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Pseudopotential Study of Bonding in the Zincblende and Rocksalt Structures*

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Abstract

The bonding nature of zincblende and rocksalt crystal structures are studied using pseudopotentials. NaCl and GaAs are used as prototypes and the characteristics of NaCl assumed to be in both crystal structures are studied. It is shown that the properties of the pseudopotential can be used to help predict crystal structure.

This paper reports an attempt to gain some understanding of the basic bonding properties of solids. It is well known that the covalent materials prefer tetrahedrally bonded structures whereas the more ionic compounds tend to crystallize in sixfold coordinated structures. However the cohesive energy differences are small. For example we can take an alkali halide, like sodium chloride and calculate[1] the cohesive energy of the crystal in the sixfold coordinated structure, including the short range repulsive energy ($\lambda e^{-r/R_o}$) only between nearest neighbors (R_o) and the Madelung[2] energy for the long range coulomb interaction. Using the same repulsive constants λ and r to calculate the cohesive energy of the crystal

for an assumed tetrahedrally bonded zincblende structure, the result shows that the cohesive energies differ by only 2% (the sixfold coordinated structure being the larger). If we had chosen potassium chloride, the cohesive energy would have been larger in the sixfold coordinated structure by about 1%. The theoretical calculation of the cohesive energies of the alkali halides in the sixfold coordinated structure by the above method agree with experimentally determined values to within about 2%.[1] From this consideration of cohesive energies alone, it is not at all obvious why the ionic alkali halides prefer the sixfold coordinated structure and not the tetrahedrally bonded structure.

Recently, using the empirical pseudopotential method (EPM), charge densities in real space have been computed for several semiconductors.[3] These results appear to yield considerable information about trends in the bonding behavior of the column IV, III-V, and II-VI semiconductors. The success of the above work has motivated us to investigate NaCl in a similar fashion.

Our calculations and discussion hinge on the idea of switching back and forth between the pseudopotential form factors in reciprocal space, V(G), and the crystal pseudopotential in the real space, $V_p(r)$. The relevant definitions and the algebra of the pseudopotential method will be reviewed here to make the subsequent discussions more transparent. The total pseudopotential $V_p(r)$ is assumed to be overlapping spherical atoms situated at the sites $R_{j\alpha}$, where j and α are respectively the lattice and basis index. Therefore,

$$V_p(\underset{\sim}{r}) = \sum_{j,\alpha} v_\alpha (\underset{\sim}{r} - \underset{\sim}{R}_{j\alpha}) \tag{1}$$

$$\underset{\sim}{R}_{j\alpha} = \underset{\sim}{R}_j + \underset{\sim}{\tau}_\alpha \tag{2}$$

where v_α is the atomic potential and $\underset{\sim}{\tau}_\alpha$ is the basis vector. In a crystal the pseudopotential may be expanded in reciprocal lattice vectors, $\underset{\sim}{G}$,

$$V_p(\underset{\sim}{r}) = \sum_{\underset{\sim}{G}} V(\underset{\sim}{G}) e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}} , \tag{3}$$

then

$$\begin{aligned} V(\underset{\sim}{G}) &= \frac{1}{N\Omega}\int V_p(\underset{\sim}{r}) e^{-i\underset{\sim}{G}\cdot\underset{\sim}{r}} d^3\underset{\sim}{r} \\ &= \sum_\alpha e^{-i\underset{\sim}{G}\cdot\underset{\sim}{\tau}_\alpha} \frac{1}{\Omega}\int v_\alpha(\underset{\sim}{r}') e^{-i\underset{\sim}{G}\cdot\underset{\sim}{r}'} d^3\underset{\sim}{r}' \\ &= \sum_\alpha S_\alpha(\underset{\sim}{G}) V_\alpha(\underset{\sim}{G}) , \end{aligned} \tag{4}$$

where

$$S_\alpha(\underset{\sim}{G}) = e^{-i\underset{\sim}{G}\cdot\underset{\sim}{\tau}_\alpha} \tag{5}$$

is the structure factor and

$$V_\alpha(\underset{\sim}{G}) = \frac{1}{\Omega}\int v_\alpha(\underset{\sim}{r}') e^{-i\underset{\sim}{G}\cdot\underset{\sim}{r}'} d^3\underset{\sim}{r}' \tag{6}$$

is the pseudopotential form factor connected to the αth atom, Ω is the primitive cell volume. The real space pseudopotential in equation (3) then becomes,

$$V_p(\underset{\sim}{r}) = \sum_{\alpha,\underset{\sim}{G}} S_\alpha(\underset{\sim}{G}) V_\alpha(\underset{\sim}{G}) e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}} . \tag{7}$$

