

Crystalline cluster model for ionic solids: NaCl*

Luiz M. Brescansin

Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Caixa Postal 1170, Campinas, Brazil

Luiz G. Ferreira

Instituto de Física, Universidade de São Paulo, Caixa Postal 20.516, São Paulo, Brazil

(Received 14 March 1979)

A crystalline cluster model for ionic crystals is presented, in the large context of the self-consistent-field multiple-scattering method, by imposing that the cluster potential has the same features as the crystal potential. The model is particularly investigated with respect to NaCl, and the results are compared with those of a conventional cluster calculation. It is seen that the main features of the electronic structure emerge from the occupied cluster states and the obtained results of our model provide a good interpretation of experimentally observed properties, e.g., the experimental one-electron spectrum.

I. INTRODUCTION

Self-consistent band-structure calculations usually require a large amount of computational work. For this reason, it is becoming increasingly popular to calculate crystalline properties by using small clusters of atoms arranged as in the crystal.¹⁻³ The cluster method can also be used to describe localized states of impurities in crystals^{4,5} and in some cases seems to be much better than the description of such states in terms of Bloch-wave expansions.

The ability of a cluster to describe a crystal depends on how well the occupied crystal orbitals can be localized in small volumes. The localized crystal orbitals are Wannier states⁶ whose spread in space is inversely proportional to the energy band gaps.⁷ Thus, one may expect to obtain a good cluster description in insulators and large-gap semiconductors.

The present work began from a simple hypothesis: large clusters should yield a better description than small clusters for a good insulator as NaCl. A self-consistent-field (SCF) cluster calculation for this material with one central Cl atom and six neighboring Na atoms gave a band gap of 8.65 eV, a quite remarkable result. Thus, we had a strong reason to suspect that clusters with more atoms, such as the $1\text{Cl}^- 6\text{Na}^+ 12\text{Cl}^- 8\text{Na}^+$, should yield even better results. Our expectations turned out to be wrong, as reported in Sec. II. On the other hand, a restudy of the cluster method showed us what was the origin of the errors, and how to correct them. This is reported in Sec. III and the results are shown therein.

II. CONVENTIONAL CLUSTER MODEL

A. Method

The conventional self-consistent multiple-scattering $X\alpha$ method of Slater and Johnson was ap-

plied to NaCl clusters. This method has been successfully applied to many molecular systems and is described in detail elsewhere.⁸⁻¹⁰ The method assumes the muffin-tin approximation for the cluster potential, in which the potential is spherically averaged inside the spheres surrounding the cluster constituent atoms, volume averaged in the region between the atomic spheres, and is again spherically averaged in the extramolecular region. The exchange parameters α for Na and Cl were taken from Schwarz's compilation¹¹:

$$\alpha_{\text{Na}} = 0.731, \quad \alpha_{\text{Cl}} = 0.723,$$

and, for the extramolecular region, a weighted average was used, resulting in

$$\alpha_{\text{out}} = 0.727.$$

The cluster model used by us consists of a central atom, six nearest neighbors, 12 next-nearest neighbors, and eight third-order neighbors, oriented in an octahedrally coordinated configuration. We used two clusters to represent the NaCl perfect crystal: one with the ion Na^+ as the central atom ($1\text{Na}^+ 6\text{Cl}^- 12\text{Na}^+ 8\text{Cl}^-$) and one with the ion Cl^- as the central atom ($1\text{Cl}^- 6\text{Na}^+ 12\text{Cl}^- 8\text{Na}^+$). Due to the charge unbalance of minus or plus one electron in each cluster, they were neutralized by distributing a charge of plus or minus one electron in the Watson sphere.¹²

The radii of the atomic and outer spheres are shown in Table I. The atomic radii were chosen so that the non-self-consistent molecular potential of the Na^+ ion, along the Na^+-Cl^- direction, was equal to the potential of Cl^- . As the ion cluster potential depends on its neighborhood, it follows that the Na^+ and Cl^- radii, calculated by this criterion, are different in the two Na^+ -centered and Cl^- -centered clusters. The radius of the surrounding outer sphere was chosen so that it touched the cluster atomic spheres. The secular

TABLE I. Radii of atomic and outer spheres of the two three-shell conventional clusters of NaCl crystal (atomic units).

