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Electronic Charge Densities for Two Layer Semiconductors - SnS_2 and $SnSe_2$

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Abstract

The total valence electronic charge densities for two semiconductors with layer structure - SnS_2 and $SnSe_2$ - are calculated using wavefunctions from pseudopotential energy band structure calculations at a representative $\vec{k}$ point. A comparison is made between the charge density distributions for these two compounds and those of ZnS in the wurtzite structure.

I. Introduction

Compounds with layer structures have attracted a great deal of attention because of their wide range and in some cases unique electronic properties.[1] Most of the optical studies on these crystals, up to now, $\overset{\text{been/}}{\text{have}}$ concentrated on the semiconductors. The authors have previously calculated[2] the electronic band structure of two compounds - SnS_2 and $SnSe_2$ using the Empirical Pseudopotential Method (EPM). The wavefunctions obtained from these calculations are now used to calculate the electronic charge distributions. These charge distributions are useful in understanding the nature of bonding in these crystals. Such calculations have primarily been done for crystals with the zincblende structure.[3,4] More recently, Joannopoulos and Cohen[5] have compared the charge distributions of ZnS in the zincblende and wurtzite structure. They showed also that the representative $\vec{k}$ - points can give to a very good approximation the total valence charge density for crystal with the wurtzite structure. In this paper, we shall report on calculations of charge densities for SnS_2 and $SnSe_2$ using one representative or mean value $\vec{k}$ - point.[6] In section II, we shall discuss the method of calculation. The results and the comparisons between the calculated charge densities and those of ZnS in the wurtzite structure are given in Section III.

II. Method of Calculation

The main steps involved in the present calculations are:

A. determination of the representative points by the method discussed in ref. 5. From Eq. (31) in ref. 5, the charge density calculated in real space from one representative point is given as

$$\rho(\vec{k},\vec{r}) = \sum_{\vec{R}_\ell} \rho(\vec{R}_\ell,\vec{r})\ \xi\ (\vec{k},\vec{R}_\ell) \tag{1}$$

where $\vec{R}_\ell$ is the lattice vector in real space, and

$$\xi(\vec{k},\vec{R}_\ell) = \frac{1}{12} \sum_{P_R} e^{i\vec{k}\cdot P_R\vec{R}_\ell} \tag{2}$$

where P_R is the symmetry operator for the crystal. Because there is confusion in ref. 2 about the axes of the two-fold rotation, we reiterate the 12 symmetry operations in D_{3d}. They are: the identity operator E, two three-fold rotations ($2C_3$) about the $\vec{c}$-axis, three two-fold rotations ($3C_2'$) about the axes in the X-Y plane and passing through the corner of the hexagon, the inversion operator i, two three-fold rotations about the $\vec{c}$-axis followed by an inversion ($2iC_3$), and three two-fold rotations followed by an inversion ($3iC_2'$).

By setting ξ equal to zero for various sets of $\vec{R}_\ell$, we solve the resulting transcendental equations for possible $\vec{k}$'s. In the present case, we obtain the mean value point,

$$\vec{k} = (0.1904,\ 0.1904,\ 0.25) \tag{3}$$

where the components are along the primitive reciprocal lattice vectors.

B. calculations of the total charge densities. The wavefunctions at $\vec{k}$ are obtained by diagonalizing the pseudopotential Hamiltonian over plane wave basis. The pseudopotentials for the two crystals are given in ref. 2. These wavefunctions are then used to calculate the total valence electronic charge density:

$$\rho(\vec{r}) = \frac{2e}{12} \sum_{\{P_R\}} \sum_{n} \sum_{\vec{G}} \sum_{\vec{G}'} \alpha_n^*(P_R^{-1}\ \vec{G})\ \alpha_n(P_R^{-1}\ \vec{G}')\ e^{i(\vec{G}'-\vec{G})\cdot\vec{r}} \tag{4}$$

where n runs over all valence bands. The $\vec{G}$'s are reciprocal lattice vectors in units of $\frac{2\pi}{a}$, and a is the lattice constant. $\alpha_n(\vec{G})$ is the component of the wavefunction for the n-th band on the $\vec{G}$-th basis state. The factor 2 is included to take account of the spin degeneracy.

