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A CALCULATION OF THE PRESSURE DEPENDENT ENERGY BANDS OF CuCl

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16.Summary/Notes

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17.Remarks

A calculation of the pressure dependent energy bands of CuCl^{+*}

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ABSTRACT

The calculation of the energy bands of CuCl by the cluster method is presented. The calculated energy bands obtained for different cluster coincide with the known experimental information available for CuCl. The calculated bands present a sudden change at 40 kbar, very suggestive of the insulator-metal transition that CuCl undergoes at such pressures.

II. THEORY

The method used in this work is the crystalline cluster method (13). It is a variation of the self-consistent multiple-scattering (MS) method of Slater and Johnson (14), developed to describe the electronic structure of ionic crystals. In this version of the MS method, the Schroedinger equation is solved in the cluster, but the Poisson equation is solved in an infinite crystal whose densities of charge in the atomic spheres are equal to the corresponding densities in the cluster. Thus, the potential used in the solution of the Schroedinger equation is the crystalline potential surrounded by an infinite potential barrier at the outer sphere. Inside the atomic spheres, the α-exchange parameters were taken the same as those tabulated for atoms (15). In the interatomic region the Kohn -Sham exchange (16) was used. Further details about the method may be found in references (13) and (14).

The crystalline density of change $\rho(r)$ can be obtained in terms of the complete ser of Bloch functions (BF) b_n $(\vec{k}, \vec{r})$ by

$$\rho(\vec{r}) = \sum_n \sum_{\vec{k}}{}' \mid b_n (\vec{k}, \vec{r}) \mid^2 \tag{1}$$

where the sums on band n and wavevector $\vec{k}$ include all occupied states, or equivalently, in terms of the complete set of Wannier functions (WF) $w_n (\vec{\ell}, \vec{r})$ by

$$\rho(\vec{r}) = \sum_n \sum_{\vec{\ell}} \mid w_n (\vec{\ell}, \vec{r}) \mid^2 \qquad (2)$$

where $\vec{\ell}$ are the lattice sites and the sum on band n include all filled bands. The relationship between the localized WF's and the delocalized. BF's is given by

$$w_n(\vec{\ell}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{\ell}} b_n (\vec{k}, \vec{r}) \qquad (3)$$

where N is the numbers of unit cells in the crystal.

Now, Ferreira and Parada (17) have shown that the width of a WF is usually smaller than the dimension of the crystal unit cell. So, the WF's that mostly contribute to $\rho(\vec{r})$ near the p-th atom are those localized in the same unit cell where the p-th atom is or those localized in the nearest neighbouring cells. The above metioned authors have also shown [17] that the width of the WF for a given band is approximately inversely proportional to the existing energy gaps between that band and the others near to it. So, the bigger the gaps between the bands, the smaller the width of the WF's and the better are the cluster results.

As CuCl is a higly ionic compound it can be assumed that the wavefunctions of the occupied (valence) states are localized in the atomic spheres. For example, the top of the valence band has a localized Cu3d orbital character. Consequently, even small clusters may

characterize well such flat bands. One may also expect that the average energy of each one of these bands depends very little on the cluster size.

However, the same arguments cannot be simply applied to the empty (conduction) states, because their wavefunctions may spread out over many atoms in the crystal. For a compound like CuCl the wavefunction for a conduction band can be written as

$$\psi(\vec{r}) = \frac{\alpha_A}{\sqrt{N}} \sum_{\vec{\ell}} a_A(\vec{r}-\vec{\ell}) \, e^{i\vec{k}\cdot\vec{\ell}} \, \frac{\alpha_B}{\sqrt{N}} \sum_{\vec{\ell}} a_B(\vec{r}-\vec{\ell}-\vec{r}_B) e^{i\vec{k}\cdot(\vec{\ell}+\vec{r}_B)} \tag{4}$$

where A and B are the two types of atoms, α is a coefficient, r_B the position of atom B in the unity cell where atom A is located at the origin and the sums are performed over all unity cells of the crystal. The localized functions a_A and a_B may be choosen in such a way that

$$\langle a_A(\vec{r}) | \, a_B(\vec{r}-\vec{\ell}) = \delta_{0,\vec{\ell}} \, \delta_{A,B} \tag{5}$$

$$\langle a_{A'}(\vec{r}) | \, H \, | a_{B'}(\vec{r}-\vec{\ell}) = E_0 \delta_{0,\vec{\ell}} \, \delta_{A',B'} \; ; \; A' = A \text{ or } B \tag{6}$$

$$\langle a_A(\vec{r}) | \, H \, | \, a_B \, (\vec{r}-\vec{\ell}-\vec{r}_B) = S \, \delta_{0,\vec{\ell}} \tag{7}$$