Sphere	Radius (a.u.)	
	1Na ⁺ 6Cl ⁻ 12Na ⁺ 8Cl ⁻	1Cl ⁻ 6Na ⁺ 12Cl ⁻ 8Na ⁺
Central sphere	2.5398	2.8508
Nearest-neighbor sphere	2.7890	2.4780
Next-nearest-neighbor sphere	2.5398	2.8508
Next-next-nearest-neighbor sphere	2.7890	2.4780
Outer sphere	12.0188	11.7078

determinant was formed using partial waves of angular momenta

$$l = 0, 1, 2, 3$$

for the outer sphere, and

$$l = 0, 1$$

for the atomic spheres, as the Na⁺ and Cl⁻ ions have only *s*- and *p*-type orbitals.

During the self-consistent procedure the core electrons of the first and second shells were frozen, and only the third-shell electrons were permitted to relax. The Na⁺-centered cluster has 112 valence electrons while the Cl⁻-centered cluster had 104. Both clusters have 270 core electrons.

B. Results

The self-consistent energy spectra of the 1Na⁺ 6Cl⁻ 12Na⁺ 8Cl⁻ and 1Cl⁻ 6Na⁺ 12Cl⁻ 8Na⁺ clusters representing a perfect NaCl crystal are shown in Fig. 1. The energy levels are labeled according to the irreducible representations of the point group *O_h*. The electron distributions for

these cluster are shown in Table II. They include atomic core electrons.

Due to the strong ionic character of the crystal, the cluster orbitals are well localized inside the atomic spheres, thus permitting an easy identification of the occupied orbitals. Then the band gap is the energy difference between the first unoccupied state and the last occupied valence state. The band gap turns out to be 4.88 eV for the Na⁺-centered cluster and 5.51 eV for the Cl⁻-centered cluster, values which are much smaller than the experimentally observed gap of 8.97 ± 0.07 eV.¹³ The reason for this failure may be understood as follows. Due to different environments, chemically identical atoms have different self-consistent potentials in the cluster. Figure 2 is a schematic plot of the Cl⁻-centered cluster potential along the direction of the touching spheres. The figure shows that the potentials of the central Cl⁻ ion and first Na⁺ shell are, respectively, deeper than those of the second (Cl⁻) and third (Na⁺) shells. Following these potential differences, there is an electronic charge migration from the outermost Na⁺ and Cl⁻ spheres to the innermost spheres. Also due to the potential differences,

TABLE II. Charge distributions of the conventional clusters 1Na⁺ 6Cl⁻ 12Na⁺ 8Cl⁻ and 1Cl⁻ 6Na⁺ 12Cl⁻ 8Na⁺ expressed in number of electrons per sphere. For the interatomic and extramolecular regions the total number of electrons is given. The self-consistent potential (Ry) is also shown.

Atom	1Na ⁺ 6Cl ⁻ 12Na ⁺ 8Cl ⁻	1Cl ⁻ 6Na ⁺ 12Cl ⁻ 8Na ⁺
Central atom	10.1984	17.0870
Nearest-neighbor atom	16.9173	10.1092
Next-nearest-neighbor atom	10.1176	16.9000
Next-next-nearest-neighbor atom	16.7002	10.0680
Extramolecular region	0.6198	0.2586
Interatomic region	14.3477	12.2444
Interatomic constant potential	-0.4850	-0.4850

