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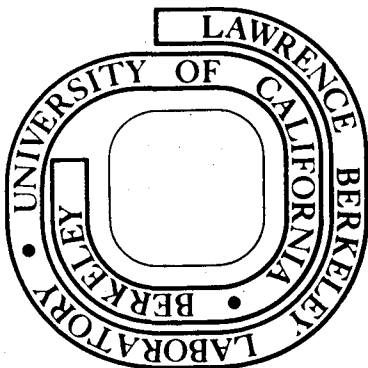
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Electronic Charge Densities in PbSe and PbTe*

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Abstract

The electronic charge densities for PbSe and PbTe are derived from recent pseudopotential band structure calculations. The results are displayed as contour plots for individual bands and for the total valence charge. Fractional amounts of charge inside touching spheres around each atom are calculated for different l -values by an angular momentum projection method. Rough estimates of the charge transfers in PbSe and PbTe are made. The charge densities for the states forming the gap at the point L of the Brillouin zone are presented and related to pressure and temperature coefficients of the fundamental gap.

I. Introduction

The calculation of electronic charge densities and their display as a function of position in real space has been used for solids with great success.¹ In this paper we present new electronic charge densities for PbSe and PbTe.

The calculations are based on recent pseudopotential band structure models² which give results consistent with a large number of optical and electronic experimental data. The calculations presented here are not the first attempts to evaluate charge densities for the lead salts. Conklin, Johnson and Pratt³ have calculated PbTe charge density parameters for various energy levels at high symmetry points using the APW method. Their results were decomposed into $l = 0, 1, 2, 3$ angular momentum components. Later Tsang and Cohen⁴ derived total charge densities and charge densities associated with states at the smallest gap at L for PbTe. Their calculations were similar to the present calculations based on pseudopotential band structures. The new pseudopotentials used in our calculations, however, differ significantly from these earlier potentials leading to several changes in the ^{calculated} optical and electronic properties,² and this is the motivation for a new investigation of PbTe. In addition we present calculations for PbSe allowing comparisons of the two salts in terms of charge transfer and trends in relative ionicity. Finally we calculate the charge profiles for states at the smallest gap at L for both salts. These results are very useful in understanding and visualizing the behavior of the gap at L as a function of hydrostatic pressure and of temperature.

II. Calculations and results

The charge density for one band can be written as

$$\rho_n(\underline{r}) = e \sum_{\underline{k}}^{\text{BZ}} \psi_{\underline{k}}^{*n}(\underline{r}) \psi_{\underline{k}}^n(\underline{r}) \quad (1)$$

with

$$\psi_{\underline{k}}^n(\underline{r}) = \sum_{\underline{G}} a_{\underline{k}}^n(\underline{G}) e^{i\underline{G} \cdot \underline{r}} \quad (2)$$

the density becomes

$$\begin{aligned} \rho_n(\underline{r}) &= e \sum_{\underline{k}}^{\text{BZ}} \sum_{\underline{G}, \underline{G}'} \left(a_{\underline{k}}^{n*}(\underline{G}') a_{\underline{k}}^n(\underline{G}' + \underline{G}) \right) e^{i\underline{G} \cdot \underline{r}} \\ &= e \sum_{\underline{k}}^{\text{BZ}} \sum_{\underline{G}} \rho_{\underline{k}}^n(\underline{G}) e^{i\underline{G} \cdot \underline{r}} \end{aligned} \quad (3)$$

The sum over \underline{k} in Eq. (3) which extends over the entire Brillouin zone can be reduced to a sum over the irreducible part of the Brillouin zone (1/48 for the lead salts) provided the $\rho_{\underline{k}}^n(\underline{G})$ are properly symmetrized. In the case of rocksalt crystals the symmetry group O_h^5 is symmorphic and the symmetrization is trivial: all $\rho_{\underline{k}}^n(\underline{G})$ with \underline{G} -vectors belonging to the same "star" have to be equal. The remaining sum over \underline{k} -states in the irreducible part of the Brillouin zone can be significantly reduced using the "special" \underline{k} -point scheme as developed by Chadi and Cohen.⁵ The total valence charge is obtained from

$$\rho(\underline{r}) = \sum_{n=1}^5 \rho_n(\underline{r}) .$$

In considering the charge densities for states at the

fundamental gap, the sum over k degenerates to one term with $k = (0.5, 0.5, 0.5)$.