Now, suppose that the crystal is represented by a cluster with a certain number of shells of atoms. The conduction band wave function of the cluster may be written in terms of the localized functions as

$$\psi_C \; (\vec{r}) = \sum_{shells} \frac{\alpha_S}{\sqrt{N_S}} \sum_p a_S \; (\vec{r} - \vec{r}_{ps}) \tag{8}$$

where N_S is the number of atoms in the s-shell, $\vec{r}_{ps}$ is the position vector of the p-atom in the s-shell and α_S is a coefficient to be determined that depends on the shell and on the cluster size.

The plot of $|(E - E_0)/zS|$, where z is the number of nearest neighbours, as function of the number of shells, both for ZNS and NaCl structures, is presented in figure 1.

insert figure 1

From this figure one can see that even in this simple approximation the forbiden gap has a very rapid convergence with the number of shells in both structures.

The crystaline cluster model, as well as the conventional MS-X$_\alpha$, method has as arbitrary parameters the radii of the atomic spheres. The usual choice of such radii consists on taking values proportional to tabulated ones in such a way that their sum gives the experimental value of the interatomic distance of the compound. In the case of CuCl there are two distinct sets of tabulated atomic radii. The first takes into account the ionic character of the crystal binding (18,19) and the second takes into account the tetrahedral coordination of the atoms (20,23). The first is called "ionic radii" and the second "tetrahedral radii".

III. RESULTS FOR ZERO PRESSURE

The lattice parameter used in the calculations was
5.406 $\overset{o}{A}$, according to reference 2. First of all, two calculations
using two-shells (five-atoms) clusters were performed. The two-
shells clusters, called CU1 and CU2, are centred in a Copper atom
but are differente in the sense that in CU1 the ionic radii (19) were
utilized and in CU2 the tetrahedral radii (21) were used as it is
shown in Table 1.

insert table 1

Figure 2 and Table 2 present the results obained for
such two-shell cluster, wich are compared with the theoretical and
experimental data available on CuCl band structure. One may easily see
from Figure 2 that the crystaline cluster results are in good
agreement with the CuCl band structure and are very little dependent
on the atomic radii. This result is not surprising due to the higly
ionic character of CuCl chemical binding.

insert table 2 and figure 2

In a further calculation a three-shells (seventeen-atoms)
cluster with ionic radii (19) was utilized in order to study the cluster
size dependence of the CCM results, which are shown in Figure 2-g
and Table 2-g. One may easily see that the crystaline cluster results are

not strongly dependent on the number of atomic shells. But the agreement between the cluster results and the available experimental data increases as the cluster does, as one may expect from the analysis of figure 1.

If one intends to compare a theoretical density of valence states (DVS) $N(E)$ with the experimental results, one has to broaden it in such a way to reproduce the experimental results. The CCM DVS is given by a sum of δ-functions weighted by the energy levels occupation. Hence, if one broadens the cluster DVS by gaussian functions of proper width the following results is obtained (24) :

$$N(\epsilon) \simeq \sum_{\substack{\text{occ.} \\ \text{st.}}} n_i \frac{e^{\frac{-(\epsilon - \epsilon_i)^2}{2\pi\sigma}}}{\sqrt{2\pi\sigma}} \qquad (9)$$

where ϵ_i is the energy of the electronic level and n_i its degeneracy.

The arbitrary parameter σ was kept fixed at 0.5 eV. The DVS's obtained by Eq. (10) are shown in Figure 3 and are comparad with the experimental DVS (1). One can see again that the cluster results are in good qualitative agreement with the experimental results and that the broadened DVS depends little on the cluster choise.

Insert Figure 3

IV. EFFECTS OF HIDROSTATIC PRESSURE

Since the results obtained for zero pressure do not differ very much for the different clusters utilized and the calculations with cluster CL1 are about ten times longer than the calculations with any one of the five-atom cluster, then cluster CU1 was used to study the pressure dependence of the band structure of CuCℓ. The main effect of pressure is to reduce the lattice parameter of the crystal. The variation of this parameter with pressure was taken from the experimental compressibility curve (12) which was extrapolated up to 50 kbar. The error in the linear extrapolation does not affect our qualitative conclusions.