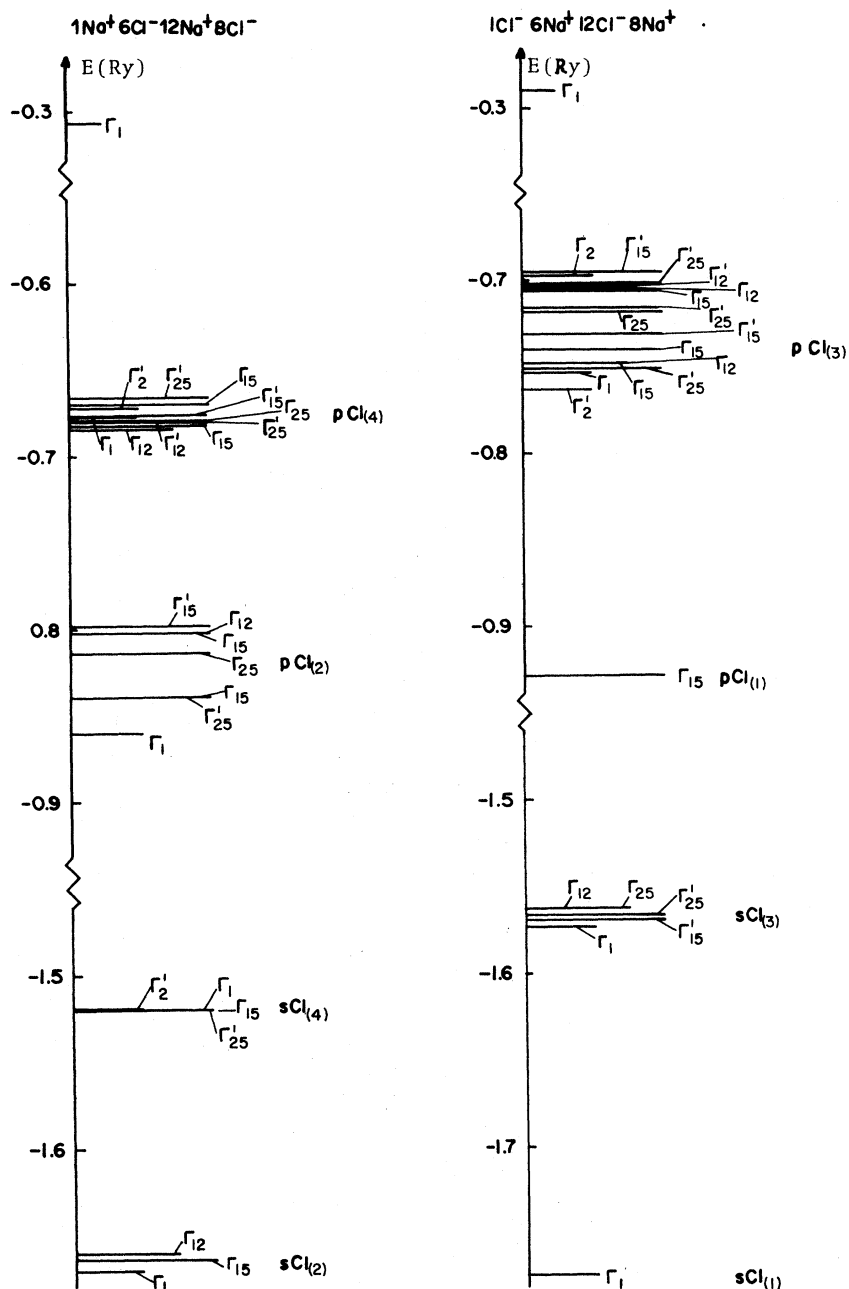


FIG. 1. Energy levels (rydbergs) of 3s and 3p Cl valence states and first conduction state for the conventional clusters $1\text{Na}^+ 6\text{Cl}^- 12\text{Na}^+ 8\text{Cl}^-$ and $1\text{Cl}^- 6\text{Na}^+ 12\text{Cl}^- 8\text{Na}^+$. $\text{Cl}_{(1)}$, $\text{Cl}_{(2)}$, $\text{Cl}_{(3)}$, and $\text{Cl}_{(4)}$ mean the Cl orbitals of the central ion, first, second, and third shells of the cluster, respectively.

