ISOMER SHIFTS AND CHEMICAL BONDING IN CRYSTALLINE Sn(II) AND Sn(IV) COMPOUNDS

by

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ABSTRACT

First-principles self-consistent Local Density calculations of the electronic structure of clusters representing Sn(II) (SnO, SnF_2, SnS, SnSe) and Sn(IV) (SnO_2, SnF_4) crystalline compounds were performed. Values of the electron density at the Sn nucleus were obtained and related to measured values of the Mössbauer Isomer Shifts reported in the literature. The nuclear parameter of [119]Sn derived was $\Delta R/R = (1.58 \pm 0.14) \times 10^{-4}$. The chemical bonding in the solids was analysed and related to the electron densities obtained.

Key-words: Sn compounds; Electronics structure; Isomer shifts.

1. INTRODUCTION

Hyperfine interactions, as measured by Mössbauer spectroscopy, may give valuable information on the chemical environment around a Mössbauer atom. However, as such interactions are described by a product of a nuclear and an electronic terms, the qualitative and quantitative interpretation of the measurements depend on a reliable estimate of the nuclear term.

The Isomer Shift δ is the product of a nuclear term of the Mössbauer isotope, which is the relative variation of the nuclear radius in the Mössbauer transition $\Delta R/R$, and an electronic term, the difference of electron density at the nucleus between absorber and source[1]. Reliable calculations of the electronic term, when coupled with the measured values of δ, may thus lead to a determination of $\Delta R/R$. The knowledge of this last, with a reasonable degree of precision, is essential for the experimentalists to interpret the measured data.

In the case of the Mössbauer isotope ^{119}Sn, reported electronic structure calculations for the investigation of hyperfine parameters have been noticeably fewer than for the better studied isotope ^{57}Fe. In the days of greater development of Mössbauer spectroscopy (the '60s), Fe was investigated theoretically with the aid of the crystal field and ligand field theories for transition metal compounds; however, no such models were available for Sn. The current, much more powerful, methods have been applied only scarcely to Sn metal, compounds and alloys; one of the reasons is probably the very complex crystal structures displayed by some of the

solids.

On the experimental side, a large number of data on Isomer Shifts of Sn metal, alloys and compounds is available in the literature[1][2]. It is thus desirable to perform electronic structure calculations both to derive a reasonably accurate value for the nuclear term and to correlate the δ values to the characteristics of the chemical bonds.

We report first-principles electronic structure calculations for clusters representing the solid compounds SnO(black), $SnF_2(\beta)$, SnS, SnSe, SnO_2 and SnF_4. The values of the electron densities at the nucleus were obtained and correlated to measured δ values reported in the literature. The choice of these compounds was made based on the following considerations: they cover a wide range of δ values; they include both Sn(II) and Sn(IV) compounds; the anions cover a wide range of electronegativities, and are thus expected to bond to Sn in different ways; the solids have well defined crystal structures and, "last but not least", they include compounds with practical and technological importance[3]. In fact, SnO_2 is a large-gap semiconductor, and its stability in the laboratory has made it widely used as source in Mössbauer spectroscopy. It has important optical properties, acting as a transparent electrode and as material for optical covering. SnS and SnS are group IV-VI semiconductors with a layered structure.

The first-principles method employed is the self-consistent Discrete

Variational (DVM)[4] in the framework of Local Density (LD) theory[5].
Calculations were performed for several clusters of different sizes, for
each compound, to test the effect of cluster size. In all clusters, the Sn
atom where the electron density was calculated was placed at the center, as
this site has no truncated bonds and thus simulates better a Sn atom in the
solid. An embedding scheme was adopted to take into account the external
infinite crystal. The electronic structures were obtained, as well as the
electron densities at the nucleus of the central Sn atom, which were related
to δ values to derive a value of $\Delta R/R$.

The organization of this paper is as follows: in Section 2 we describe
the theoretical method, in Section 3 we present and discuss our results
pertaining to the Isomer Shifts, correlating them to the chemical bonding in
the solids and in Section 4 we give a brief summary of our main conclusions.

2 THEORETICAL METHOD

The purpose of the Discrete Variational method[4] is to solve the set
of one-electron Kohn-Sham[6] equations of Local Density Theory for the
cluster (in Hartree atomic units):

$$h\psi_i(\vec{r}) = [-1/2 \, \nabla^2 + V_c(\vec{r}) + V_{xc}(\vec{r})]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r}) \tag{1}$$

In Eq. (1), the Coulomb potential $V_c(\vec{r})$ includes the electron-nucleus attraction and electron-electron repulsion, and $V_{xc}(\vec{r})$ is the exchange-correlation potential, which we have chosen in the form derived by Hedin and Lundqvist[7]. $V_{xc}(\vec{r})$ is a functional of the electron density calculated with the cluster orbitals $\psi_i(\vec{r})$, with occupation n_i:

$$\rho(\vec{r}) = \sum_i n_i |\psi_i(\vec{r})|^2 \qquad (2)$$

The cluster orbitals are expanded[8] on a basis of numerical symmetrized atomic orbitals χ_μ^a:

$$\psi_i(\vec{r}) = \sum_\mu \chi_\mu^a(\vec{r}) c_\mu^i \qquad (3)$$

The Discrete Variational scheme leads to the secular equations,

$$([H]-[E][S])[C] = 0 \qquad (4)$$

where the matrix elements of the Hamiltonian matrix [H] and overlap matrix [S] are summations over a 3-dimensional grid of points $\vec{r}_j$

$$\sum_j w(\vec{r}_j)\chi_\mu^{q*}(\vec{r}_j)h(\vec{r}_j)\chi_\nu^{q}(\vec{r}_j) \qquad\qquad (5)$$

and

$$\sum_j w(\vec{r}_j)\chi_\mu^{q*}(\vec{r}_j)\chi_\nu^{q}(\vec{r}_j)$$

and $w(\vec{r}_j)$ is the weight per point. The 3-dimensional grid is regular inside a sphere, around the central Sn atom, of radius equal to $2a_0$, where a precise polinomial integration is performed[9]; outside this sphere, and around all other atoms, the pseudorandom Diophantine point generator provides the points. The total number of points employed here were in the range 15,000-19,000.

