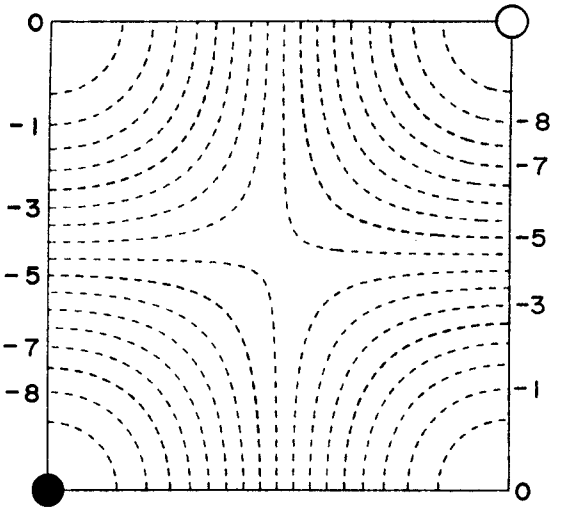

Fig. 5. Contour map of the dipole polarization energy ΔE_1 computed from (1) for Ar at 0.3 nm above the (001) surface plane of NaCl. The values are in units of meV.

good accuracy is desired. This is especially true for the case $n=1$, namely, the Coulomb potential case, which we have to deal with for calculating the electric field and its gradients in the vicinity of an ionic crystal surface. The evaluation of (4) for $n=1$ is

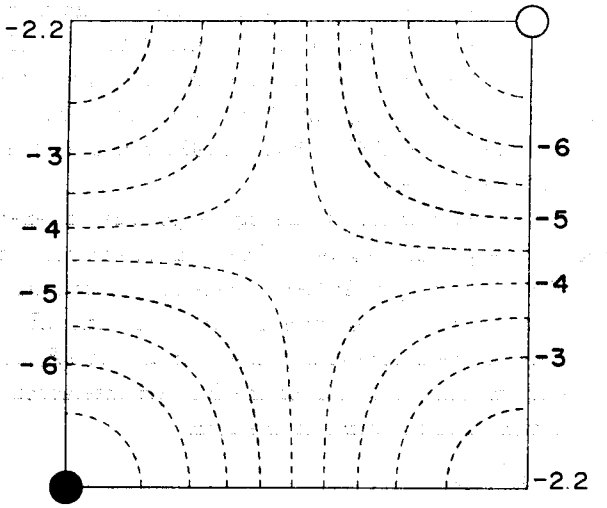

Fig. 6. Contour map of the quadrupole polarization energy ΔE_2 computed from (2) for Ar at 0.3 nm above the (001) surface plane of NaCl. The values are in units of meV.

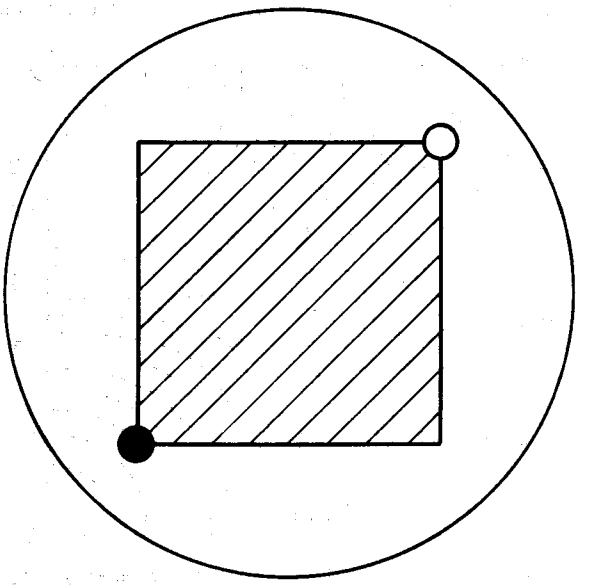

Fig. 7. Size of the Ar atom (circle) as compared with that of the hatched area in Fig. 1.

quite similar to the calculation of the Madelung constant for the Coulomb energy of an ionic crystal. It is well-known that the latter calculation has to be carried out carefully enough[8] (otherwise it would lead to unsatisfactory results). In general the use of the Fourier expansion method rather than the direct summation is efficient and desirable.[5,6,7,9,10]

The electrostatic potential at the location $\vec{r}$ near the surface of a semi-infinite NaCl crystal is given by the lattice sum (4) provided that we put $n=1$, $C_p=e$ for cation sites and $C_p=-e$ for anion sites. Let us consider the Fourier expansion of the lattice sum:

$$U(\vec{r}) = \sum_{\vec{G}} \exp(i\vec{G}\cdot\vec{r}_{/\!/})\, A(\vec{G}, z) \qquad (5)$$

where $\vec{G}$ is a two-dimensional reciprocal lattice vector and $\vec{r}_{/\!/}=(x, y)$. Assuming that the crystal surface is the (001) surface shown in Fig. 1, we write

$$\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2 \qquad (m_1 \text{ and } m_2 \text{ are integers}),$$

where $\vec{b}_1$ and $\vec{b}_2$ are vectors reciprocal to the primitive translation vectors, $\vec{a}_1$ and $\vec{a}_2$ shown in Fig. 1. We calculate the Fourier coefficient $A(\vec{G}, z)$ by the standard method,[5,9] and find

$$A(\vec{G}, z) = -\frac{4\pi e}{Ga^2}\left(1-(-1)^{m_1+m_2}\right)\frac{e^{-Gz}}{1+e^{-Ga/2}} \qquad \text{for} \quad \vec{G}\neq\vec{0}. \qquad (6)$$

Thus (6) vanishes if m_1+m_2 is even. We may take

$$A(\vec{0}, z) = 0$$

because of the neutrality condition for the crystal.[5]

Now that $U(\vec{r})$ of (5) with (6) gives the electrostatic potential, the expressions for the electric field are readily found by differentiating (5) with respect to the coordinates. The convergence of the series (5) is found very fast at $z=0.3$ nm and even more so at larger values of the distance z.

In the present study, numerical calculations and graphical plotting were carried out by using the facilities of the Hokkaido University Computing Center. We thank Mr. M. Chiba and Miss A. Hiratuka for their help.

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