the energy levels corresponding to the Cl^- orbitals of the second shell lie between the valence levels of the Cl^- central ion and the orbital corresponding to the Na^+ ion (the conduction energy state). Thus, whenever molecular clusters of ionic materials made up by more than one shell of atoms are investigated, the identification of the crystal band edges from the cluster spectrum turns out to be misleading and one gets an energy gap much smaller than the experimental one. On

the other hand, the valence-band width of the NaCl crystal, which is an interesting feature of its energy-level structure, is also not properly described by this method: One sees from Fig. 1 that the states are spread too much in energy.

The failure reported above motivated the work described in Sec. III. As will be seen shortly, the main idea is to make the cluster potential as periodic as possible, thus avoiding the effect sketched in Fig. 2.

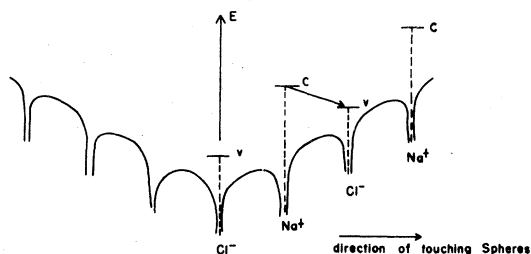


FIG. 2. Schematic profile of the potential in a conventional cluster of an ionic crystal. v and c designate, respectively, a valence and a conduction state centered at the ion. The figure explains the shrinkage of the gap in the energy spectrum.

III. CRYSTALLINE CLUSTER MODEL

A. Method

We show in this section the modifications to be introduced in the conventional SCF- $X\alpha$ multiple-scattering method with which the one-electron cluster potential acquires crystalline properties. Among the many Na^+ and Cl^- atoms of the cluster, we select two atoms as representatives of the families. Practically, the selected atoms are the innermost of the cluster. Let

$$n_p(r)$$

be the electronic density of the representative of the family of atoms p . Let b_p be its sphere radius. A perfect crystal made up of atoms identical to the representatives would have an average electronic density n_{II} in the intersphere region given by

$$\Omega_{\text{II}} n_{\text{II}} = \sum_p Z_p - \sum_p 4\pi \int_0^{b_p} r^2 n_p(r) dr, \quad (1)$$

where Z_p are the proton numbers and Ω_{II} is the intersphere volume in the unit cell of the crystal.

The determination of the crystal Coulomb potential due to densities

$$n_p(r),$$

inside the spheres, and n_{II} in the intersphere region, is a solved classical problem. One considers two charge distributions. The first has neutral spheres with electronic densities

$$n_p(r) - n_{\text{II}}$$

and proton numbers equal to

$$Z_p - B_p.$$

Since the spheres are neutral, one has

$$Z_p - B_p = 4\pi \int_0^{b_p} r^2 n_p(r) dr - \frac{4\pi}{3} b_p^3 n_{\text{II}}, \quad (2)$$

from which one determines the values of B_p . The second charge distribution has a uniform electronic density n_{II} and nuclei with B_p protons. The potential due to this latter distribution is determined by the Ewald method.¹⁴ The sum of the potentials due to the two distributions has the following expressions.

(i) Inside the sphere p ,

$$v_p(r) = -\frac{2Z_p}{r} + \frac{8\pi}{r} \int_0^r r'^2 n_p(r') dr + 8\pi \int_r^{b_p} r' n_p(r') dr - 4\pi b_p^2 n_{\text{II}} - 2 \sum_q B_q M(\vec{R}_{pq}), \quad (3)$$