The various sets of eigenspinors $\{a_k^n(\underline{G})\}$ in Eq. (2) were obtained from pseudopotential calculations² which included non-local as well as spin-orbit effects. To visualize the charge densities we first compute $\rho_n(\underline{r})$ for a grid of 2500 points in a (100) plane and then display the contours of constant density. The charge densities for PbTe computed individually for each of the five valence bands are given in Figs. 1a and 1b. The values are indicated in units of e^- per unit cell volume $\Omega_c = a^3/4$. In addition we have calculated the fractional charge decomposed into angular components inside touching spheres around each atom (Table 1). The computational procedure for this is discussed in Ref. 2. The numbers listed in Table 1 represent fractional amounts of charge inside the spheres around each atom and thus differ from previously published⁷ values of fractional angular-character of charge which have been obtained by scaling the different charges with the respective sphere volumes. The sphere radii were chosen consistent with the total charge distribution to be $r_{\text{cation}} = 1.29 \text{ \AA}$, $r_{\text{anion}} = 1.94 \text{ \AA}$ for PbTe and $r_{\text{cation}} = 1.22 \text{ \AA}$, $r_{\text{anion}} = 1.83 \text{ \AA}$ for PbSe. These volumes agree within 10% with the quoted⁶ ionic radii for Pb^{++} and $\text{Se}^{--}/\text{Te}^{--}$. All values are normalized to 100% i.e. it has been implied that all charge is totally concentrated within the spheres around each atom. This assumption is

of course not exactly true; it is however a reasonable approximation (within 10-20%) for ionic compounds crystallizing in the rocksalt structure.

The relationship between the numbers in Table 1 and the charge contours in Figs. 1a and 1b is clearly recognizable. The lowest valence band accommodates almost exclusively anion s-electrons. The next higher band contains mainly cation s-states with some contributions from anion s- and p-states. The relative amount of the calculated s- or p-character of the anion states depends somewhat on the sphere radius r_{anion} used in the calculations. Some of the more spread-out charge around the cation is interpreted as anion p-like charge if r_{anion} is increased. The bands 3 to 5 (Fig. 1b) represent mainly the anion p-states with varying admixtures of cation s- and p-character. As seen from Table 1, all valence bands exhibit only very little d-character. An interpretation of the valence bands in PbSe and PbTe on the basis of only s- and p-states therefore seems to be well justified. Moreover, the differences between PbSe and PbTe are relatively small, so the individual band charge densities of only PbTe need to be discussed.

In Fig. 2 the total valence charge distributions for both PbSe and PbTe are presented. The charge around the cation sites is mainly of s-character whereas around the anion sites it clearly exhibits contributions from both s- and p-states. In PbTe there is less charge transfer from

cation to anion than in PbSe. The relative amounts of total charge within the touching spheres are indicated in Table 1. They do not differ much from the simple "totally ionic" model, in which 2 electrons of the cation are transferred to the anion. The calculated effective charges of cation and anion (in units of electron charge) are $\sqrt{2.1}$ and 7.9 for PbSe and 2.5 and 7.5 for PbTe. Though these numbers are very approximate the ratios between the PbSe and PbTe values bear physical significance.

In the discussion of the pressure and temperature dependence of the gap at L the symmetry of the different states involved plays an important role.⁷ As a general rule one can state that with regard to pressure s-like states rise faster in energy than do p- or d-like states and that with regard to temperature (constant volume-Debye-Waller effect) p- and d-like states rise faster in energy than do s-like states. These results were obtained from a detailed analysis of pressure coefficients and Debye-Waller type temperature coefficients in terms of charge Fourier components $\rho_k^n(\underline{G})$.⁷ In an actual case cancellation effects can occur; therefore the exact pressure and temperature (Debye-Waller) coefficients can only be obtained by direct calculation. Nevertheless the general rules stated above may be used with caution to inspect charge density plots of individual states and this helps to interpret and illustrate the physical origins of the various effects. We thus present in Figs. 3ab charge density plots of the two states L(5) and L(6) forming the gap at L for PbSe and PbTe.