It has been shown (10) that the insulator-metal transition of CuCℓ is an effect that seems to depend more on the crystal features than on impurity effects. For an intrinsic semiconductor, the resistivity ρ is related to the band gap ϵ_G by (25)

$$\rho \sim \exp \frac{\epsilon_G}{2kT}$$

The calculated band gap variation with pressure is shown in Figure 4 as well as the experimental pressure dependence of the resistivity. One sees that at about 40 kbar the cluster energy band gap has a sharp decrease and that both theoretical and experimental curves have the same shape.

V. CONCLUSION

The crystalline-cluster model seems to reproduce very well the band structures of CuCl,an ionic compound. The results do not depend strongly on parameters like the atomic radii and the number of atomic shells used in the cluster.

The theoreticaly calculated band gap presents a sharp decrease with pressure at about 40 kbar, does indicating that the insulator-metal transition of CuCl is an intrisic effect.

ACKNOWLEDGMENT

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TABLE 1. Parameter used in our band calculation of CuCℓ at zero pressure.

cluster		CU1	CU2	CL1
number of atomic shells		2	2	3
number of atoms		5	5	17
inner atom		Cu	Cu	Cl
atomic radii		ionic	tetrahedal	ionic
R_{Cu}		2.108	2.541	2.108
$R_{Cℓ}$		2.315	1.882	2.315
	Cu	0.707	0.707	0.707
α exchange	Cℓ	0.723	0.723	0.723
parameter				
	interatomic	0.667	0.667	0.667

TABLE 2. Band structure calculations of CuCℓ at zero pressure

	a	b	c	d	e	f	g	h
band gap	3.43	1.0	4.4	-	4.56	4.01	3.79	3.4
band width	19.94	15.0	24.2	16.26	13.51	13.46	14.28	15.8
upper valence band	Cu 3d	Cℓ 3p	Cu 3d	Cℓ 3p	Cu 3d	Cu 3d	Cu 3d	Cu 3d

a- ref. 4
b- ref. 5
c- ref. 6
d- ref. 7
e- cluster CU1
f- cluster CU2
g- cluster CL1
h- experimental, ref. 2

FIGURE CAPTIONS

FIG. 1 - Variation of the cluster forbidden energy band with the number of atomic shells.

FIG. 2 - Different band structure calculations of $CuC\ell$ at zero Pressure. a - ref. 4; b - ref. 5; ref. 6; d - ref. 7; e - cluster CU1; f - cluster CU2; g - cluster CL1; h - exp., ref. 2.
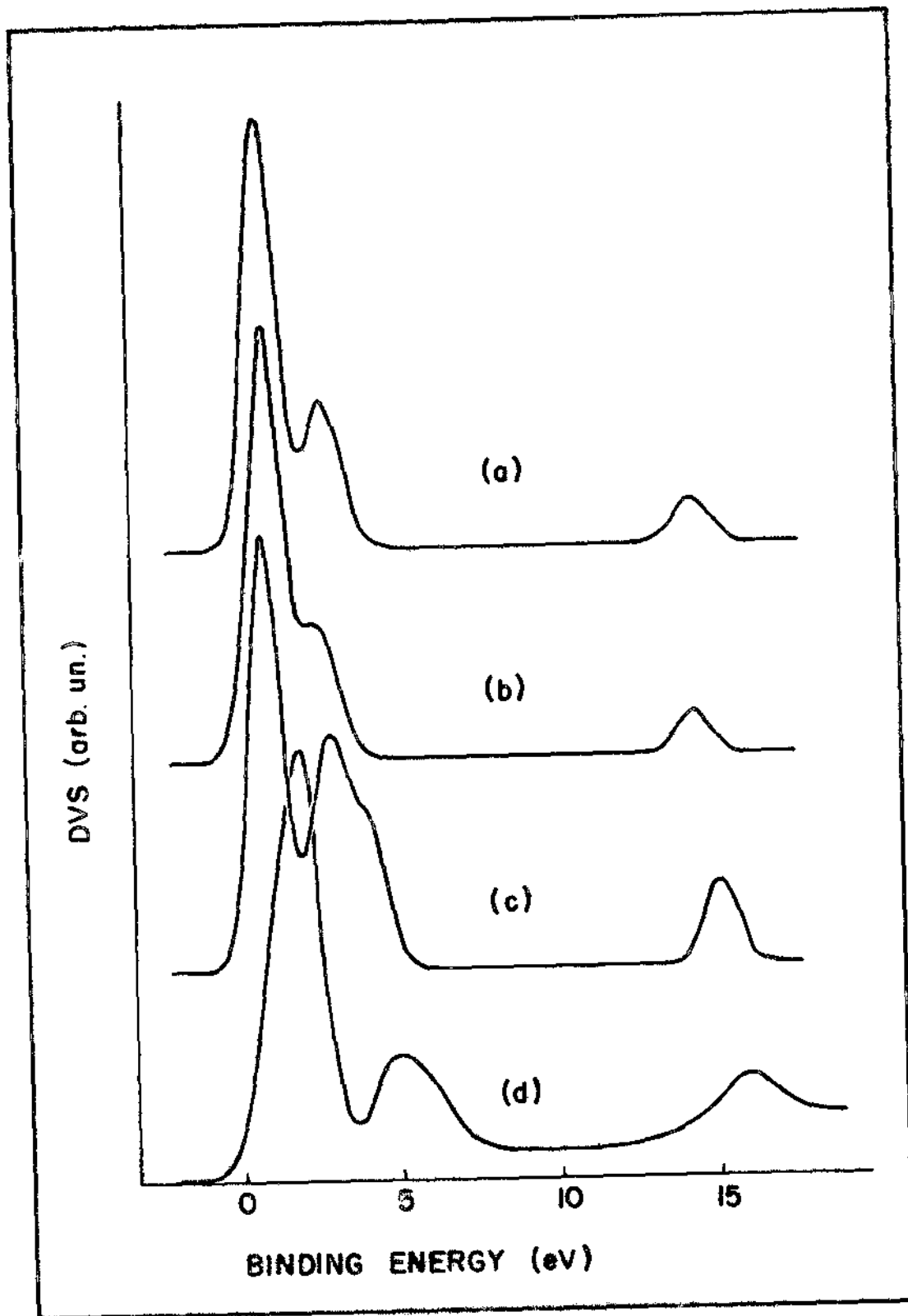
FIG. 3 - DVS of $CuC\ell$ at zero pressure. a - cluster CU1; b - cluster CU2; c - cluster CL1; d - exp., ref. 1.