To facilitate the computation of the electron-electron repulsion term, a model charge density $\rho_M(\vec{r})$ is used in place of the exact cluster charge density[10]

$$\rho(\vec{r}) \stackrel{\sim}{=} \rho_M(\vec{r}) = \sum_{n\ell I} d_{n\ell}^I \rho_{n\ell}^I(\vec{r}) \qquad\qquad (6)$$

where $\rho_{n\ell}^I(\vec{r})$ are overlapping charge densities centered at each atom q, calculated with the radial atomic functions of the basis

$$\rho_{n\ell}^I(\vec{r}) = \sum_q{}' |R_{n\ell}^q(r_q)|^2 Y_0^0(\hat{r}_q) \; ; \qquad\qquad (7)$$

the summation is over a previously defined set of atoms and I represents a particular set. In the present calculations, the central Sn atom (Sn_c), which is better represented in all clusters and where δ will be calculated, is kept as a set by itself. All peripheral Sn atoms (Sn_p) constitute another set. As for the anions, they will be kept in the same set if all anions are equivalent in the crystal (SnO, SnO_2, SnS, SnSe); otherwise, there will be a different set for each type of anion (SnF_2, SnF_4). The coefficients $d_{n\ell}^I$ are obtained variationally by a least-squares procedure[10], with the condition that $\rho_M(\vec{r})$ integrates to the total number of electrons in the cluster. Self-consistency is achieved through convergence of these coefficients, since they ultimatly define the cluster potential.

In the calculations reported here, the atomic basis functions were obtained from numerical self-consistent atomic LD calculations. Basis functions in the variational space were 4s, 4p, 4d, 5s and 5p for Sn_c, 5s and 5p for Sn_p, 3s and 3p for S and 4s and 4p for Se. For O and F all orbitals were included.

Core orbitals not kept in the variational space were orthogonalized to the valence basis functions in the first iteration, and kept "frozen" subsequently.

An embedding scheme was adopted to take into account the effect of the atoms external to the cluster in the solid. At each site of several layers of atoms is placed a numerical atomic charge density, truncated at the core

region to simulate the Pauli exclusion principle[11]. More distant charges were taken into account by an Ewald procedure[12].

Cluster calculations for these ionic and partially ionic solids poses a number of questions derived from the truncation of bonds to form the cluster. One of these questions is the definition of the charge on the cluster. We have approached this problem by employing a scheme by which the charge on the cluster is not defined beforehand, but is consistent with the atomic charges found in the calculations. The scheme is as follows: to start the self-consistent procedure, the atoms are considered neutral. Accordingly, basis functions are generated for neutral atoms, neutral atoms also are placed in the external shells of the embedding, and the cluster charge is zero. After self-consistency is achieved, a Mulliken[13] population analysis is performed and charges are obtained for the atoms. New basis functions are generated for the atoms with the charges and configurations obtained, as well as new charge densities for the embedding. For Sn, the central atom is considered, since it is better described. A new charge for the cluster is defined; for example, if the charge found for Sn_c is +1 in $[SnO_8Sn_{12}]$ representing SnO, the Oxygens are assumed to have charge -1 and the charge of the cluster is thus +5. This charge defines the total number of electrons for the next set of iterations. This computer-time consuming procedure is repeated until the charges and configurations of the cluster atoms, the atoms generating the basis functions and the atoms of the embedding are similar. With this procedure we reduce spurious effects of basis truncation and of finite cluster size, since basis functions and external atoms are consistent with the results for the cluster.

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The Isomer Shift δ is defined as[1],[2]

$$\delta = \frac{4}{5} \pi Z e^2 S'(Z) R^2 \Delta R / R \left[\rho_A(0) - \rho_S(0) \right]$$ (8)

where R is the radius of a spherical nucleus, Z is the atomic number, S'(Z) a correction for relativistic effects and the term in brackets is the difference of the electron density (Eq.(2)) at the nucleus between absorber and source. Alternatively, δ may be expressed as

$$\delta = \frac{2}{3} \pi e^2 Z S'(Z) \Delta \langle r^2 \rangle \left[\rho_A(0) - \rho_S(0) \right]$$ (9)

where $\Delta \langle r^2 \rangle$ is the change in the mean square radius of the nucleus in the Mössbauer transition. The value of S'(Z) for ^{119}Sn (2.306) was taken from Shirley's early derivation[14]; more accurate relativistic and non-relativistic Local Density atomic calculations have demonstrated that this linear correction is quite adequate[15].

3 ISOMER SHIFTS AND CHEMICAL BONDING

In Table I is given structural information on the solid compounds and on the clusters chosen to represent them[16]-[21]. The crystal structures are complex, resulting in very low point symmetries around the central Sn atom for the clusters, in most cases. In Figs. 1 to 5 are depicted clusters chosen to represent the crystals. Convergence of the value of $\rho(0)$ with cluster size was tested for all compounds, and it was verified to be adequate; accordingly, the largest cluster considered for each compound was chosen to represent the solid. This study of the influence of cluster size on a given property, however time-consuming, has made clear that caution is needed with cluster calculations of Isomer Shifts. For example, the addition of the four topmost Oxigen atoms (see Fig. 1) to the smallest cluster representing SnO ($[SnO_4Sn_8]$) changes the value of $\rho(0)$ significantly; further inclusion of the four peripheral Sn atoms to form $[SnO_8Sn_{12}]$, however, has a small effect on $\rho(0)$. The value of $\rho(0)$ for $[SnS_7Sn_2]$ representing SnS is very different from that obtained for $[SnS_7Sn_6]$; $\rho(0)$ for this last cluster, however, does not differ much from that obtained for $[SnS_7Sn_8]$. Accordingly, SnS and SnSe, which have the same crystal structure, were represented by $[SnS_7Sn_8]$ and $[SnSe_7Sn_8]$, respectively. The two Sn(IV) compounds SnO_2 and SnF_4 have six-fold coordinated nearest neighbors; however, it was verified that inclusion of more distant Sn and anion atoms to the minimal clusters $[SnO_6]$ and $[SnF_6]$ (see Table I) is essential to obtain accurate values of $\rho(0)$.