The top of the valence bands has L_6^+ symmetry originating in both compounds from an L_1^+ orbital in the absence of spin-orbit coupling. Group theory allows this state to be s- and d-like around the cation and p-like around the anion, which is also reflected in Table 1. The bottom of the conduction bands has L_6^- symmetry originating from a L_2^- orbital in PbSe and from a L_3^- orbital in PbTe. In both cases the states are p-like around the cation and s- and d-like around the anion. However, the details, the individual amounts of charge and the symmetry of the cation p-like orbitals are different. It is this difference which for example accounts for the very different effective mass anisotropies in the two compounds² and for the different Debye-Waller effects.⁷ The different symmetries of the cation p-like orbitals can be recognized from Figs. 3ab. While in PbSe the p-lobes point along the four equivalent (111) directions (a (100)-cut shows the charge maxima along (110)); in PbTe the charge maxima appear along the six equivalent (100) directions. These patterns can be understood as originating from the L_2^- and L_3^- states respectively, keeping in mind that for states at L the axis of quantization points along (111) and that the displayed charges are combinations symmetrized over all four inequivalent L-points. The inclusion of spin-orbit coupling mixes the L_2^- and L_3^- states and washes out the difference in the symmetry of the orbitals. In both compounds the valence states L(5) contain considerably

more s-like charge than the conduction states L(6) which in turn results in negative pressure coefficients for the gap. To understand the Debye-Waller temperature effect we focus on the amount of p-like charge in valence- and conduction bands. There the situation is not so clear, since both bands in both compounds contain considerable p-like charge. Moreover these p-like charges have to be weighted by different mean squared displacements of the different vibrating atoms to give a measure for the Debye-Waller temperature shift. Calculations⁷ show that the valence bands shift upwards in energy with temperature with comparable rates. Moreover, the different amounts of p-like charge on the cations in PbSe and PbTe shift the conduction bands upwards with sufficiently different rates so as to overcompensate for the valence band shift in PbTe but not in PbSe. Added to a positive lattice dilation coefficient,⁷ the different shifts thus produce a positive (Debye-Waller) temperature coefficient for the gap in PbTe which is in agreement with experiment, but result in a negative coefficient for the gap in PbSe in contradiction to experiment. It has been suggested in Ref. 7 that the inclusion of incoherent electron-phonon scattering might remove this inconsistency.

III. Conclusion

Electronic charge densities are calculated for individual bands for PbSe and PbTe. The calculations are based on recent

pseudopotential band structure models.² The charge densities are displayed as a function of position in real space. In addition the amount of charge within spheres around each atom is computed and decomposed into $\ell = 0, 1, 2$ angular components. The results exhibit the strong ionic character of both compounds. An approximate charge transfer of 1.9 (in units of electron charge) and 1.5 λ can be estimated for PbSe and PbTe respectively. Individual charge densities for states forming the smallest gap at L illustrate (based on the amount of s-like charge) the negative pressure coefficient of the gap in both compounds. An analysis in terms of p-like charge helps in analyzing the different Debye-Waller contributions to ^{the} temperature dependence of the gap in PbSe and PbTe.

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- 1. M. L. Cohen, Science 179, 1189 (1973).
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Table Caption

Table 1. Calculated fractional charges (in percent) inside touching spheres around anions and cations in terms of $l = 0, 1, 2$ atomic angular functions. The values are given for each valence band individually and for the total valence charge. Also indicated are values for the states L_6^+ (L(5)) and L_6^- (L(6)) forming the smallest gap at the point L of the Brillouin zone.

Table 1

band	PbSe						PbTe					
	Pb			Se			Pb			Te		
	s	p	d	s	p	d	s	p	d	s	p	d
1	1	1	0	97	1	0	3	1	0	95	1	0
2	55	0	0	18	24	3	70	0	0	13	13	4
3	0	12	0	0	85	3	0	16	0	0	81	3
4	5	8	1	1	80	5	4	10	2	0	79	5
5	21	2	2	0	70	5	12	2	3	0	80	3
total	16	4	1	23	52	4	18	6	1	22	50	3
	21			79			25			75		
total for a simple ionic model	20	0	0	20	60	0	20	0	0	20	60	0
L(5)	45	0	1	0	54	0	29	0	2	0	69	0
L(6)	0	43	0	28	0	29	0	58	0	9	0	33

Figure Captions

Figure 1a. Charge density contours in a (100) plane for PbTe for the lowest two s-like valence bands. The values are given in units of electrons per unit cell volume.