In all the diamond, zincblende, and rocksalt structures, there is a basis of two atoms per lattice site; often it is convenient to express equation (7) in terms of symmetric and anticymmetric structure factors ($S^S(\underset{\sim}{G})$, $S^A(\underset{\sim}{G})$) and form factors ($V^S(\underset{\sim}{G})$, $V^A(\underset{\sim}{G})$). The symmetric terms are simply a sum of the structure factors for each α and the antisymmetric terms are the difference. Only a few discrete form factors $V_\alpha(\underset{\sim}{G})$ are needed to fit the band structure of a perfect crystal. If a smooth curve is drawn through the discrete points $V_\alpha(\underset{\sim}{G})$, one obtains the continuous Fourier transform of the atomic pseudopotential,

$$V_\alpha(\underset{\sim}{q}) = \frac{1}{\Omega} \int v_\alpha(\underset{\sim}{r}') e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}'} \, d^3\underset{\sim}{r}' \quad . \tag{8}$$

Equation (8) is particularly useful if one is concerned with interpolating $V_\alpha(\underset{\sim}{q})$ between the points of $V_\alpha(\underset{\sim}{G})$. With the further assumption that the atomic pseudopotential $v_\alpha(\underset{\sim}{r}-\underset{\sim}{R}_{j\alpha})$ in equations (6) and (8) is invariant to changes in crystal structure, the above algebra provides us with a simple scheme of obtaining the crystal pseudopotential in real space for any crystal structure and lattice desired. This is provided one has a set of form factors, $V_\alpha(\underset{\sim}{G})$ (alternately, $V^S(\underset{\sim}{G})$, $V^A(\underset{\sim}{G})$) and the lattice constant for the crystal of interest.

The band structure of NaCl has been calculated by the EPM.[4] In Figure 1 we plot the crystal pseudopotential $V_p(\underset{\sim}{r})$ in real space along a [100] direction in the rocksalt structure; $V_p(\underset{\sim}{r})$ is expressed in eV and $|\underset{\sim}{r}|$ is expressed in units of lattice constant a. If NaCl were to crystallize in the zincblende structure, an important question to ask is: what does

the potential $V_p(r)$ look like along the direction of a tetrahedral bond ([111] axis)?

To explore the above question, we need the lattice constant for the zincblende phase. Minimizing the short range repulsion plus Madelung energy will give the equilibrium nearest neighbor distance $R_o = 2.673$ Å for the zincblende NaCl. This implies a lattice constant $a = 4/\sqrt{3}\, R_o = 6.172$ Å. The nearest neighbor distance and lattice constant in rocksalt NaCl are 2.815 Å and 5.63 Å respectively. The solid line in Figure 2A displays the $V_p(\underset{\sim}{r})$ for the imaginary zincblende NaCl along the [111] direction. If d were the body diagonal of the unit cell, i.e. $d = \sqrt{3}\, a$, then the sodium will be situated at o and d and the chlorine atom at d/4. The distance $|\underset{\sim}{r}|$ in Figure 2A is expressed in units of the body diagonal, d. As a reference for the discussion of $V_p(\underset{\sim}{r})$ in the zincblende structure, the $V_p(\underset{\sim}{r})$ for GaAs, which actually crystalizes in the zincblende structure (with a lattice constant of 5.64 Å) is also computed. The EPM form factors for GaAs are obtained from Zucca, et al.[5] The $V_p(\underset{\sim}{r})$ for GaAs along the [111] direction is shown in Figure 2B.

The potential at and very near the atom site arises from pseudopotential form factors having large $\underset{\sim}{G}$ values, and therefore it is very sensitive to the behavior of the tail of $V_a(\underset{\sim}{q})$ in equation (8). For a band structure calculation which deals with the properties of the upper valence bands and the conduction bands, the inner core region is of little interest and the form factor is usually cut off at high G (i.e. $V(G^2 \geqq 16) = 0$), both to facilitate computation and to give a more uniquely defined set of

pseudopotential form factors. The cut off has some consequences for the present calculation. Since the reciprocal lattice vector $\underset{\sim}{G}$ is inversely proportional to the lattice constant, the tail region of $V_a(\underset{\sim}{q})$ is sensitive to the lattice constant chosen. To illustrate this, $V_p(\underset{\sim}{r})$ for the imaginary zincblende NaCl with a lattice constant identical to its rocksalt counterpart (a = 5.63 Å) is also computed, this $V_p(\underset{\sim}{r})$ is plotted as the dashed curve in Figure 2A. Note the change in shape at the inner cores of sodium and chlorine for the two lattice constants; note also the resemblance of this dashed curve to Figure 1, the $V_p(\underset{\sim}{r})$ for the rocksalt structure, in the inner core regions. Despite the absence of this structure for larger lattice constants we don't expect this region to affect the conclusions about bonding and we assume that for our purposes, we can neglect the region very close to the core in discussing the bonding of these crystals.