(ii) In the intersphere region,

$$V_{\text{II}} = \frac{8\pi}{\Omega_{\text{II}}} \sum_p \left(\frac{B_p b_p^2}{2} + \frac{2\pi}{15\Omega} b_p^5 \sum_q B_q + \frac{b_p^3}{3} \sum_q B_q M(\vec{R}_{pq}) \right), \quad (4)$$

where \vec{R}_{pq} is the radius vector from nucleus p to nucleus q , both in the unit cell, and

$$M(0) = \lim_{G \rightarrow \infty} \left(\frac{4\pi}{\Omega} \sum_{\vec{g} \neq 0} \frac{e^{-\vec{g}^2/4G^2}}{g^2} - \frac{\pi}{G^2 \Omega} - \frac{2G}{\sqrt{\pi}} \right), \quad (5a)$$

$$M(\vec{R}) = \lim_{G \rightarrow \infty} \left(\frac{4\pi}{\Omega} \sum_{\vec{g} \neq 0} \cos \vec{g} \cdot \vec{R} \frac{e^{-\vec{g}^2/4G^2}}{g^2} - \frac{\pi}{G^2 \Omega} \right) \quad (5b)$$

are Madelung-like constants expressed as sums in the reciprocal-lattice vectors \vec{g} , and where Ω is the volume of the unit cell.

Once the crystal potential is calculated, we select a piece of the crystal, the cluster, and envelop it with a sphere outside which we set the potential equal to zero. As a matter of fact, it is convenient to set the outside potential equal to a positive constant sufficiently higher than the intersphere potential V_{II} so as to avoid the cluster electrons escaping outside the enveloping sphere. The value of the positive constant is irrelevant and a few Rydbergs will do.

B. Results

We have selected to investigate two Cl^- -centered clusters whose geometric parameters are presented in Table III. The two clusters are of the type $1\text{Cl}^- 6\text{Na}^+ 12\text{Cl}^- 8\text{Na}^+$ and differ by the sphere radii. Cluster $\text{Cl}^- 1$ has radii proportional to ionic radii, while in cluster $\text{Cl}^- 2$ the radii are chosen to minimize the integrated

$$\int [v(\vec{r}) - \bar{v}(\vec{r})]^2 d\vec{r}$$

squared deviation of the potential $v(\vec{r})$ from its muffin-tin average $\bar{v}(\vec{r})$. The α parameters for

TABLE III. Radii of atomic and outer spheres of the two three-shell crystalline clusters of NaCl crystal (atomic units).

Sphere	Radius	
	Cluster Cl ⁻ 1	Cluster Cl ⁻ 2
Cl ⁻ central sphere	3.4580	2.9308
Na ⁺ internal sphere	1.8708	2.3980
Cl ⁻ external sphere	3.4580	2.9308
Na ⁺ external sphere	1.8708	2.3980
Outer sphere	11.1006	11.6278

Na⁺, Cl⁻, and the outer-sphere region are the same as in the conventional cluster calculation.

The self-consistent energy spectra of the clusters Cl⁻ 1 and Cl⁻ 2 are shown in Fig. 3. The energy levels are labeled according to the irreducible representations of the octahedral point group O_h . The 104 valence electrons fill the valence levels up to the last Γ_{15} level and there is no difficulty in identifying the crystal energy gap as the difference between the first unoccupied state and the last Γ_{15} valence state. The energy gap found in this way is 9.29 eV in the Cl⁻ 1 cluster and