In Table II are given the values found for the electron densities $\rho(0)$ at the nucleus of the neutral Sn atom for the largest clusters representing the Sn(II) and Sn(IV) compounds. The contribution due to the deep core orbitals of Sn was not included, since these orbitals were "frozen". In the Table, the total $\rho(0)$ is divided in the contribution due to the "shallow core" (cluster orbitals dominated by 4s, 4p and 4d Sn orbitals) and valence contribution, dominated by Sn(5s); this separation, however, was done primarily as an aid in the understanding of the origin of the Isomer Shifts, since a small mixture of "shallow core" and valence orbitals is always present. It is seen from the Table that differences among the "shallow core" contributions are much smaller than differences among valence $\rho(0)$; however, they are by no means negligible. This shows the importance of including these inner orbitals in the calculations of δ; their small participation in bonding generates non-negligible differences in $\rho(0)$, due to the enhancement brought in by the much greater $\rho(0)$ of Sn(4s), relative to Sn(5s). Deeper core orbitals may be expected to have approximatly equal values of $\rho(0)$ in all compounds, thus contributing negligibly to Isomer Shifts.

Regarding the valence $\rho(0)$, it may be verified that, as expected, the Sn(IV) compounds SnO_2 and SnF_4 present a much smaller value, relative to Sn(II) compounds; this is in accord with the much lower values of δ, since the nuclear term in Eq. (8) (or Eq. (9)) is expected to be positive for ^{119}Sn. As for the Sn(II) compounds, values of $\rho(0)$ are close together for SnF_2, SnS and SnSe; accordingly, δ values are similar. SnO has a lower δ

and, for this compound, a smaller $\rho(0)$ was obtained with the calculations.

In Table II are also given the charges and 5s and 5p populations at the central Sn atom, obtained by a Mulliken population[13] analysis of the cluster orbitals. It may be observed that charges for Sn(II) and Sn(IV) compounds are very far from the formal +2 and +4. There is a high degree of 5s-5p hybridization in all compounds. Values of $\rho(0)$ are inversely proportional to the charge on Sn_c, for the Sn(II) compounds, with the exception of SnF_2. In fact, SnO, SnS and SnSe present a large degree of covalency, evidenced by charges on Sn much smaller than +2 and by a high degree of 5s-5p hybridization; on the other hand, SnF_2 has a much larger positive charge and smaller s-p hybridization, with a configuration which resembles more the ionic $Sn^{2+}(5s^2 5p^0)$.

Qualitative analysis of Isomer Shifts of Sn(II) compounds have stressed the importance of the role played by the "lone pair" electrons of Sn^{2+}. In fact, in Figs. (1)-(3) it may be seen that in Sn(II) compounds the crystals allow a portion of 3-dimensional space around a Sn atom to accomodate the "lone pair". In a Molecular Orbital (or Cluster Orbital) picture like the present one, the "lone pair" is described by one or more molecular orbitals (or cluster orbitals) presenting a high degree of hybrid 5s and 5p character, since the "lone pair" electrons are accomodated in a directional orbital. For SnO (see Fig. (1)) the "lone pair" is in the z axis, for SnS and SnSe (see Fig. (3)) in the xy plane.

The Mulliken population analysis of the Sn(II) compounds shows that the

5s charge is distributed among a large number of valence cluster orbitals in SnO, SnS and SnSe, in accordance with their covalent nature; for SnF_2, which is much more ionic, this feature is much less pronounced. In all cases one may point out to one or two orbitals with considerable 5s-5p populations at Sn_c, which may be identified with "lone pair" orbitals of the central Sn atom. These are given in Table III; two orbitals ($13a_1$ and $15a_1$) may be classified in this manner for SnO, and one ($28a'$) for SnS and SnSe. These orbitals have similar 5s and 5p character on Sn_c. In contrast, the 5s-5p hybrid orbital of SnF_2 ($58a$) has a much higher 5s to 5p ratio, in accordance with the more ionic configuration similar to $5s^2 5p^0$, for Sn_c (see Table II).

In Table III are also given the contributions to $\rho(0)$ of the "lone pair" orbitals, and compared to the total valence $\rho(0)$. It is seen that, due to the distribution of the 5s charge among a large number of cluster orbitals in SnO, SnS and SnSe, the contribution of the "lone pair" orbitals to total $\rho(0)$ is small for these compounds; in contrast, most of the 5s character of Sn_c in SnF_2 is concentrated in the $58a$ "lone pair" orbital, which, accordingly, contributes with 58% of the total valence $\rho(0)$.

It must be emphasized that the self-consistent method adopted here takes into account simultaneously all aspects of the chemical bonding that may influence the Isomer Shifts, such as covalency, charge transfer, potential distortion and changes in the shape of the wave functions due to the Pauli exclusion principle (sometimes denominated "overlap distortion").

In Fig. 6 we present the correlation between $\rho(0)$ ("shallow core" and

valence) and experimental values of δ. It is seen that an approximatly linear correlation is obtained; by a least-squares fit of the points, the values $\Delta R/R=(1.58\pm0.14)\times10^{-4}$ (according to Eq. (8)) and $\Delta<r^2>=(6.61\pm0.58)\times10^{-3}fm^2$ (according to Eq. (9)) were derived.

In Fig. (6), results for the Sn(IV) compounds $SnCl_4$, $SnBr_4$ and SnI_4 were also included; these were the subject of a previous publication[22], together with SnF_4 which, however, was represented by the smaller cluster $[SnF_6]$. In this previous work, the DVM method with a slightly different (less accurate) model potential was used, in which the coefficients of the expansion of the density ρ (Eq. (6)) were taken to be the Mulliken populations of the atomic orbitals. To make all results exactly comparable, calculations for $SnCl_4$, $SnBr_4$ and SnI_4, which form isolated tetrahedral units in the crystals and were thus represented by tetrahedral clusters, were repeated with the same model potential (Eqs. (6) and (7)) as was adopted in the present calculations of Sn(II) and Sn(IV) compounds.

In Fig. (7), the present linear correlation between δ and $\rho(0)$ is compared to that obtained from our previous investigation for SnF_4, $SnCl_4$, $SnBr_4$ and SnI_4, in which a slightly different model potential was used and SnF_4 was represented by the smaller cluster $[SnF_6]$[22]. The steeper inclination obtained for the straight line in this previous calculation resulted in a higher value for $\Delta R/R$ (2.20×10^{-4}) than the present value $\Delta R/R=(1.58\pm0.14)\times10^{-4}$. The present value is more reliable, due to the use of an improved model potential and to the fact that both Sn(II) and Sn(IV) compounds have been included, covering a much wider range of Isomer Shift

values.