III. Results

The charge densities of SnS_2 and $SnSe_2$ are displayed on two different planes; these planes are shown in Fig. 1. The charge densities in plane OABC are shown in Figs. 2a and 2b. These contours show the charge distributions among different metallic ions in the same layer. The contours in plane DEFG (Figs. 3a and 3b) show the distribution between the ions on different layers and the distribution between the metallic ions and the chalcogen ions forming the SnX_2 molecules. In Figs. 2 and 3, we use a mesh of 784 points and 703 points respectively. The charge densities within the dotted circles (~19%, 8% and 11% of the length $\overline{OA}$ for Sn^{4+}, S^{6+} and Se^{6+} respectively[7]) are not expected to be accurate because these distributions are calculated by using pseudowave functions. They are not orthogonalized to the core wavefunctions, therefore, the charge densities at the ions are not representative of the true charge densities. The unit of the charge density is measured in $-e$, the charge of an electron.

In Figs. 2a and 2b, the metallic ions are located at the corners of the parallelogram. One of the chalcogen ion is located $\frac{1}{4}$ of c above the plane, where c is the lattice constant in the $\vec{z}$ direction. We used a dot to indicate its location. The other chalcogen ion is located at same distance below the plane. This location is indicated by a small circle. The nearest neighbours of either the S ion or Se ion are three Sn ions which are equi-distance away. We expect from crystal field point of view that the bonding charge of the chalcogen ions will point toward the Sn ions. The contours with density at value of 31.9 in SnS_2 and 36.5 in $SnSe_2$ are due to the bonding charge intersected by the X-Y plane. In Fig. 2b, the density of $SnSe_2$ in the region just outside the dotted circle of the metallic ion is larger than the corresponding distribution of SnS_2, so that the charge distribution of $SnSe_2$ is more uniform than SnS_2. This difference between the two crystals is more evident in Figs. 3a and 3b, and shows that SnS_2 is more covalently bound than $SnSe_2$. This is consistent with the results of the band structure calculations. The fundamental energy gap of SnS_2 is 2.07eV and the value for $SnSe_2$ is 0.97eV. The sites of Sn and S or Se ions for nearest layers are explicitly indicated in these two figures. The bonding charge within the layer can be clearly seen, which is concentrated between the Sn and the chalcogen ions forming the SnX_2. These bonding charges are p-like in character. The asymmetric shape of the charge distribution around the S or Se ion can be explained as follows: The p-like states of the chalcogen ion extend into the interlayer region. The repulsive interaction between the p-states of nearest layers pushes the charge distribution toward the ions. Furthermore, the metallic ion at the nearest layer exerts a weak attractive force on the p-like states. The effect of this attractive interaction is to pull the charge toward the Sn atom of the nearest layer. The charge distribution for one layer form almost a closed shell. This illustrates that the binding between the layers is weak. The contours around the Sn ions in both crystals have bulged toward the S or Se ion at nearest layer. The free Sn atom is like C, Si and Ge to form sp^3 orbitals. However, the sp^3 orbitals do not consistent with the crystal symmetry at the site of Sn. Most of the charge in the orbitals form bounding charges with the chalcogen ions. The residue charge distribution on Sn will try to persist in the form of sp^3 orbitals.

It is interesting to compare these results with the charge distribution of ZnS in the wurtzite structure. We reproduce Fig. 8 of ref. 5 as Fig. 4 in order to facilitate the discussions. Comparing the magnitudes of the charge densities near the metallic ions in Figs. 2, 3 and 4, we find that ZnS is more ionic than the two compounds in layer structure. The densities at the bonds within the layer for SnS_2 and $SnSe_2$ have values comparable to the case of ZnS. The largest difference between these two different kinds crystal structure is shown in Fig. 4 and Figs. 3a and 3b. In Fig. 4, the Zn ions at different coordinates in the $\vec{z}$ direction are covalently bound to the S ions. However, the Sn ions in Figs. 3a and 3b do not have similar bonding properties as the Zn ions. The

Sn ions interact weakly with closed shell charge distribution around the chalcogen ions of nearest layers. The covalent bonding between the Sn and the chalcogen ions happens only within the SnX_2 molecules. These crystalline effects are showing clearly in the present comparison.