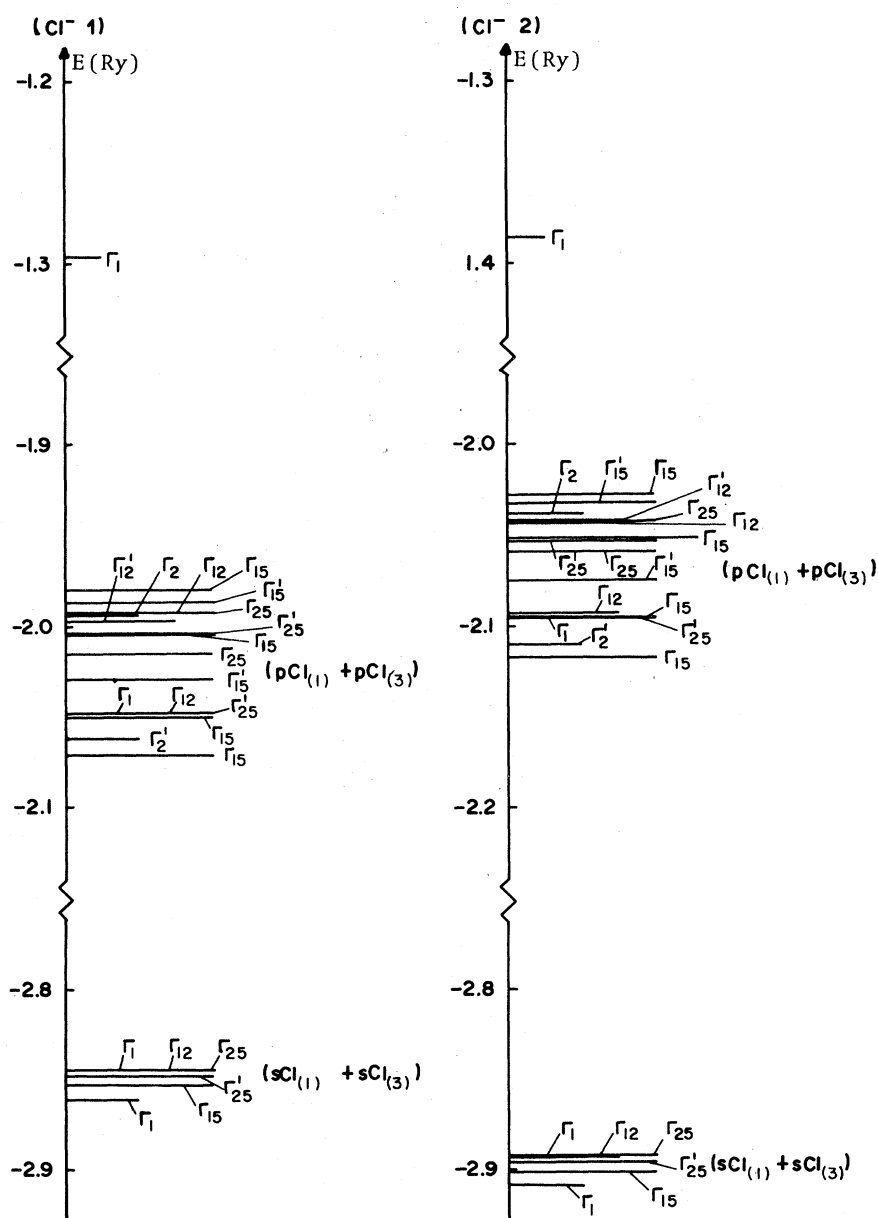


FIG. 3. Energy levels (rydbergs) of the valence states and first conduction state for the crystalline clusters Cl⁻ 1 and Cl⁻ 2. Both clusters are of the type 1Cl⁻ 6Na⁺ 12Cl⁻ 8Na⁺ but have spheres with different radii. The energy zero was arbitrarily chosen.

TABLE IV. Charge distribution of the crystalline clusters Cl⁻ 1 and Cl⁻ 2 expressed in number of electrons per sphere. For the interatomic and extramolecular regions the total number of electrons is given.

Atom	Cluster Cl ⁻ 1	Cluster Cl ⁻ 2
Central atom	17.5323	17.0661
Nearest-neighbor atom	9.8636	10.0806
Next-nearest-neighbor atom	17.5323	17.0661
Next-next-nearest-neighbor atom	9.8636	10.0806
Extramolecular region	0.1379	0.0878
Interatomic region	5.4755	11.6247

8.73 eV in the Cl⁻ 2 cluster. Both values are in very good agreement with the experimental findings.^{13,15} The upper valence band arises from the 3*p* states of the Cl⁻ atoms. According to Page and Hygh,¹⁶ the width of this band is 0.57 eV. From Figs. 1 and 3 it is immediately seen that the valence-band width of NaCl calculated by the crystalline-cluster model compares much better with the mentioned value, although the bandwidth is still larger than the experimental one.