The Isomer Shift calibration of ^{119}Sn has been the subject of investigation of other theoreticians. Early attempts were based on atomic models and resulted in a wide range of values proposed for $\Delta R/R$ [23] (from -2.5 to +3.6x10^{-4}). Semi-empirical calculations for Sn molecules were also employed [24]. Band-structure calculations of Sn metal and Sn compounds (SnO$_2$, SnMg$_2$, SnSb and SnTe) were performed [25] with the scalar-relativistic linear muffin-tin orbital method (LMTO), for valence electrons only, resulting in the value $\Delta R/R=(1.34\overset{+}{-}0.07)$x10^{-4}. The same method was applied to investigate the pressure dependence of δ measured in Sn metal [26], by performing calculations of $\rho(0)$ for different lattice constants. The value of $\Delta R/R$ derived (1.53x10^{-4}) is the closest that we found to the one reported here.

Other properties related to the electronic structures of the Sn(II) and Sn(IV) crystalline compounds investigated, such as densities of states and electric field gradients, will be reported in a forthcoming publication [27].

4. CONCLUSIONS

The first-principles Local Density cluster calculations reported here have proved to be quite accurate in describing the linear correlation between Isomer Shifts and $\rho(0)$ for Sn(II) and Sn(IV) solid compounds. Cluster size effects are found to be important, suggesting that caution must

be exercised when selecting a cluster to investigate a property of a given

crystal, even when very localized as the one studied here. Charges found

are quite different from the formal +2 and +4. Of the four Sn(II) compounds

considered, SnO, SnS and SnSe are very covalent and SnF_2 is ionic; for this

last compound, the "lone pair" electrons are more localized.

ACKNOWLEDGEMENT

FIGURE CAPTIONS

Figure 1

The smallest and the largest clusters selected to represent SnO (black).

Figure 2

a) Closest F neighbor environment surrounding a Sn atom in SnF_2. Dots represent "lone pair" electrons. F1 and F2 are the two types of F atoms in SnF_2 crystal. Sn-nearest neighbor distances are also given (in $\mathring{A}$).

b) Smallest cluster selected to represent SnF_2. The largest cluster is not depicted due to complexity of low-symmetry structure.

Figure 3

Largest cluster considered to represent isomorphous SnS and SnSe.

Figure 4

Largest cluster selected to represent SnO_2.

Figure 5

Largest cluster selected to represent SnF_4.

Figure 6

Correlation between Isomer Shifts δ and electron densities $\rho(0)$ ("shallow core" and valence) at the nucleus of the central Sn atom, for the

largest clusters representing Sn(II) and Sn(IV) compounds.

Figure 7

Correlation between Isomer Shifts δ and electron densities $\rho(0)$ at the nucleus of Sn$_c$. ● Present calculations. ■ Calculations reported in ref. (22), performed with a different model potential (see text).

TABLE CAPTIONS

Table I

Information on the crystal structures of Sn(II) and Sn(IV) solids, clusters for which calculations were performed and point symmetry around central Sn atom. (a) See ref. (16). (b) From ref. (17). (c) From ref. (18). (d) From ref. (19). (e) From ref. (20). (f) From ref. (21).

Table II

Electron densities $\rho(0)$ at the nucleus of the central Sn atom for the largest clusters representing Sn(II) and Sn(IV) compounds. "S.core" stands for "shallow core" (4s, 4p and 4d-containing cluster orbitals). Also given in Table are charges and Mulliken populations on central Sn atom. (a) From ref. (2); relative to SnO_2.

Table III

Energy and charge distribution of the "lone pair" cluster orbitals of the largest clusters representing Sn(II) compounds, as well as their contribution to the electron densities $\rho(0)$ at the nucleus of the central Sn atom.
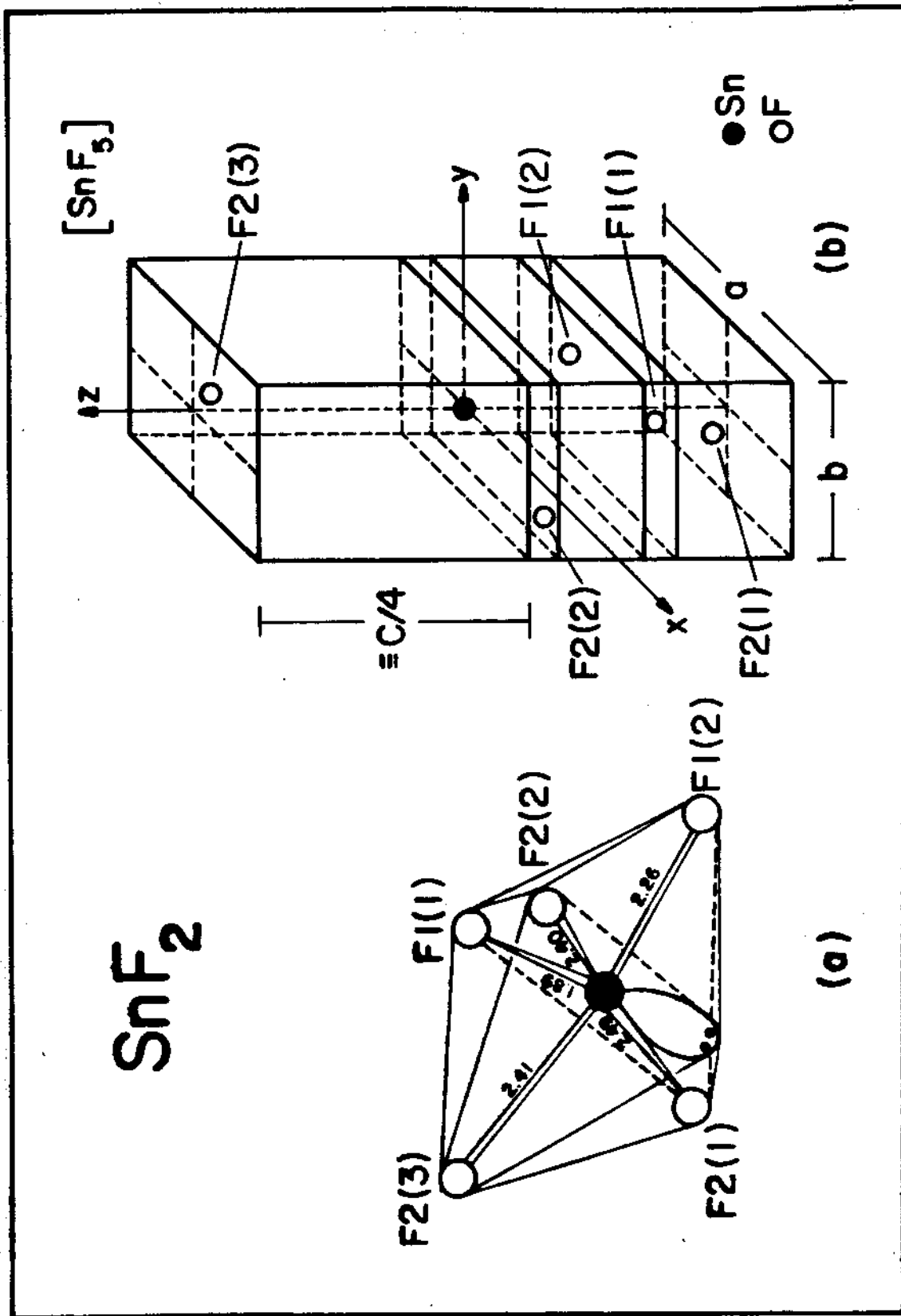
SnO