In conclusion, we have presented charge density calculations for layer structure compounds. The charge densities show that there is strong covalent bonding between the metalic ion and chalcogen ions within the same layer. Ions at nearby layers interact very weakly. By comparing the results with ZnS in the wurtzite structure, we find ZnS to be the most ionic, followed by SnS_2 and finally $SnSe_2$ is the least ionic of the three crystals. (The fundamental energy gaps for these crystals are 3.8, 2.07 and 0.97 eV respectively.)

Acknowledgement

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Figure Captions

Fig. 1. Planes in real space used to display the charge density calculations.

Fig. 2a. Total charge density of SnS_2 in OABC plane.

Fig. 2b. Total charge density of $SnSe_2$ in OABC plane.

Fig. 3a. Total charge density of SnS_2 in DEFG plane. (A reduction of 0.67 in scale).

Fig. 3b. Total charge density of $SnSe_2$ in DEFG plane. (A reduction of 0.67 in scale).

Fig. 4 Total charge density of ZnS in (110) plane.

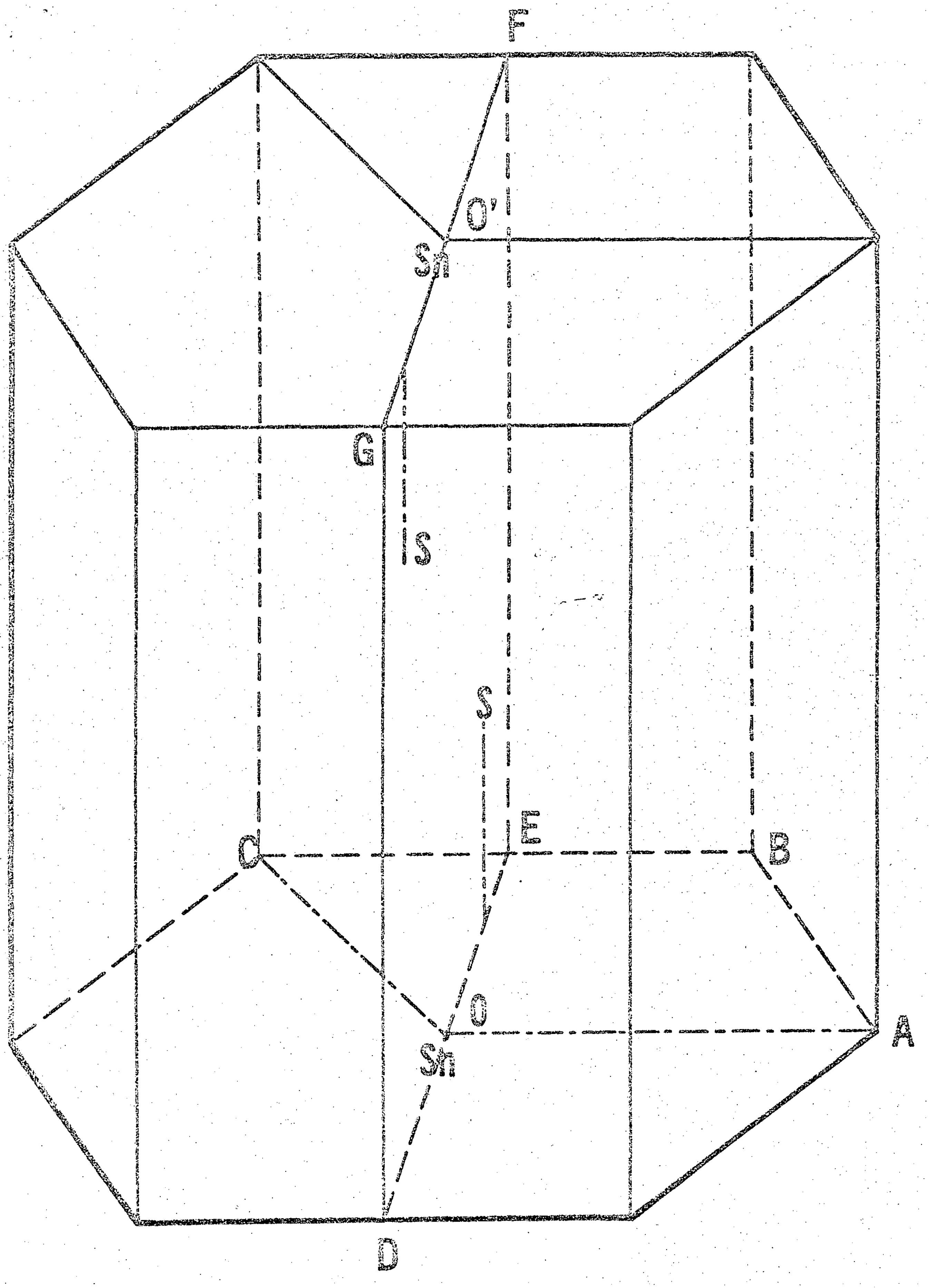

F
O'
Sn
G
S
S
E
C
B
O
A
Sn
D

FIG. 1

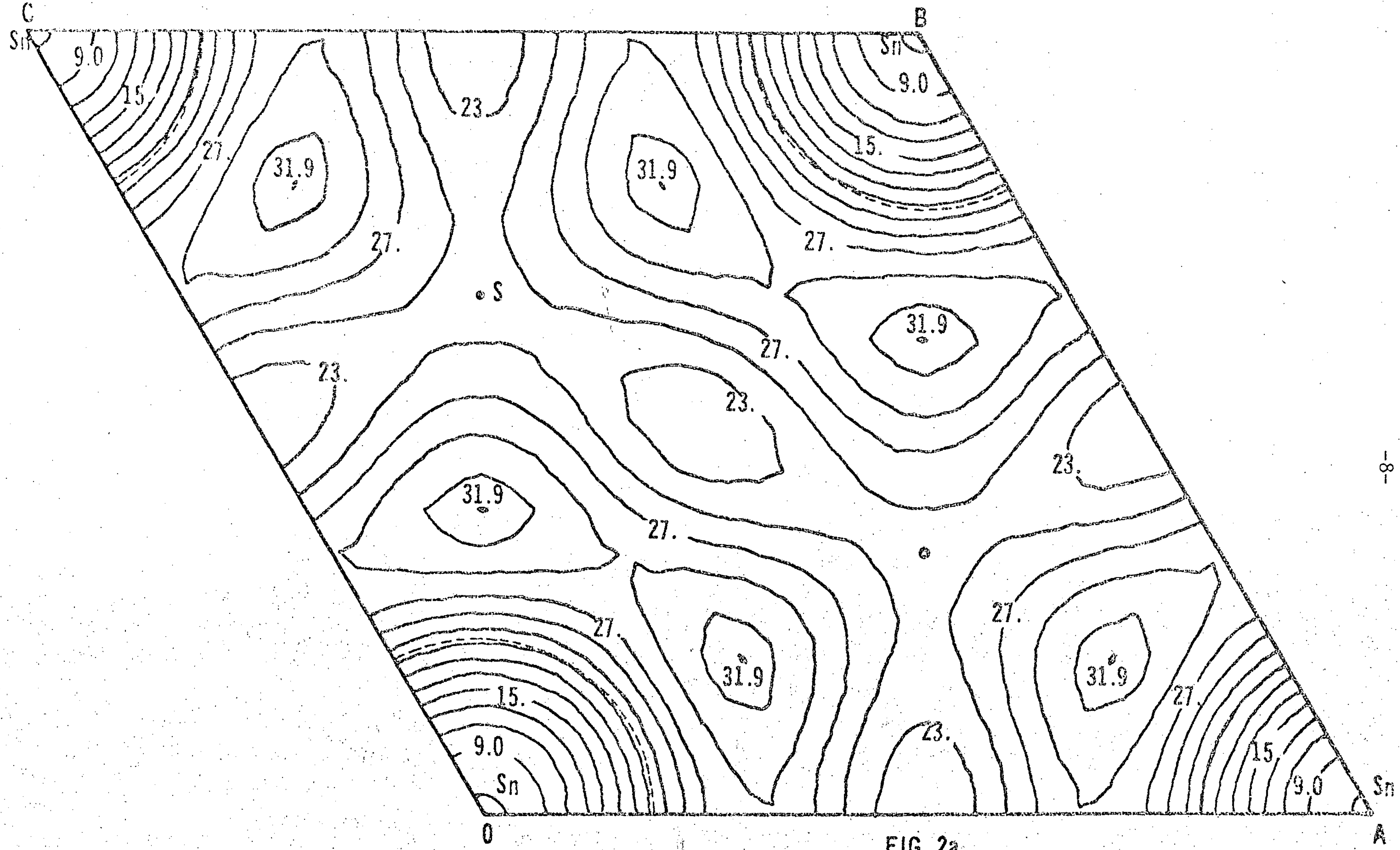

C
Sn
9.0
15
27.
31.9
23
B
Sn
9.0
15.
27.
S
23.
27.
31.9
23.
31.9
23.
27.
27.
31.9
27.
31.9
15.
9.0
Sn
23.
21.
15
9.0
Sn
0
A