The charge density, $\rho(\underset{\sim}{r})$, for the sum of the valence electrons follows the potential $V_p(\underset{\sim}{r})$. Figure 2B for GaAs therefore predicts a piling up of valence electrons between Ga at 0 and As at d/4, slightly displaced towards As. On the other side of As, the potential rises, reaching a maximum barrier at 5/8d, the mid-point between As at d/4 and the next Ga at d along the body diagonal. This is characteristic of the diamond and zincblende crystals. One thus obtains a picture from the potential shown here that the valence electrons will tend to avoid the region between As (at d/4) and Ga (at d) and they will prefer to stay between As (at d/4) and Ga (at 0). In other words, the potential for GaAs favors a zincblende structure which is characterized by (1) tetrahedral

bonding and (2) an asymmetric positioning of As relative to the Ga atom in its own primitive cell (d/4 away) and the Ga atom in the next primitive cell along the body diagonal (3d/4 away).

On the other hand (Figure 2A), the potential for NaCl is seen to be generally not very repulsive between Cl at d/4 and Na at d by comparison to that of GaAs. The highest potential barrier moves from 5/8d to approximately 9/10d, i.e. very near the Na at d. The shape of the potential Figure 2A suggests that the upper valence electrons would tend to stay in the region near d/2 and this potential would not favor the "asymmetric" zincblende structure. The potential pushes charge to the Cl and gives an electronic configuration more consistent with the rocksalt structure. Another way of saying this is: GaAs bonds in the zincblende structure but NaCl antibonds in the zincblende structure. This can be seen by the charge pile up along the line from d/2 to d.

To understand the cause for the qualitative change in shape of the potential in going from GaAs to NaCl in the zincblende structure, we did the following calculation. Starting again with the EPM form factors, we forced $V_{Cl}(\underset{\sim}{G})$ and $V_{Na}(\underset{\sim}{G})$ to vanish separately. The resultant $V_p(\underset{\sim}{r})$ for each case is plotted respectively in Figures 3A and 4A. We then did a similar calculation for $V_{As}(\underset{\sim}{G})$ and $V_{Ga}(\underset{\sim}{G})$; these $V_p(\underset{\sim}{r})$ are plotted in Figure 3B and 4B. For NaCl, a rocksalt lattice constant for the zincblende structure of 5.63 Å rather than the calculated equilibrium value 6.172 Å is used. This choice of 5.63 Å is almost the same as the GaAs lattice constant 5.64 Å. This is convenient in a comparison of Figures 3A and B,

Figures 4A and B. The features in $V_p(\underset{\sim}{r})$ that give rise to bonding properties are not sensitive to the lattice constant chosen.

Figures 4A and 4B indicate what the crystal potential will look like if one were to leave the Na and Ga sites vacant respectively in the usual zincblende configuration. The two potentials have similar qualitative features. Figures 3A and B show the crystal potential if one would remove the Cl and As respectively from NaCl and GaAs. A striking feature of Figure 3A is the extremely large size of the sodium pseudopotential core. The Na potential becomes negative at and beyond its nearest neighbor, i.e. at the empty chlorine site. Ga has a much smaller pseudopotential core. The potential is negative near the bond site and becomes repulsive at and beyond the empty As site. The $V_p(\underset{\sim}{r})$ of NaCl in Figure 2A may be thought of as a superposition of Figure 3A and Figure 4A (see equation (1)). Similarly, the $V_p(\underset{\sim}{r})$ of GaAs in Figure 2B may be thought of as a superposition of Figure 3B and Figure 4B. It is then clear from Figure 4A that the extent of the sodium core plays a crucial role in giving rise to the antibonding character of NaCl in the zincblende structure.

In the rocksalt structure, a Cl ion has two symmetrically situated nearest neighbor Na ions. Hence the negative Na potential at the chlorine site results in a definite minimum potential at the chlorine core giving rise to an ionic crystal. In the zincblende structure, a Cl ion has its nearest neighbor Na ion at a distance of d/4 on one side; it also has another Na neighbor at a distance 3d/4 on the other side looking along a tetradedral bond (body diagonal) direction. The large repulsive core of the Na nearest

to Cl makes the potential between these nearest neighbors more repulsive than on the opposite side of the "bond." In fact the overall potential shows a dip on the opposite side of the "bond," or right side of the Cl in Figure 2A. Electrons will want to localize in this dip. The result will be an antibonding configuration.