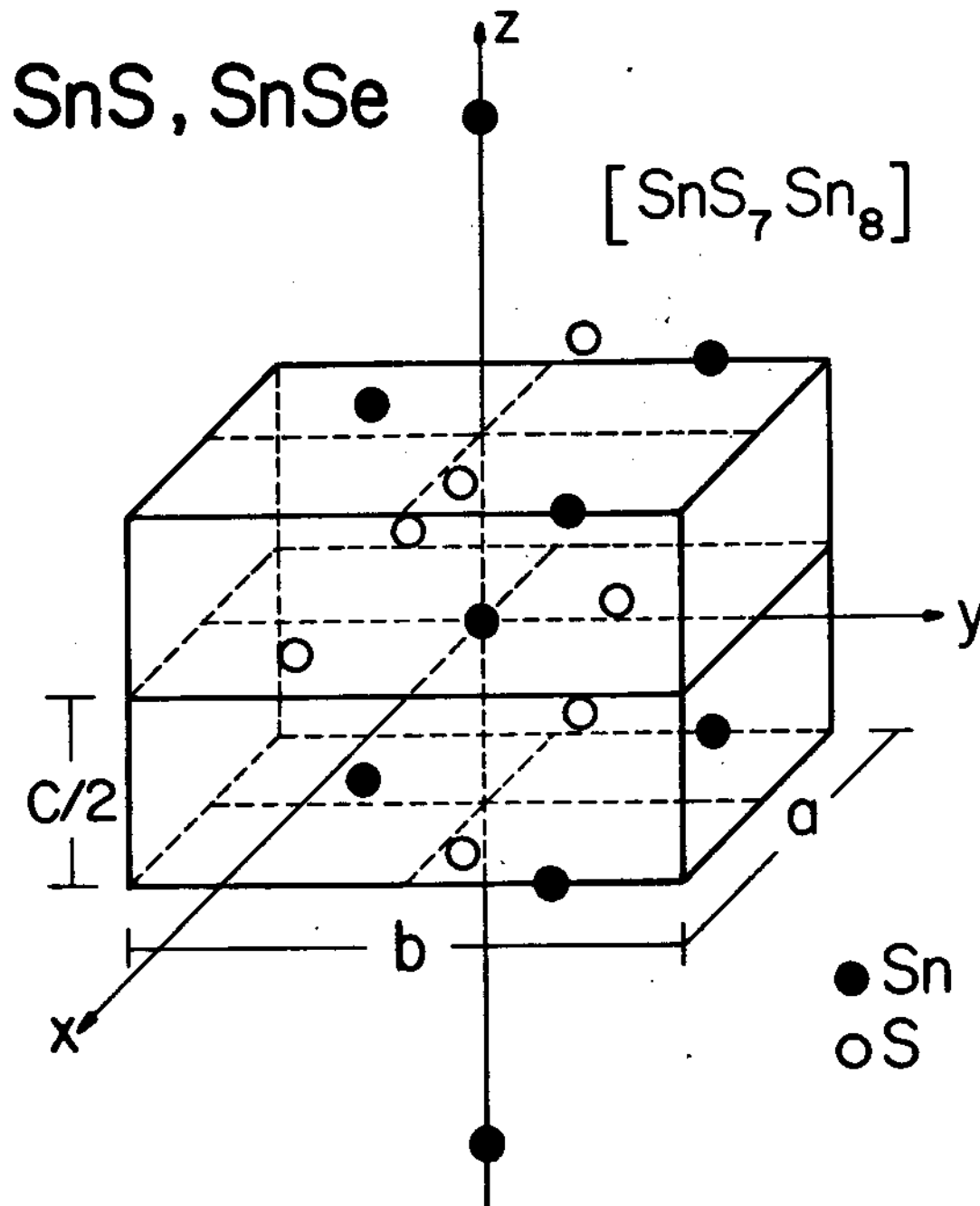$[SnO_4 Sn_8]$

$[SnO_8 Sn_{12}]$

Sn ●

O ○

FIG. 1

SnF_2

F1(1)

F2(2)

F2(3)

F2(1)

F1(2)

(a)

$[SnF_5]$

F2(3)

y

F1(2)

F1(1)

≡C/4

F2(2)

x

F2(1)

z

a

b

(b)