FIG. 2a

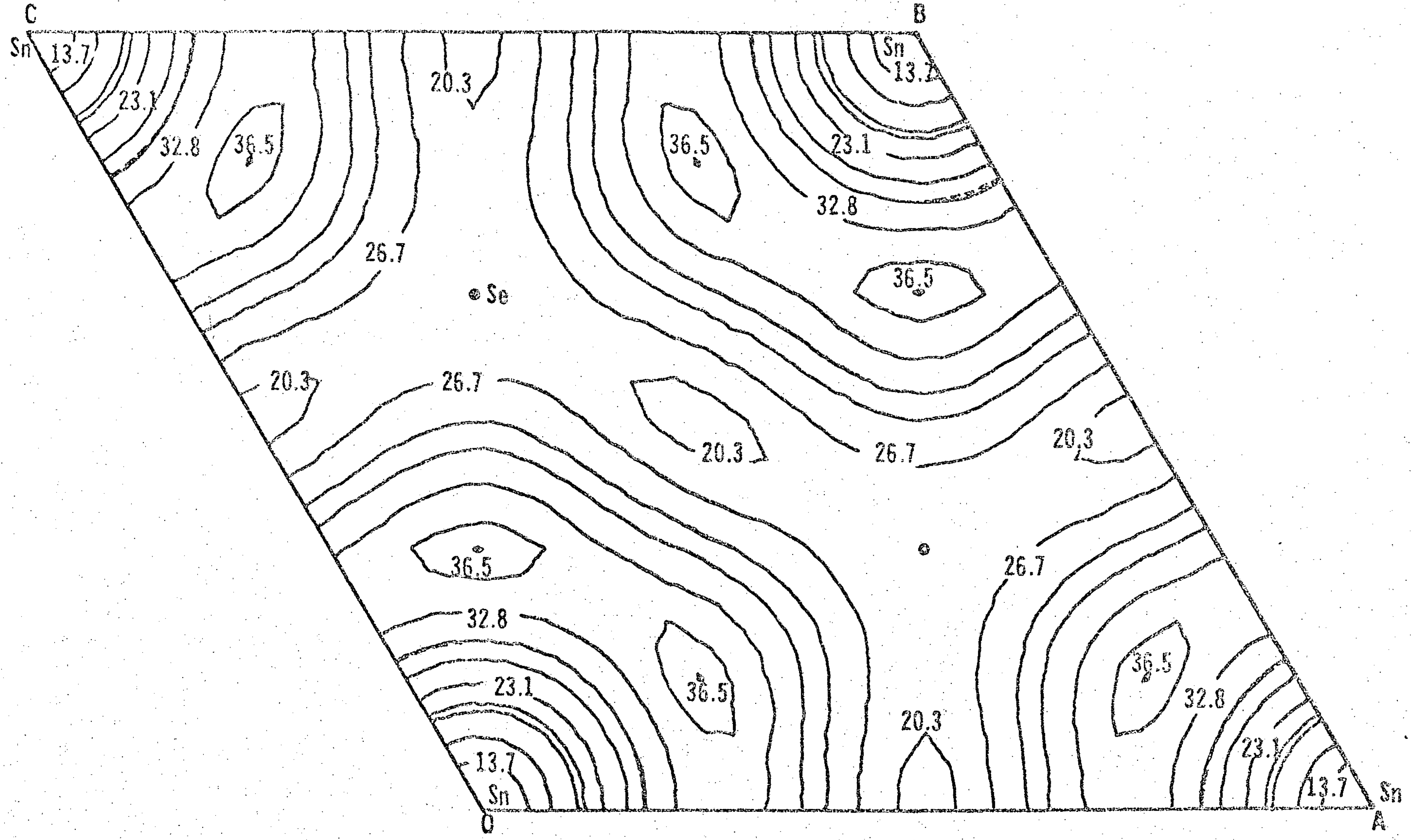

C
B
Sn
13.7
13.7
23.1
32.8
36.5
20.3
26.7
Se
20.3
26.7
20.3
26.7
20.3
36.5
32.8
23.1
13.7
Sn
O
A
Sn