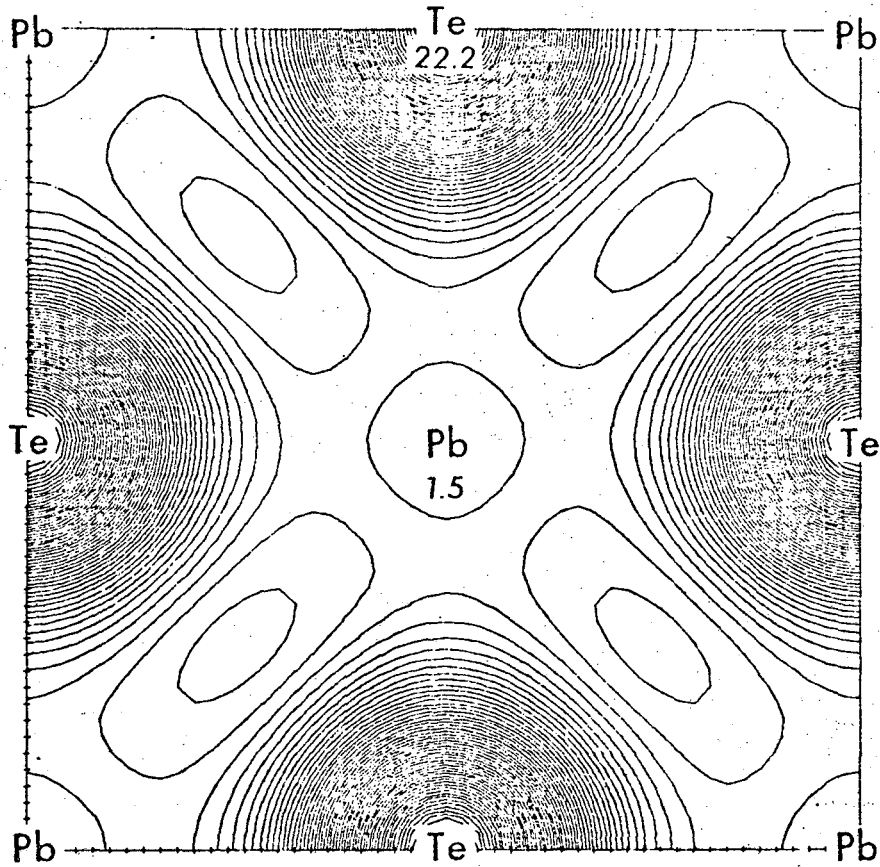
Figure 1b. Charge density contours for the third, fourth and fifth valence band of PbTe.

Figure 2. Total valence charge density for PbSe and PbTe.

Figure 3a. Charge density contours for PbSe and PbTe for the valence state L(5).

Figure 3b. Charge density contours for PbSe and PbTe for the conduction state L(6).