The shape of a typical pseudopotential in Fourier space, $V_a(\underset{\sim}{q})$, usually resembles the potential shown in Figure 5. The value of $|\underset{\sim}{q}|$, where the curve crosses the zero potential, denoted by q_o, gives some indication of the size of the pseudopotential core. In Table I, we reproduce Cohen and Heine's tabulation[6] of q_o derived from both model and fitted pseudopotentials for elements ranging from column I to column VII in the periodic table. The alkali metals Li and Na indeed have exceptionally small q_o compared with elements in all other columns. The small q_o implies a large pseudopotential core. The pseudopotential core is physically different than the actual ionic core radius; these are 0.98 Å for Na^+ and 1.81 Å for Cl^-. It is more appropriate to think of the pseudopotential core as being related to the "electronegativity," which Pauling defines as "the power of an atom in a molecule to attract electrons to itself." In this sense, "crystal" would substitute for "molecule" in the present context. In Figure 3, the gallium and the sodium core potential are repulsive in the respective GaAs and NaCl crystals, whereas (Figure 4) the arsenic and chlorine potentials have an attractive core region crystals of GaAs and NaCl indicating that As and Cl are the more electronegative atoms in each crystal. The exceptionally large core size of the sodium pseudopotential

relative to atoms in all the other columns of the periodic table is related to the fact that the sodium atom has little affinity for valence electrons. This pseudopotential then gives rise to a metal in the Na element, but an insulator in the compounds like NaCl when it is coupled with the very electronegative chlorine.

Based on this investigation, we are led to conclude that the pseudopotential core size in the alkali metals is important to the favoring of the rocksalt crystal structure in the ionic alkali halides. Our conclusion is strengthened also by the following observation. The molecular orbital theory for chemical bonding[8] says an $A^N B^{8-N}$ crystal will have fourfold coordination when the s and p valence electrons hybridize to form sp^3 directed valence orbitals. Hybridization does not occur in the more ionic sixfold coordinated structure. If one were to look at the band structure of NaCl,[4] indeed one finds the s band is well separated from the three p bands and all valence bandwidths are narrow. When NaCl is assumed to be in the zincblende structure and its energy bands are calculated using the EPM, the above features of the bands remain. There is a narrow s band well separated from the three narrow p bands, i.e. little hybridization occurs when the change in crystal structure is imposed.

In conclusion, it appears that it is possible to investigate the bonding properties of compounds through studies of the pseudopotentials of the elements making up the compounds. Since the charge density reflects the properties of the potential, it is possible to predict qualitatively the bonding nature of the charge density without calculating the charge density.

This latter idea was checked by direct computation in several cases and found to be true. The scheme presented here indicates that it is possible to use a catalogue of real space pseudopotential curves extracted from experiment for elements to make some predictions of the crystal structure of compounds made from these elements.

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8. See for example A. Streitwiesser, Jr., Molecular Orbital Theory (John Wiley and Sons, Inc., New York, 1961).

Table I

q_o (atomic units)

	Model Potential	Fitted Pseudopotential
Li	0.91	---
Na	0.87	0.97
Be	1.44	---
Mg	1.13	1.13
Zn	1.42	1.42
Cd	1.28	1.28
Hg	1.27	1.33
B	1.87	---
Al	1.35	1.38
Ga	1.40	1.49
In	1.32	1.43
Tl	1.39	---
C	2.25	---
Si	1.50	1.53
Ge	1.53	1.60
Sn	1.42	1.46
Pb	1.47	1.50
P	1.64	1.68
As	1.63	1.65
Sb	1.48	1.57
Bi	1.45	1.70
O	---	2.00
S	---	1.77
Se	1.67	1.75
Te	1.53	1.64
Cl	---	1.70

Table Caption

Table I Values of q_o in atomic units for the Model Potentials and the Fitted Pseudopotentials.

Figure Captions

Figure 1: Pseudopotential $V_p(\underset{\sim}{r})$ along the [100] axis for NaCl in the rocksalt crystal structure.

Figure 2: Pseudopotential $V_p(\underset{\sim}{r})$ along the [111] axis for (A) NaCl and (B) GaAs in the zincblende crystal structure. The solid line in (A) corresponds to a lattice constant of 6.172 Å; the dashed line is for a lattice constant of 5.63 Å. In 2B the Ga potential is at 0 and d.

Figure 3: Pseudopotential $V_p(\underset{\sim}{r})$ along the [111] axis for (A) NaCl (setting $V_{Cl} = 0$) and (B) GaAs (setting $V_{As} = 0$) in the zincblende crystal structure.

Figure 4: Pseudopotential $V_p(\underset{\sim}{r})$ along the [111] axis for (A) NaCl (setting $V_{Na} = 0$) and (B) GaAs (setting $V_{Ga} = 0$) in the zincblende crystal structure.

Figure 5: Schematic shape of a typical pseudopotential V(q), showing the limit at q = 0, the q_o where it crosses the axis, the maximum point at q_m, and the characteristic tail off to zero at q_c. In fitting band structure data it is often desirable to use a form cutoff at q_t.