FIG. 2b

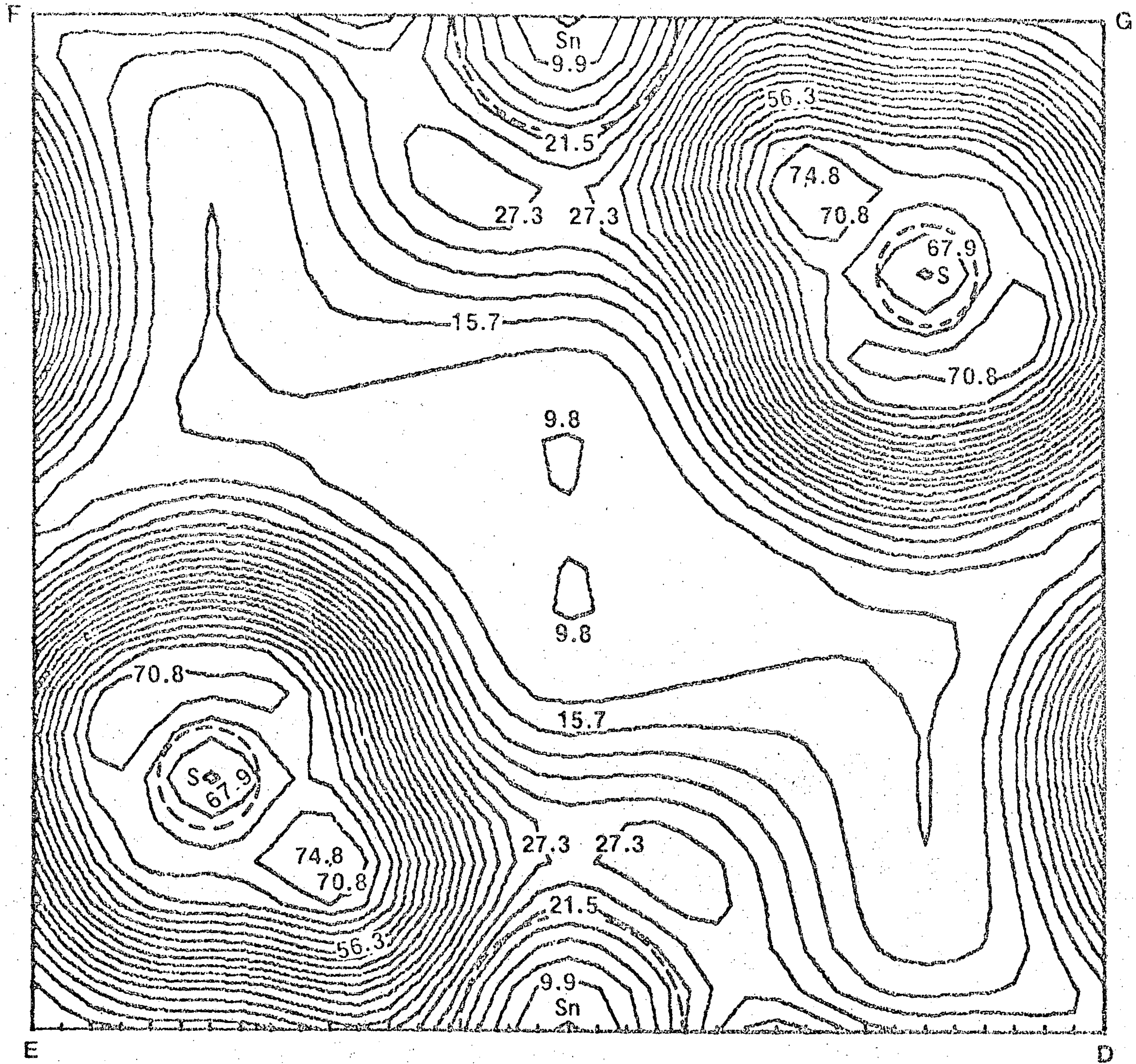