● Sn
○ F

FIG. 2

SnS, SnSe

$[SnS_7 Sn_8]$

z

y

c/2

a

b

x

● Sn
○ S

FIG. 3

SnO_2

$[Sn\, O_{10}\, Sn_{10}]$

● Sn
○ O

FIG. 4

SnF_4

$\left[Sn\,F_{22}Sn_4\right]$

$0.2\overset{T}{\underset{\perp}{3}}7C$

● Sn
● Sn (not considered)
○ F

FIG. 5

$\delta (mm/s)$

$\rho (0)(a_0^{-3})$

FIG. 6

FIG. 7

Table I
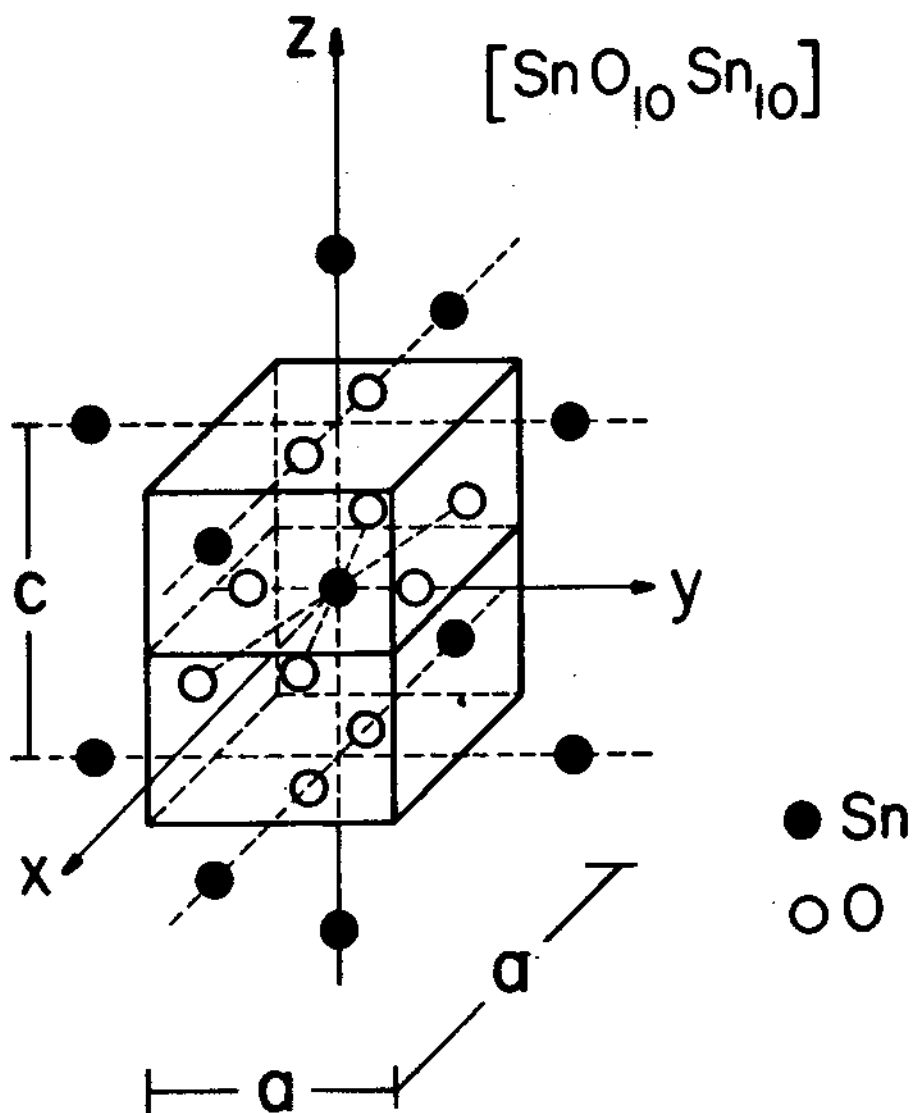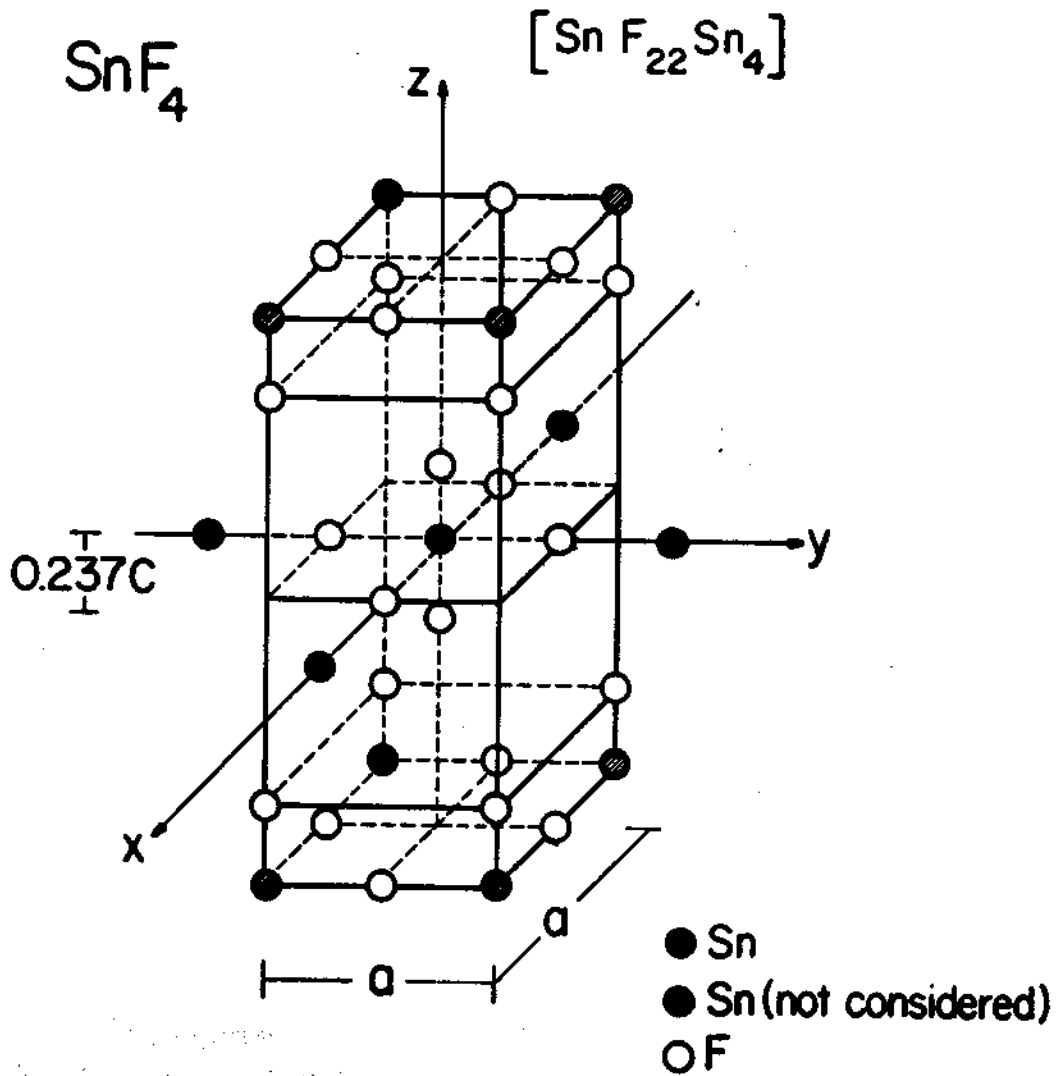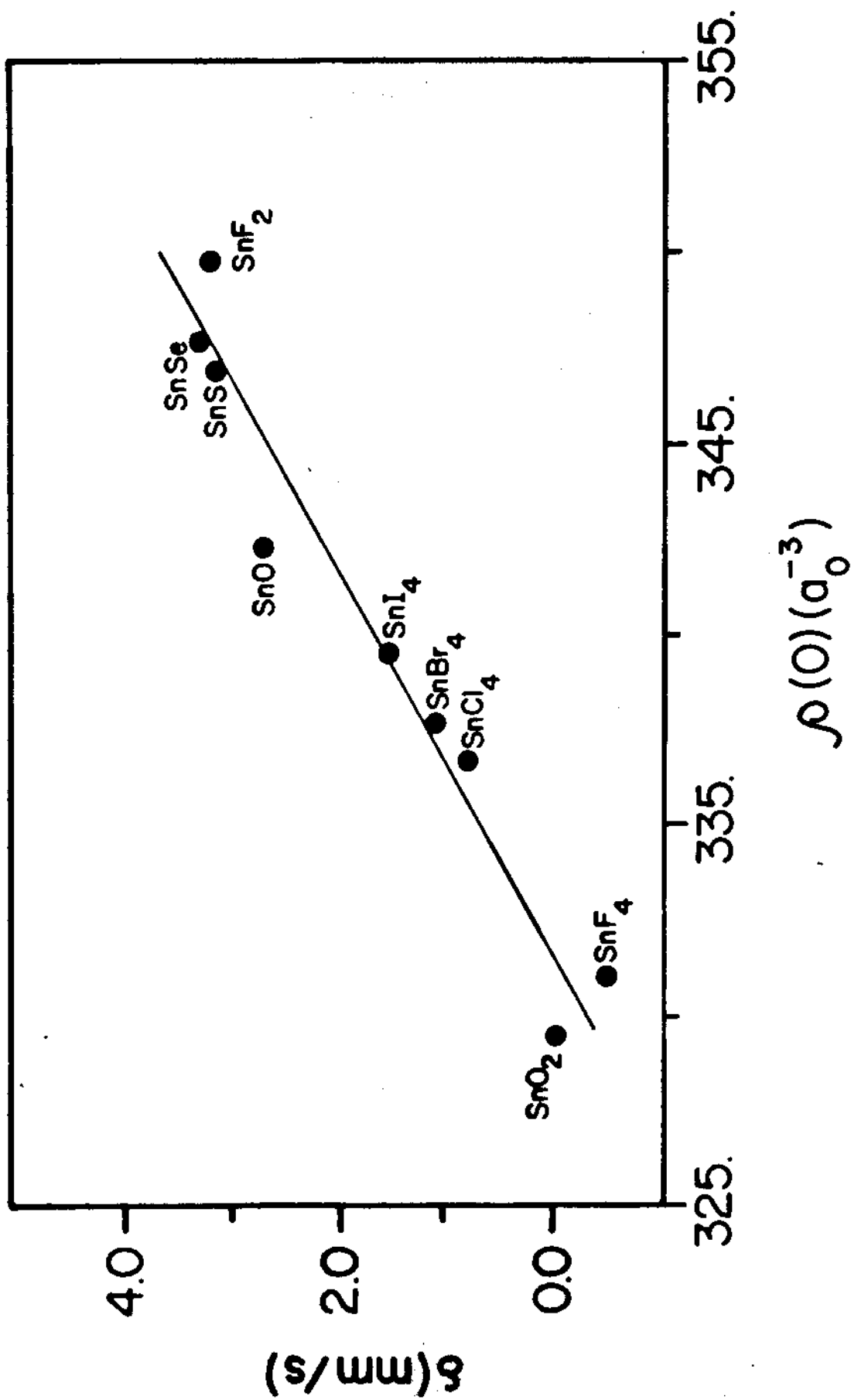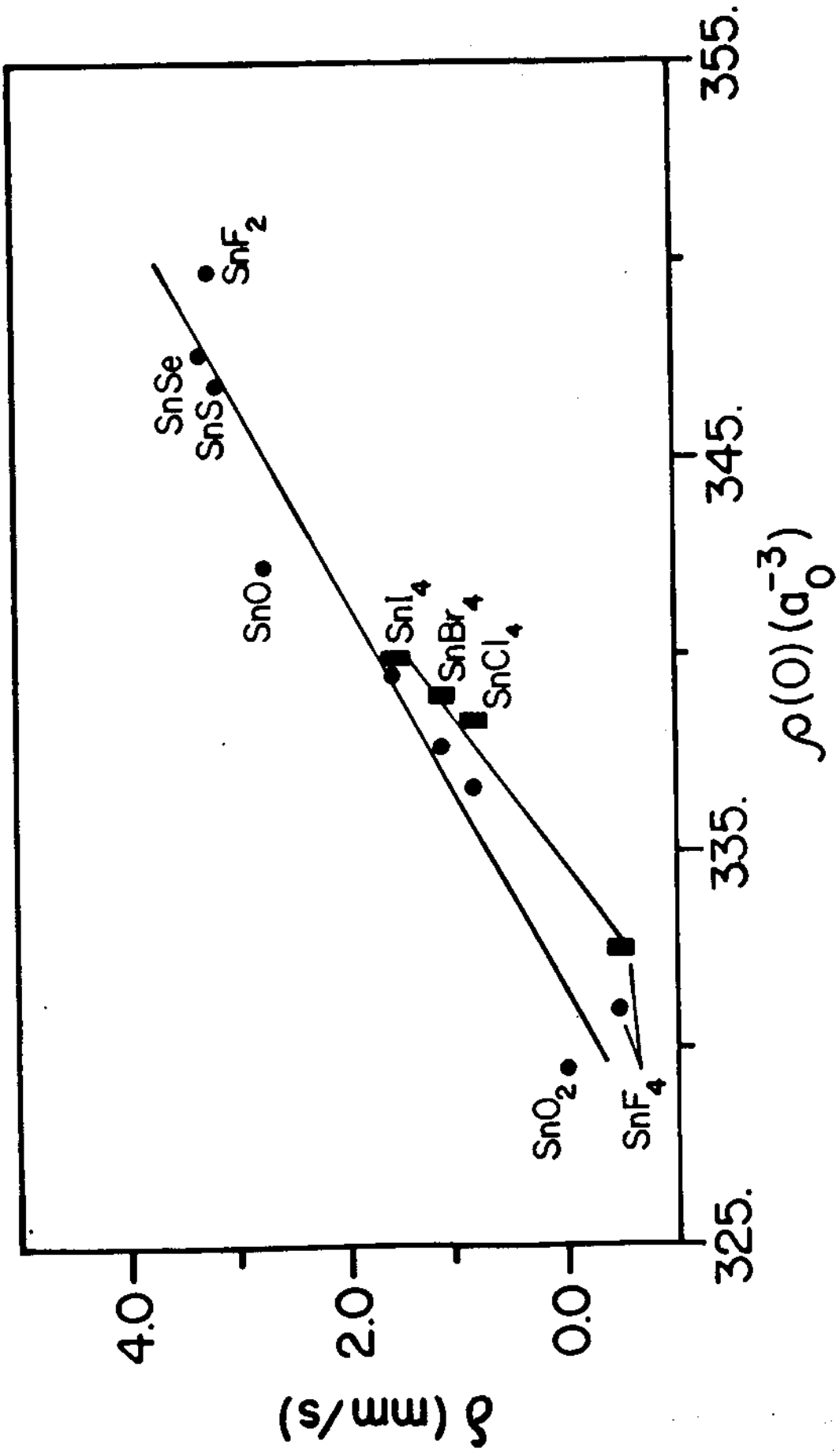
Compound	Crystal Structure [a]	Lattice Parameters (Å)	Sn-X nearest-neighbor distances (Å)	Clusters	Local Symmetry