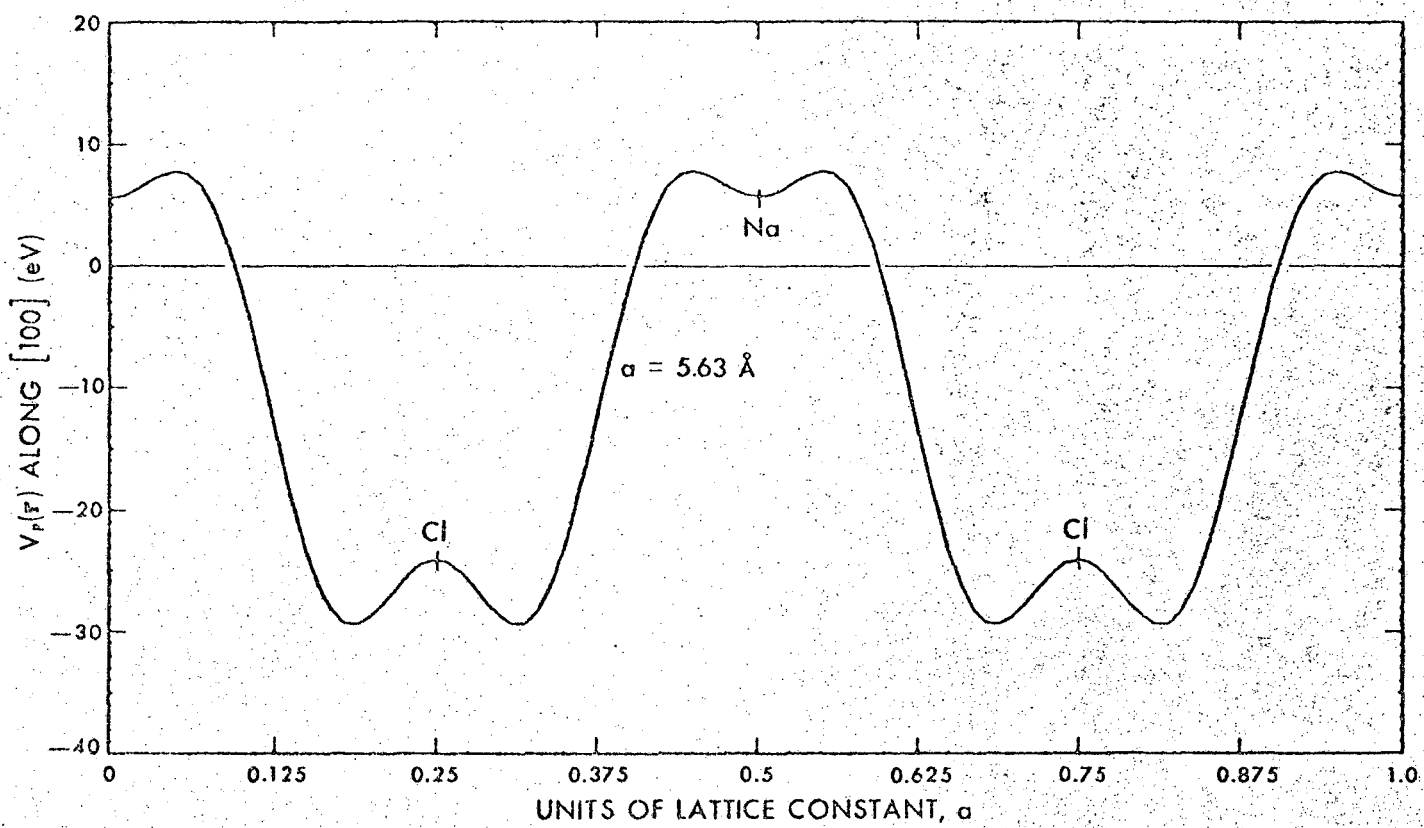
20
10
0
−10
−20
−30
−40
$V_p(\vec{r})$ ALONG [100] (eV)
Na
a = 5.63 Å
Cl
Cl
0
0.125
0.25
0.375
0.5
0.625
0.75
0.875
1.0
UNITS OF LATTICE CONSTANT, a