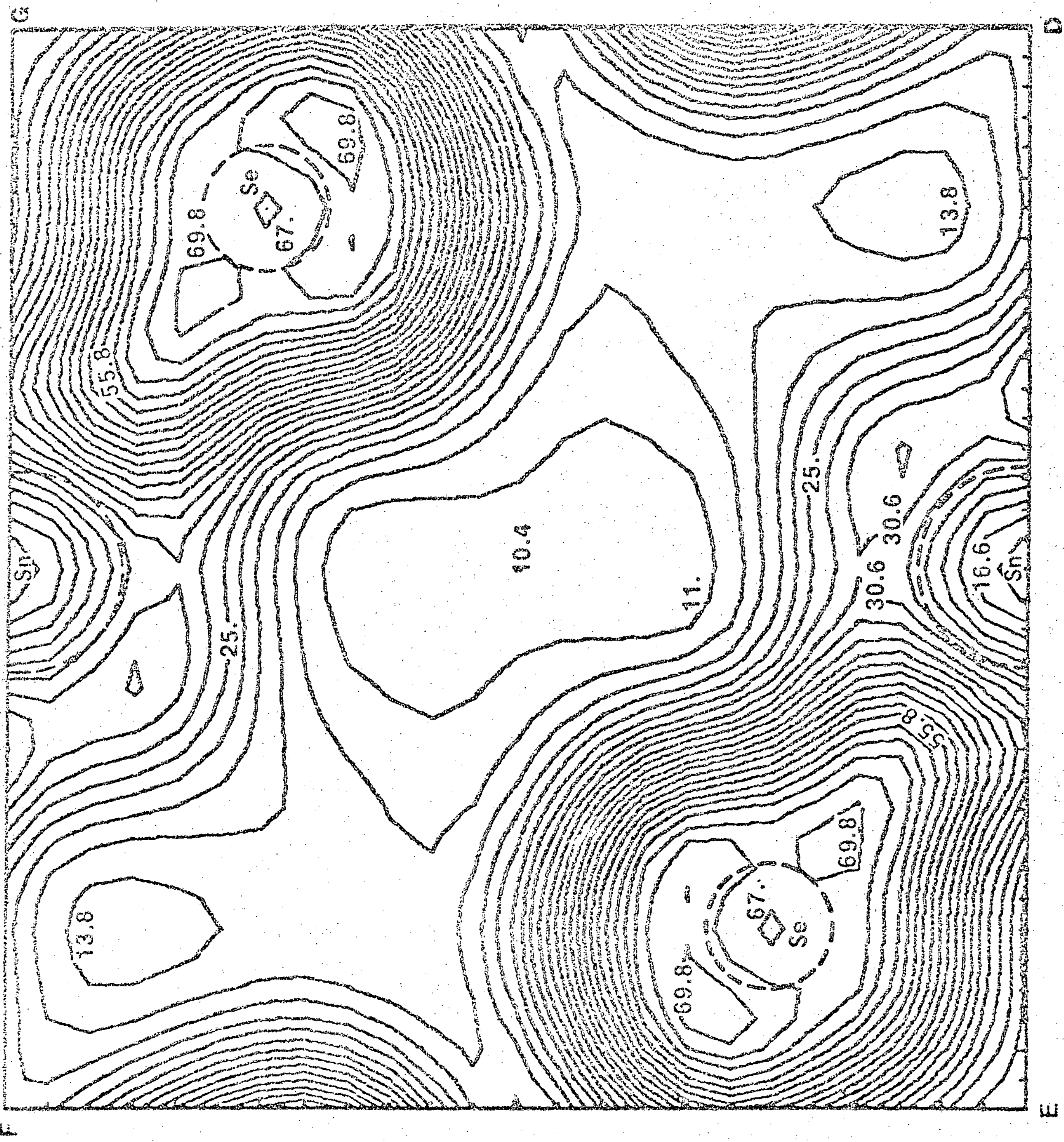