PbTe first valence band



PbTe second valence band

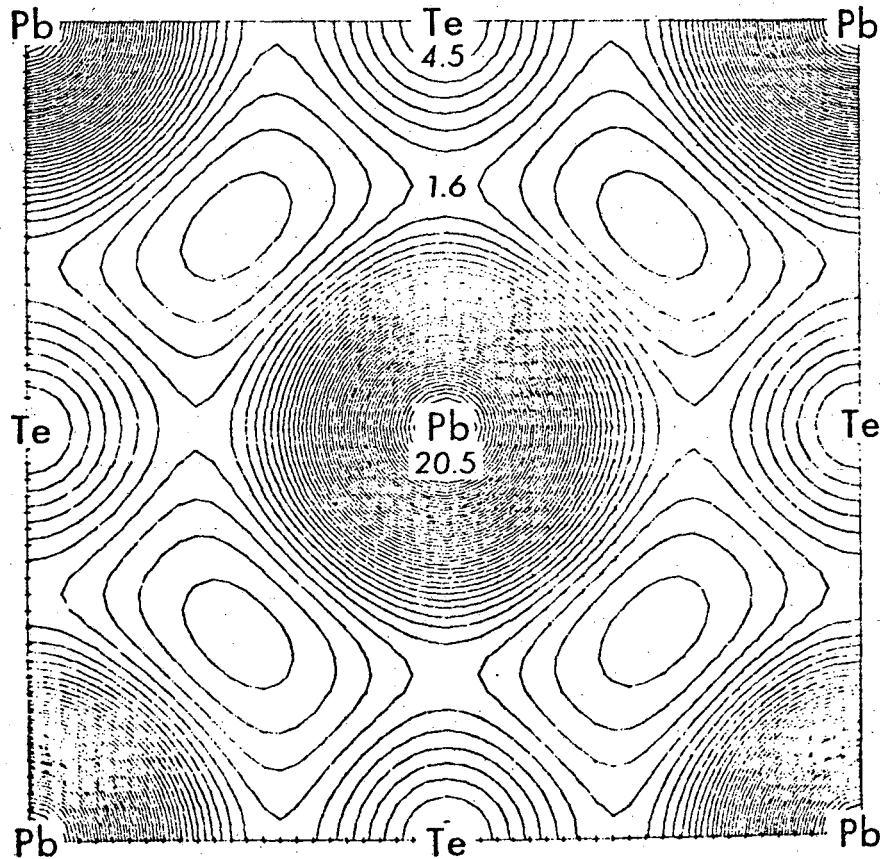


Figure 1a