Figure 1

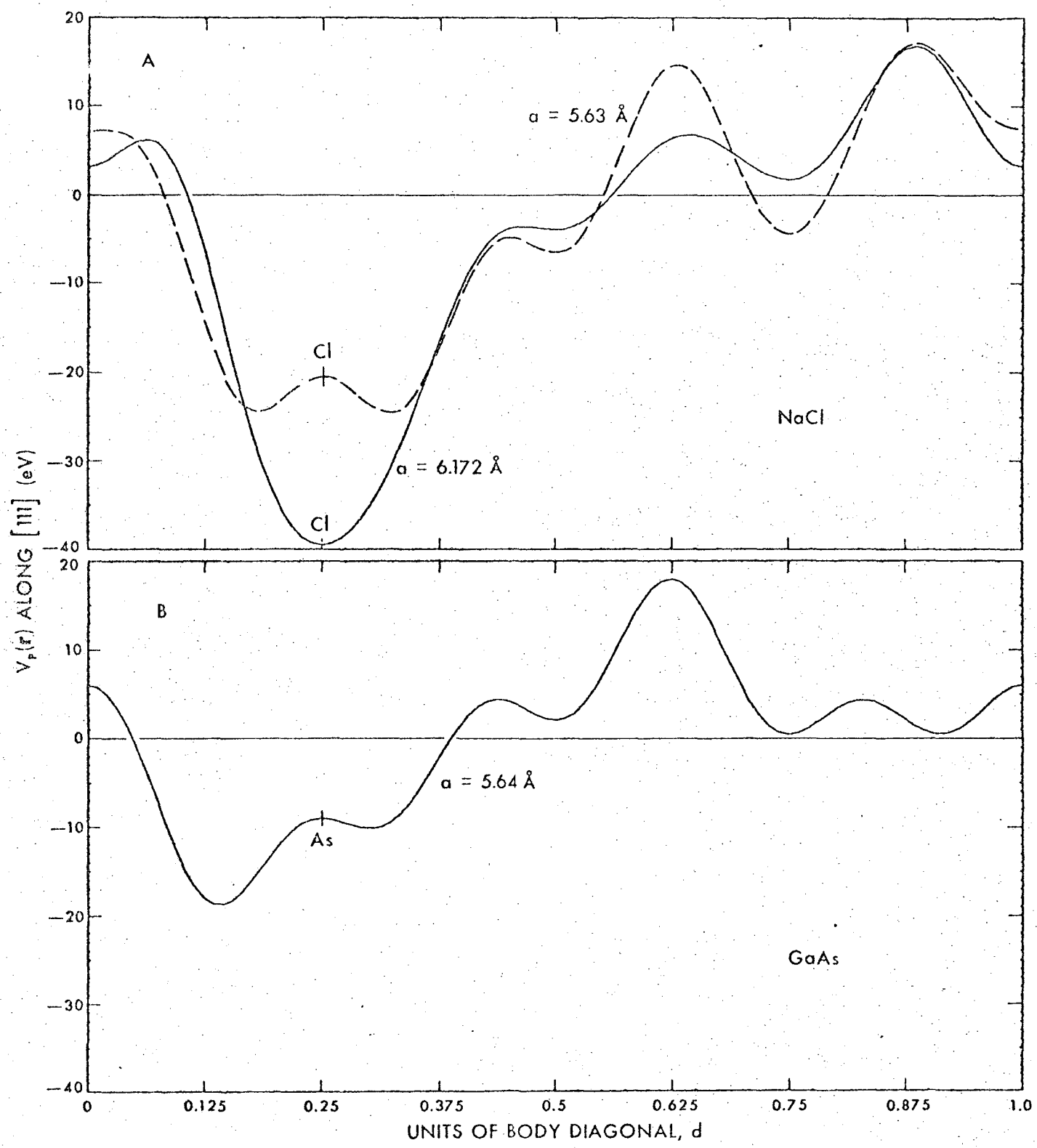
A
a = 5.63 Å
a = 6.172 Å
Cl
Cl
NaCl
B
a = 5.64 Å
As
GaAs
$V_p(r)$ ALONG [111] (eV)
UNITS OF BODY DIAGONAL, d
20
10
0
−10
−20
−30
−40
0
0.125
0.25
0.375
0.5
0.625
0.75
0.875
1.0