FIG. 4 - a - experimental resistivity variation with pressure, according · to ref. 10. b - theoretical variation of energy gap with pressure, according to this work.

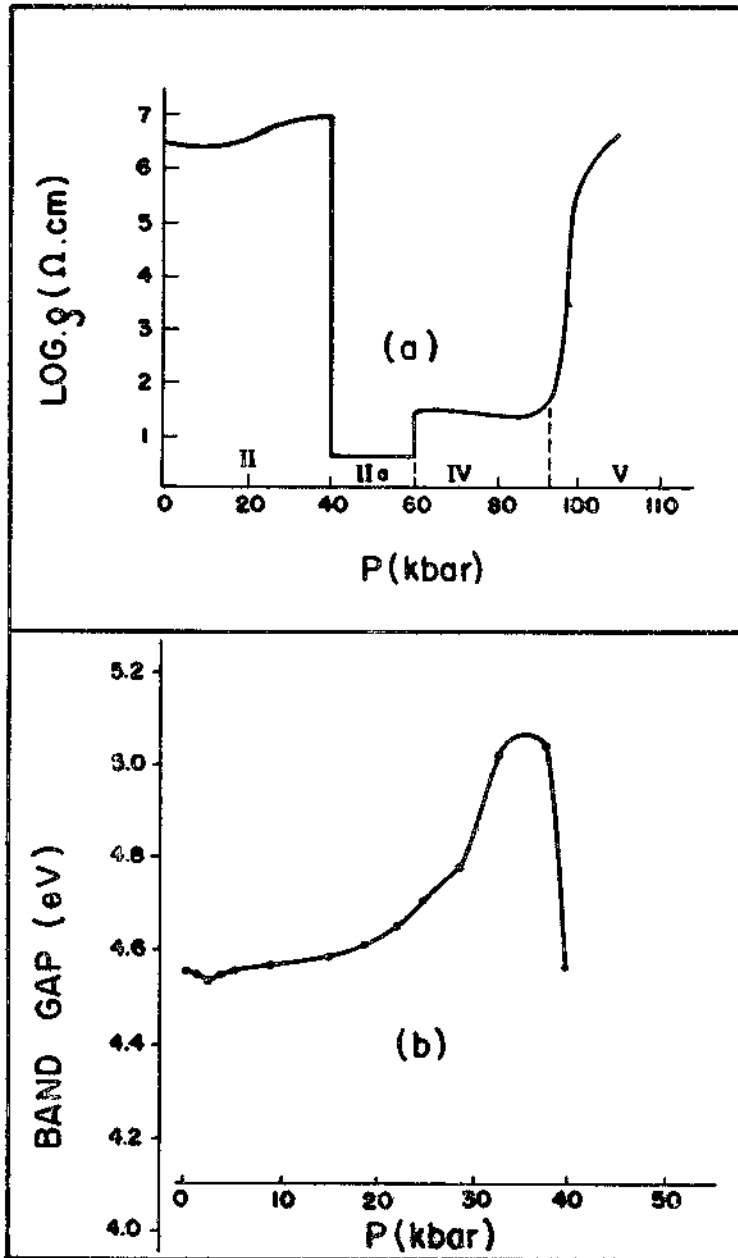Guimarães, Parada and Ferreira – Fig. 2
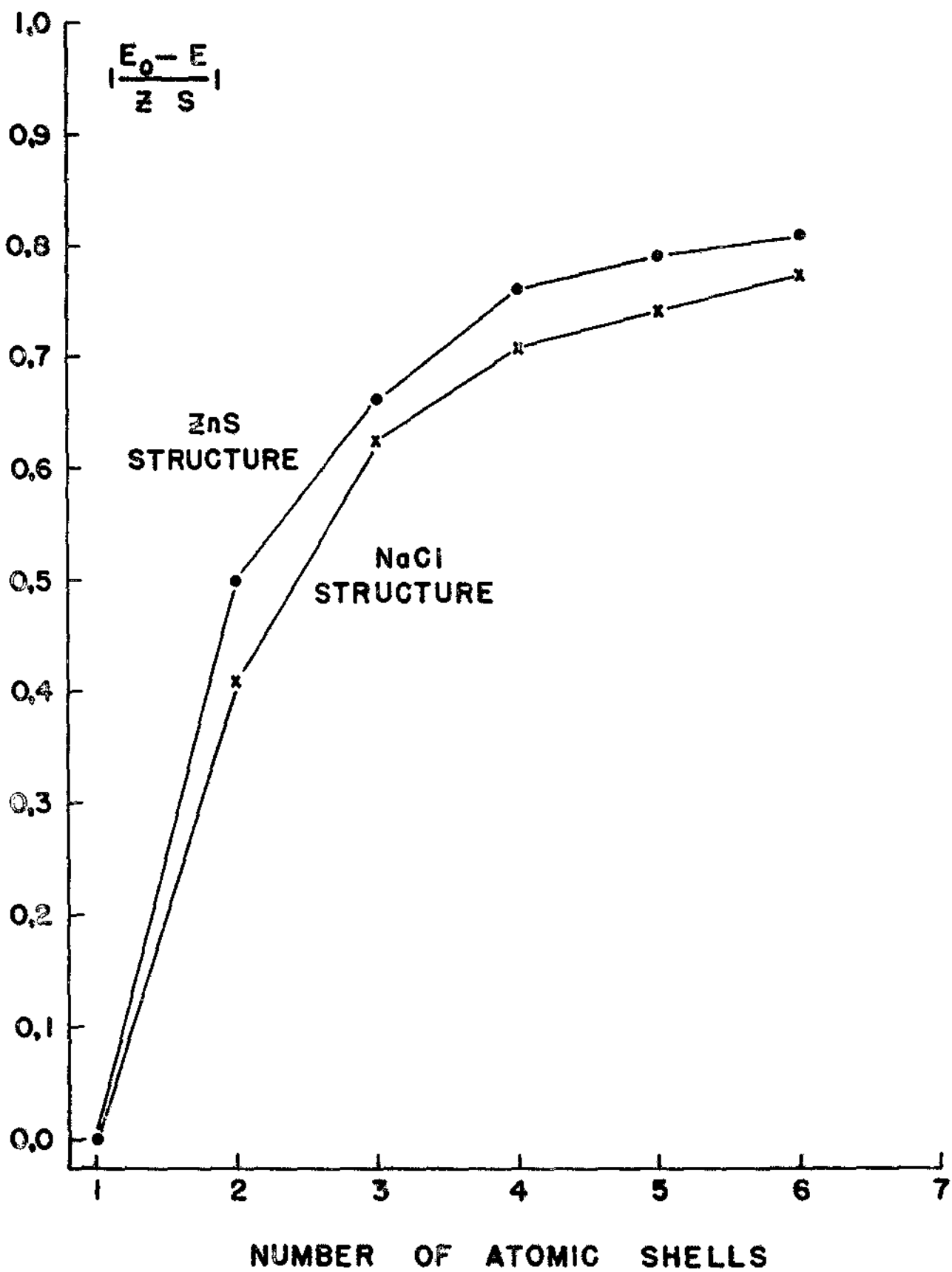
Guimarães, Parada and Ferreira - Fig. 3

Guimarães, Parada and Ferreira - Fig. 4