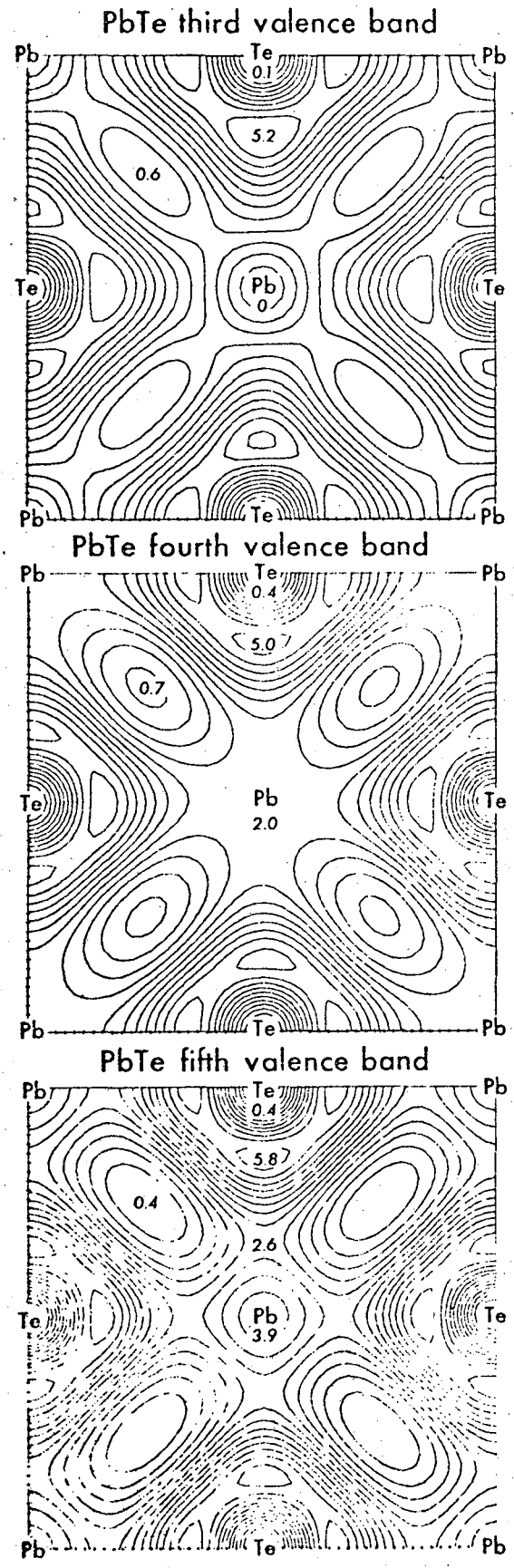


Figure 1b

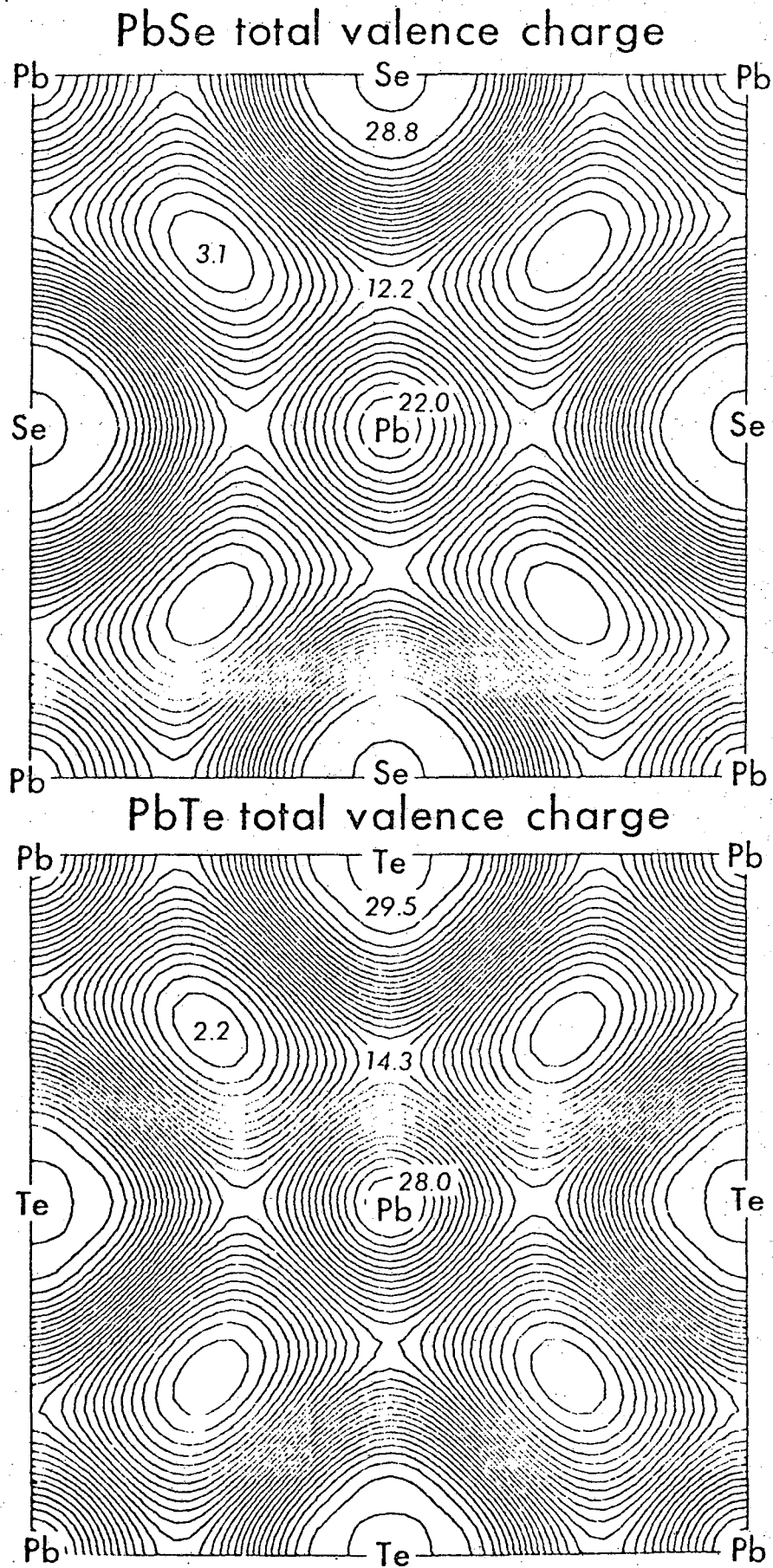
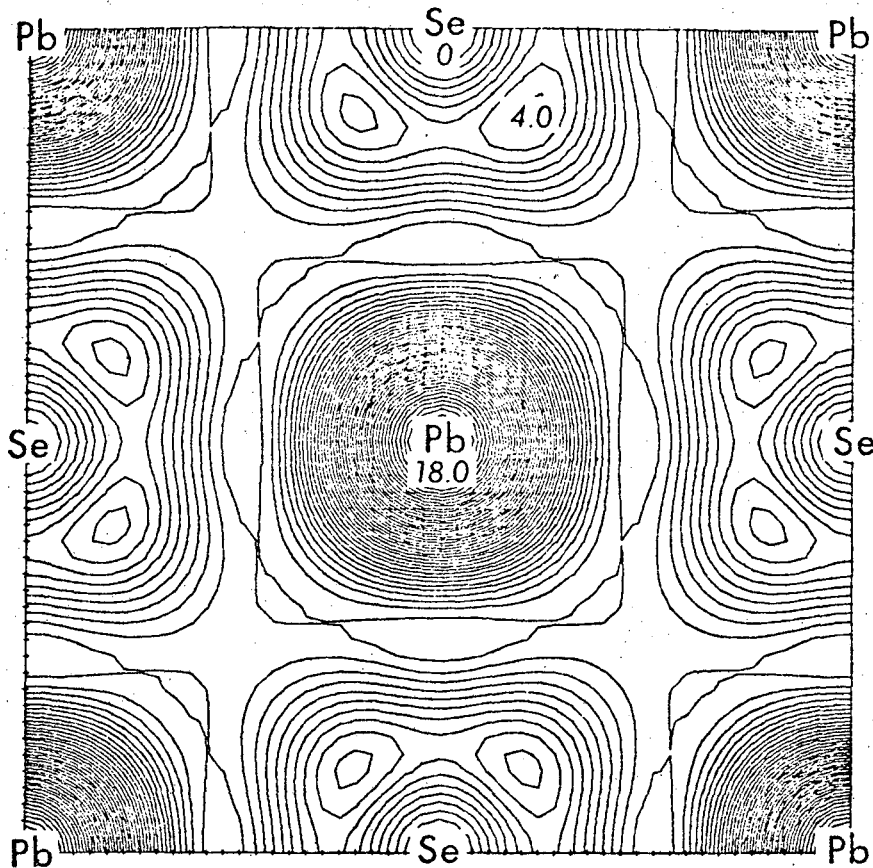