SnO(black) [b]	tetragonal	a=3.80 c=4.84	4(O)2.22	$[SnO_4Sn_8]$ $[SnO_6Sn_8]$ $[SnO_8Sn_{12}]$	C_{4v}
SnF_2 (β) [c]	orthorhombic	a=4.98 b=5.14 c=8.48	1(F)1.89 1(F)2.26 1(F)2.40 1(F)2.41 1(F)2.49	$[SnF_5]$ $[SnF_{11}Sn_4]$	C_1
SnS [d]	orthorhombic	a=4.33 b=11.18 c=3.98	1(S)2.62 2(S)2.68 2(S)3.27 1(S)3.39	$[SnS_7Sn_2]$ $[SnS_7Sn_6]$ $[SnS_7Sn_8]$	C_s
SnSe [d]	orthorhombic	a=4.46 b=11.57 c=4.19	1(Se)2.77 2(Se)2.82 2(Se)3.35 1(Se)3.47	$[SnSe_7Sn_8]$	C_s
SnO_2 [d][e]	tetragonal	a=4.74 c=3.19	2(O)$_y$ 2.06 4(O)$_{xz}$ 2.05	$[SnO_6]$ $[SnO_6Sn_2]$ $[SnO_{10}Sn_{10}]$	D_{2h}
SnF_4 [f]	tetragonal	a=4.04 c=7.93	4(F)$_{xy}$ 2.02 2(F)$_z$ 1.88	$[SnF_6]$ $[SnF_{14}Sn_4]$ $[SnF_{22}Sn_4]$	D_{4h}