Figure 2

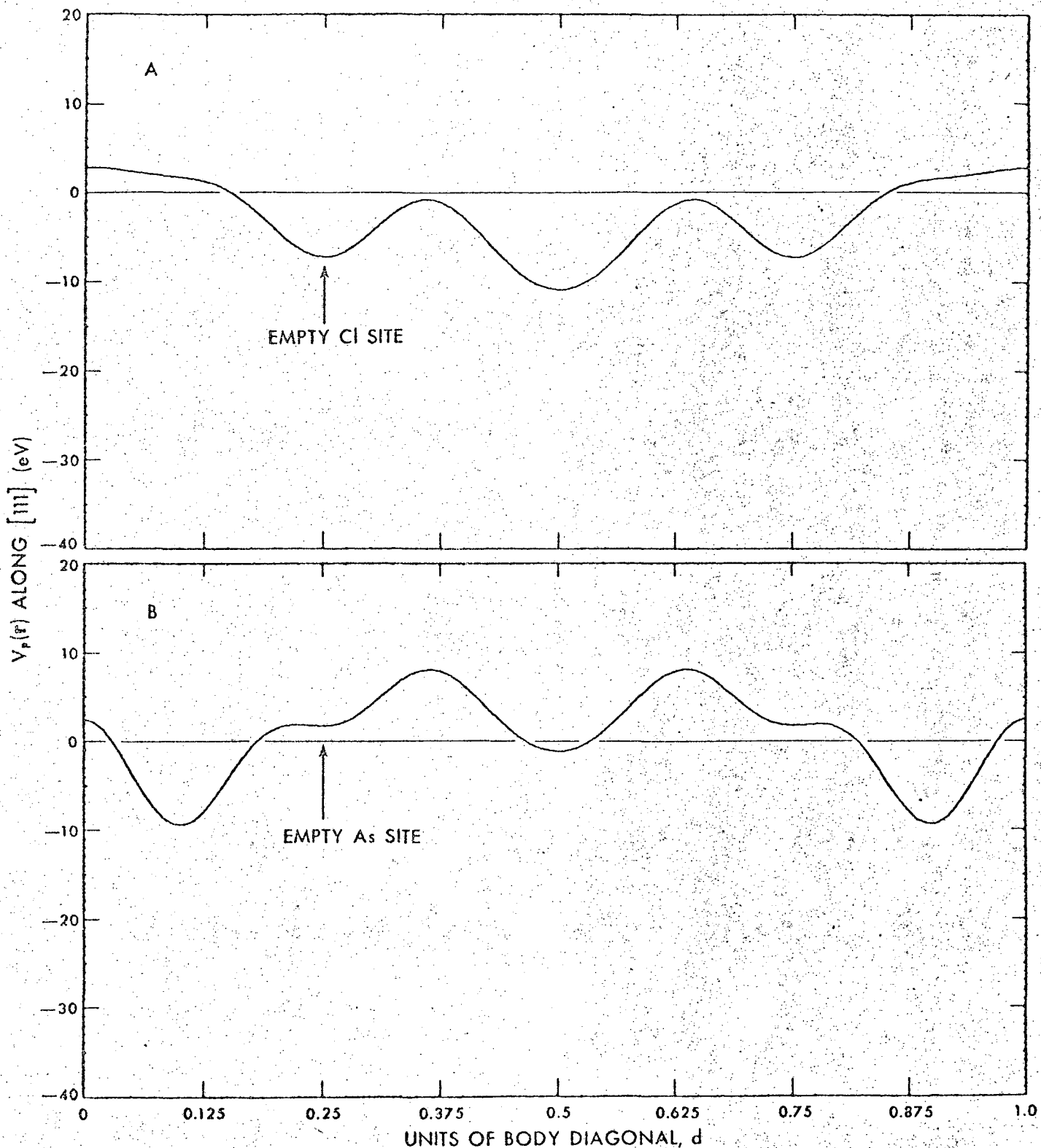
A
B
EMPTY Cl SITE
EMPTY As SITE
$V_p(\mathbf{r})$ ALONG [111] (eV)
UNITS OF BODY DIAGONAL, d
20
10
0
−10
−20
−30
−40
0
0.125
0.25
0.375
0.5
0.625
0.75
0.875
1.0