Figure 2

PbSe L(5) valence band



PbTe L(5) valence band

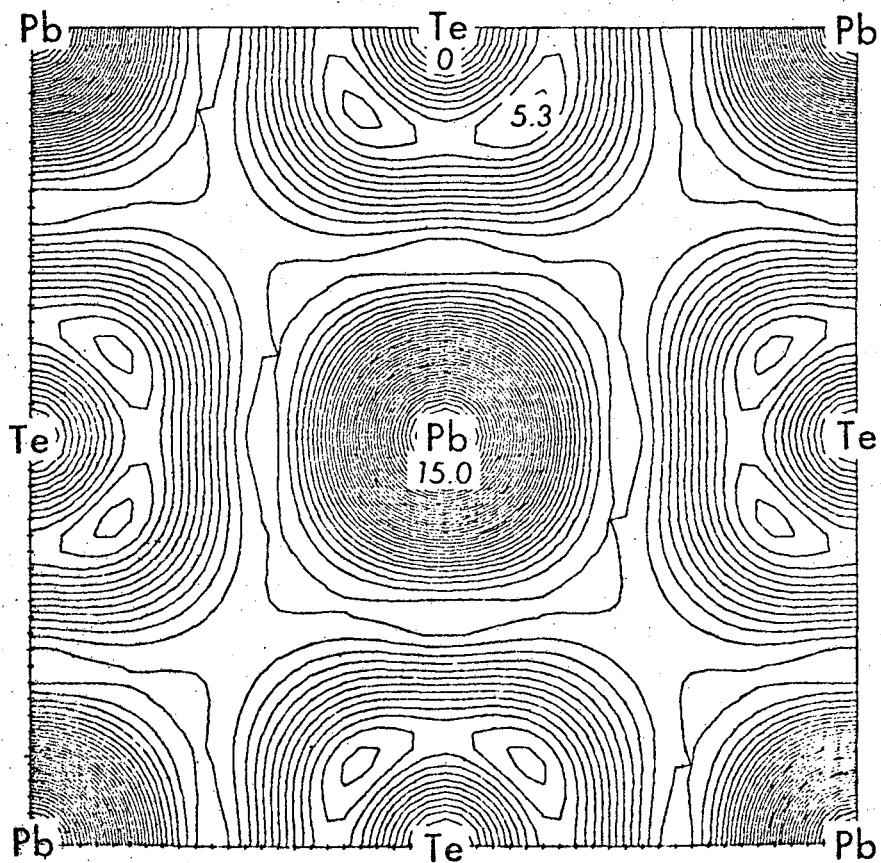
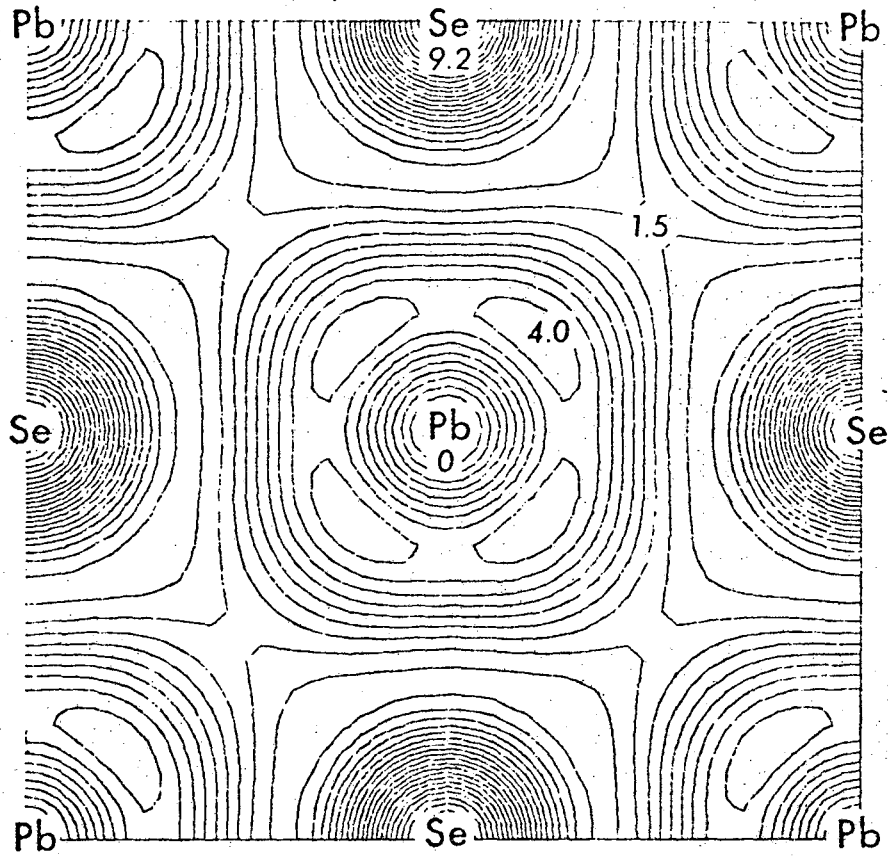