The conduction-band states are supposed to be rather delocalized and could not be well described by a small cluster. Therefore, no attempt was made by us to investigate and identify the higher unoccupied levels with optical spectroscopy data from band-to-band transitions, even for the crystalline-cluster calculations.

The charge distributions of the clusters Cl⁻ 1 and Cl⁻ 2 are shown in Table IV. They are expressed in numbers of electrons per region, including the atomic core electrons. One readily sees there no longer is the inconvenient effect of charge migration from one sphere to another chemically equivalent.

IV. CONCLUSIONS

We have shown in this paper how a cluster-model technique may be successfully utilized to describe electronic structure and related properties of ionic compounds. The case of Na⁺Cl⁻ clusters, containing up to 27 atoms (three shells), was particularly studied, involving two kinds of cluster

calculations. Our presented results show that the conventional cluster method applied to the three-shell cluster of Na⁺Cl⁻ leads to a wrong energy spectrum for the bulk material; however, by proposing a new way of calculating the cluster potential, we have shown that a localized description of the electronic structure is satisfactory. It appears as a good alternative to the conventional band theory description, for the main aspects of the electronic energy structure emerge from the cluster occupied states. We believe that the crystalline-cluster technique developed for NaCl should be useful whenever one deals with insulators, for which the occupied orbitals are well localized, and especially for ionic materials, when the self-consistent calculation in conventional clusters may result in very dissimilar potentials for identical atoms. Of course, our model is not suitable for describing crystal-surface properties, in which the differing potentials for the same chemical species as a function of position is clearly meaningful.

ACKNOWLEDGMENTS

Helpful discussions with Professor Huberto Closs and Professor P. S. Guimarães during the calculations are gratefully acknowledged. Thanks are also due to Professor N. J. Parada and C. M. C. Castilho for their encouragement and constant help during the implementation of the program at the Universidade de Campinas.

*Paper based on a doctoral thesis submitted to the Universidade Estadual de Campinas by one of the authors (L.M.B.).

¹B. G. Cartling, *J. Phys.* C **8**, 3171 (1975).

²D. R. Salahub and R. P. Messmer, *Phys. Rev. B* **16**, 2526 (1977).

³A. Fazzio, J. R. Leite, and M. L. de Siqueira, *J. Phys.* C **11**, 513 (1979).

⁴R. P. Messmer and G. D. Watkins, *Phys. Rev. B* **7**,

2568 (1973).

⁵L. A. Hemstreet, *Phys. Rev. B* **15**, 834 (1977).

⁶L. G. Ferreira and N. J. Parada, *Phys. Rev. B* **2**, 1614 (1970).

⁷L. G. Ferreira and N. J. Parada, *J. Phys. C* **4**, 15 (1971).

⁸K. H. Johnson, *J. Chem. Phys.* **45**, 3088 (1966).

⁹J. C. Slater and K. H. Johnson, *Phys. Rev. B* **5**, 844 (1972).

- ¹⁰K. H. Johnson, in *Advances in Quantum Chemistry*, edited by Per-Olov Löwdin (Academic, New York, 1973), Vol. 7, p. 143.
- ¹¹K. Schwarz, Phys. Rev. B 5, 2468 (1972).
- ¹²R. E. Watson, Phys. Rev. 111, 1108 (1958).
- ¹³D. W. Roessler and W. C. Walker, Phys. Rev. 166, 599 (1968).
- ¹⁴F. S. Ham and B. Segall, Phys. Rev. 124, 1786 (1961).
- ¹⁵C. Gout and F. Pradal, J. Phys. Chem. Solids 29, 581 (1968).
- ¹⁶L. J. Page and E. H. Hygh, Phys. Rev. B 1, 3472 (1970).