Figure 3

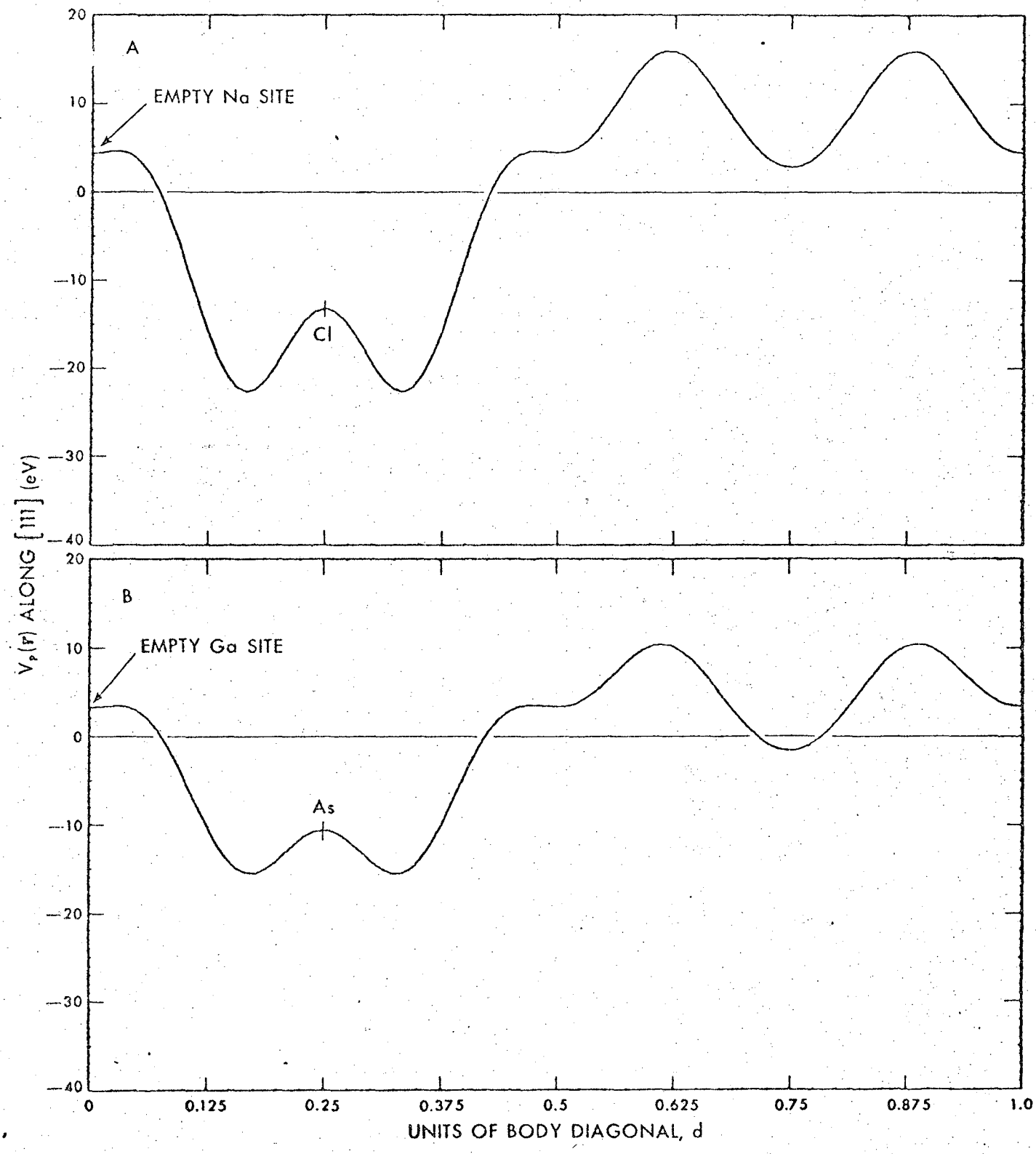
A
EMPTY Na SITE
Cl
B
EMPTY Ga SITE
As
$V_p(r)$ ALONG [111] (eV)
20
10
0
−10
−20
−30
−40
0
0.125
0.25
0.375
0.5
0.625
0.75
0.875
1.0
UNITS OF BODY DIAGONAL, d

Figure 4

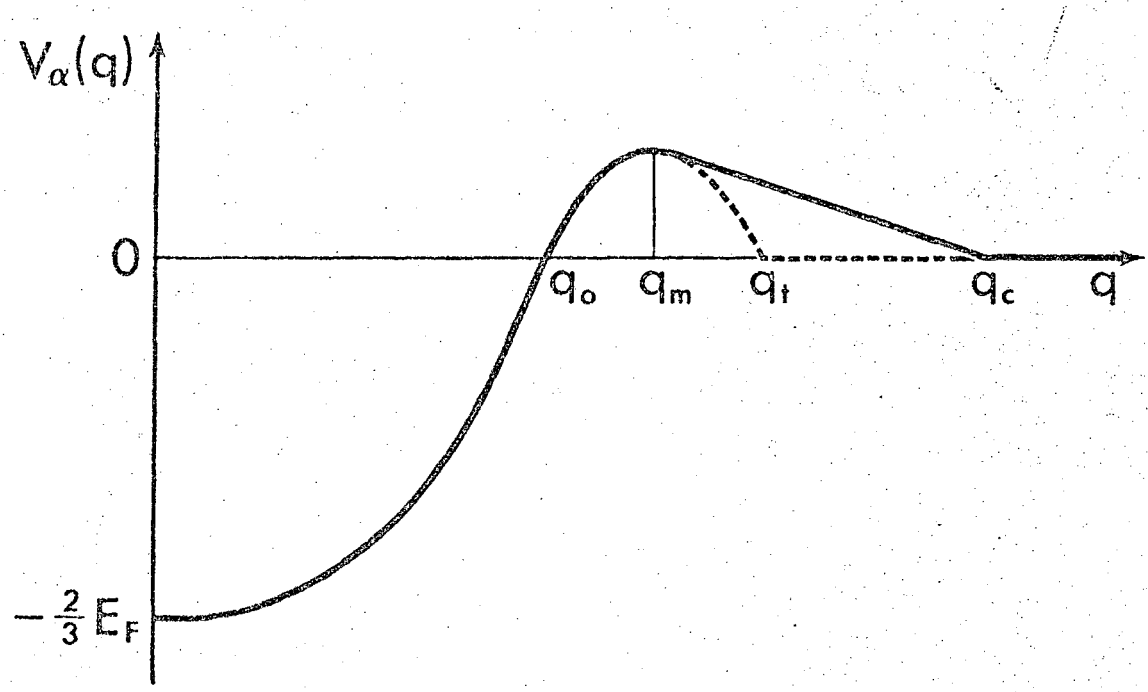

Figure 5

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