F
G
E
D
Sn
9.9
56.3
21.5
74.8
70.8
27.3
27.3
67.9
S
15.7
70.8
9.8
9.8
70.8
S
67.9
15.7
27.3
27.3
74.8
70.8
21.5
56.3
9.9
Sn

FIG. 3a


G
D
F
E
Se
Se
67.
67.
69.8
69.8
69.8
69.8
69.8
69.8
55.8
55.8
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25.
13.8
13.8
Sn
Sn
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11.
30.6
30.6
16.6

FIG. 3b

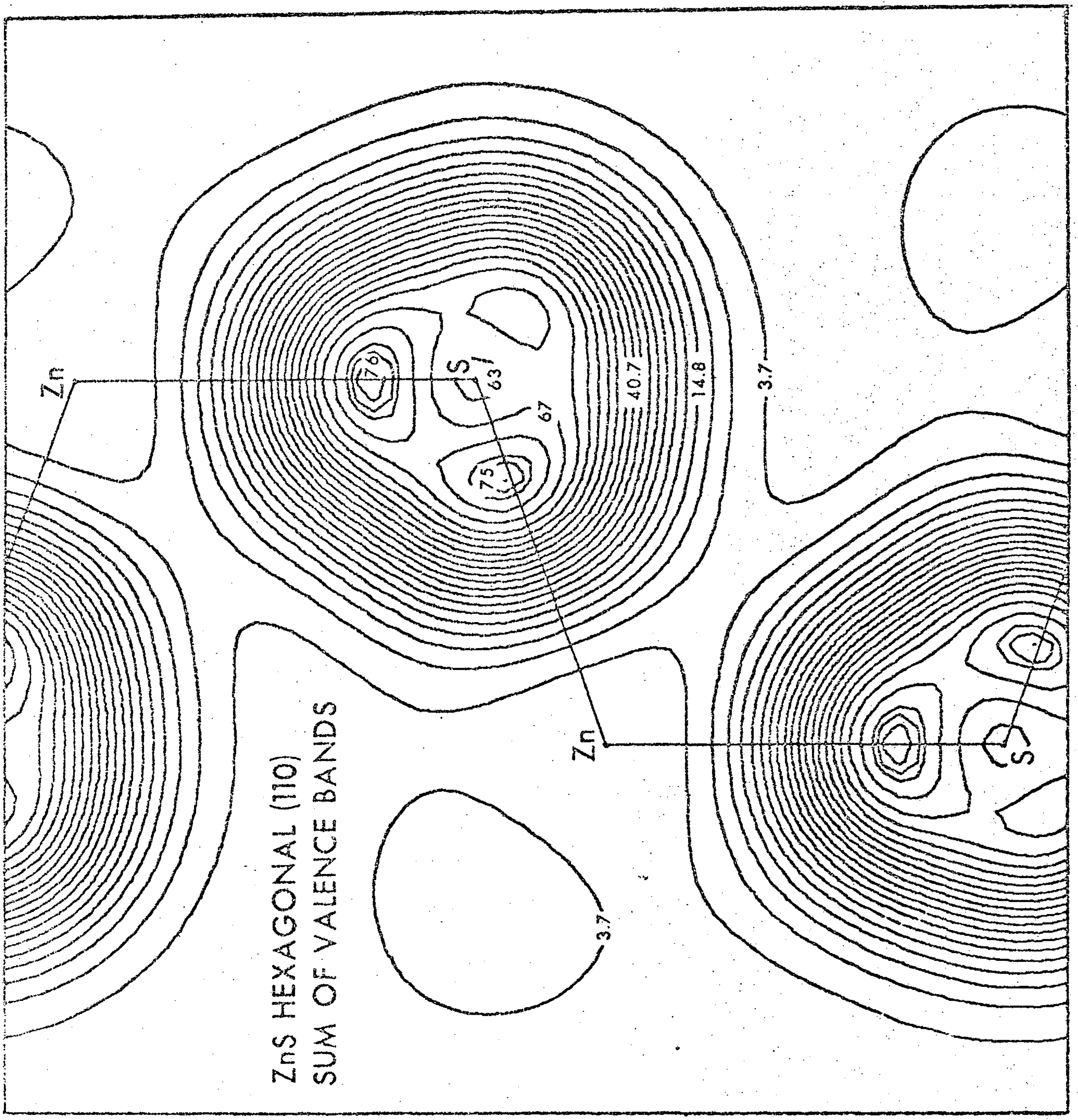
ZnS HEXAGONAL (110)
SUM OF VALENCE BANDS
Zn
S
76
63
67
75
40.7
14.8
3.7
Zn
S
3.7

FIG.4

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