Table II

Compound	Cluster	$\rho(0)(a_0^{-3})$		Charge on Sn_c	Populations on Sn_c		$\delta^{(a)}$ (mm/s)
SnO	$[SnO_8Sn_{12}]$	s.core valence Total	314.90 27.40 342.30	+1.25	5s 5p	1.37 1.39	2.71
SnF_2	$[SnF_{11}Sn_4]$	s.core valence Total	314.73 35.04 349.77	+1.68	5s 5p	1.66 0.67	3.20
SnS	$[SnS_7Sn_8]$	s.core valence Total	315.64 31.29 346.93	+1.03	5s 5p	1.61 1.36	3.16
SnSe	$[SnSe_7Sn_8]$	s.core valence Total	315.51 32.17 347.68	+0.86	5s 5p	1.71 1.43	3.30
SnO_2	$[SnO_{10}Sn_{10}]$	s.core valence Total	315.76 13.71 329.47	+2.82	5s 5p	0.49 0.70	0
SnF_4	$[SnF_{22}Sn_4]$	s.core valence Total	315.81 15.29 331.10	+2.80	5s 5p	0.57 0.64	-0.47

Table III

Compound	Cluster	Orbital	Energy (eV)	Population analysis (in %)				Contribution to $\rho(0)(a_o^{-3})$	Total valence $\rho(0)$ (a_o^{-3})
				$Sn_c(5s)$	$Sn_c(5p)$	Sn_p	Anion		
SnO	$[SnO_8Sn_{12}]$	$13a_1$	-12.22	8.6	$8.5(5p_z)$	54.8	28.1	3.59	27.40
		$15a_1$	-10.49	13.6	$20.1(5p_z)$	36.3	30.0	5.54	
SnF_2	$[SnF_{11}Sn_4]$	58a	-6.38	49.9	12.9	11.7	25.5	20.30	35.04
SnS	$[SnS_7Sn_8]$	28a'	-9.35	12.8	$14.9(5p_x,5p_y)$	18.5	53.8	6.46	31.29
SnSe	$[SnSe_7Sn_8]$	28a'	-8.19	14.2	$14.3(5p_x,5p_y)$	15.9	55.6	7.24	32.17

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