Figure 3a

PbSe L(6) conduction band



PbTe L(6) conduction band

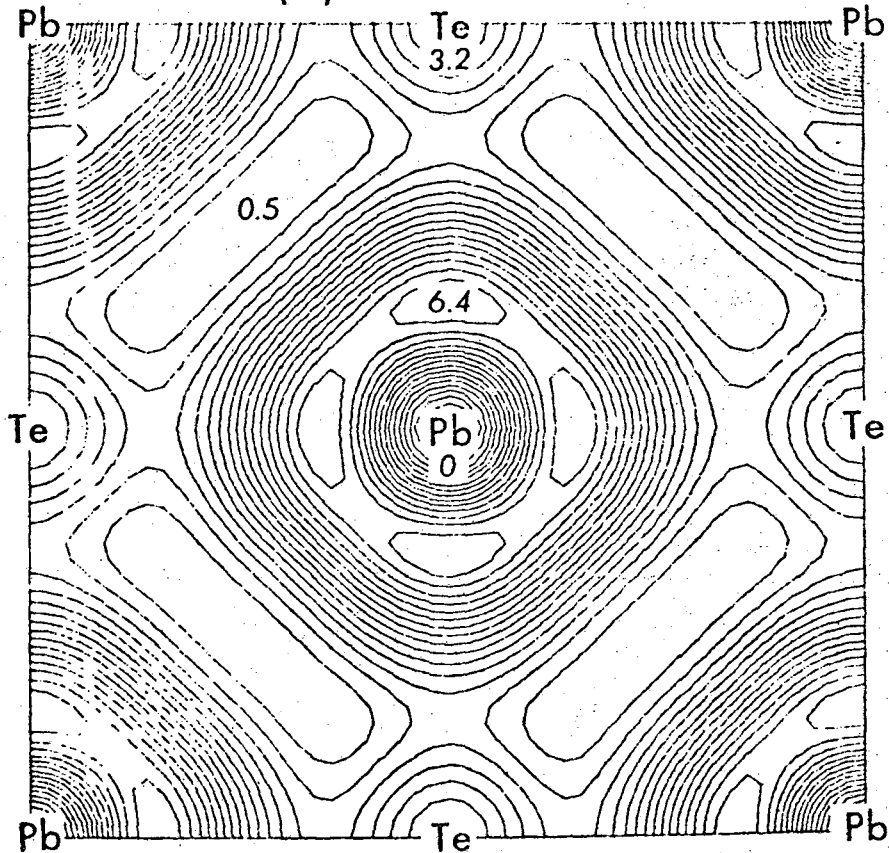


Figure 3b

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