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THE ELECTRONIC CHARGE DENSITIES IN SEMICONDUCTING LAYER AND CHAIN STRUCTURES*

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Abstract—From calculations of the pseudo-wavefunctions the charge densities of the valence electrons in the semiconducting crystals SnSe_2 , PbI_2 , GaSe , Se and Te have been determined. The results are compared with the valence bond description of semiconductors which can thus be confirmed and refined. Insight is gained into the accommodation in the valence bands of the excess s-electrons in PbI_2 and GaSe . For Te the transformation from the trigonal to the simple cubic modification has been simulated on the computer. The changes of the charge densities occurring in this semiconductor-to-metal transition are discussed.

1. INTRODUCTION

From pseudopotential calculations Cohen and coworkers [1-3] have recently determined the charge densities of the valence electrons as functions of position in the unit cell of series of semiconductors crystallizing in zincblende, diamond, rocksalt and wurtzite structures. They have shown that in spite of the deviations of pseudowavefunctions from the exact one-electron wavefunctions such as are e.g. derived from the selfconsistent orthogonal plane-wave model [4] a very satisfactory description of the distribution of the valence electrons in the lattice can be obtained: In regions outside the atomic cores the pseudo charge densities are qualitatively correct. Their pictorial representations therefore afford a confirmation or infirmation of the chemist's image of the bonding in solids.

Semiconductors are particularly gratifying objects for a confrontation of the chemist's intuition with the physicist's calculations because they tend to be predominantly covalent and the bonds in them are saturated. There is thus a particularly pronounced covalent charge build-up between two bonded atoms and the picture of the shared electron pair bond is particularly adequate. These facts are of

course at the basis of the success of the valence bond description of semiconductors [5-7] which in establishing a relationship between chemical composition and atomic coordination led the way to a coherent crystal chemistry of semiconductors [8, 9]. It follows from the discussions of the present paper that if the chemist's views are somewhat oversimplified their general traits are, nevertheless, confirmed by calculation. The main discrepancies arise from the inexistence of an unequivocal correlation between bonds and bands. As might be expected the information derived from the knowledge of the charge densities renders the bond picture more complex but this complexity is a small price to pay for the insight gained.

In recent years compounds crystallizing in layer structures have retained the attention of many physicists [10]. By means of the empirical pseudopotential method we therefore have calculated the bandstructures of a series of such compounds including the semiconductors GaSe , SnS_2 , SnSe_2 , PbI_2 and GeI_2 . For three of them, i.e. for GaSe , SnSe_2 and PbI_2 we have evaluated the charge densities of the valence bands. The investigated compounds all have hexagonal structures and the computer programs developed for calculating their electronic states and wavefunctions afford handling of any trigonal and hexagonal crystals and in particular of the chain structures of Se and Te . These elemental structures

*The present article is an extended version of a paper read at "Sagamore IV" in Minsk, August 1973.

are of particular interest since they are closely related to the simple cubic structure of the heaviest group VI element Po. By gradually changing the lattice parameters in Te we have simulated on the computer the transition from the trigonal to the cubic modification and we have followed the evolution of the charge densities through this semiconductor-to-metal transition.

2. BANDSTRUCTURES AND WAVEFUNCTIONS

The electronic wavefunctions used in determining the charge densities were obtained from empirical pseudopotential band calculations. For GaSe, SnSe₂, SnSe₂, Se and Te the details of the calculations have been described by Schlüter and Schlüter [11-13]. For PbI₂ they will be published elsewhere [14] together with a discussion of the importance in PbI₂ of spin-orbit coupling. In the present considerations relativistic effects are neglected because they do not greatly affect quantities which like the charge densities are the result of an integration over one or more bands.

A small but significant deviation of the present calculations from standard procedures is noteworthy. Because the extension of the unit cell along the *c*-axis is quite big in some of the considered structures (16 Å in GaSe) some of the reciprocal lattice vectors are rather small. The number of atomic form factors $V(q)$ which had to be taken into account (90 for each kind of atom in GaSe) is therefore much larger than, e.g. in the diamond structure and it was preferable to express $V(q)$ in terms of the interpolation formula

$$V(q) = \frac{a(q^2 - b)}{\exp[c(q^2 - d)] + 1}. \quad (1)$$

The free parameters a , b , c and d were adjusted such that the present pseudopotentials approximate those of earlier calculations. The pseudo Hamiltonians were diagonalized in bases of symmetrized plane waves. Waves for which $|\mathbf{k} + \mathbf{K}|^2 \leq E_1$ were included exactly, waves for which $E_1 < |\mathbf{k} + \mathbf{K}|^2 \leq E_2$ were accounted for by second order perturbation

theory [15]. The cut-off energies E_1 and E_2 and the corresponding approximative numbers of plane waves are listed in Table 1. The resulting bandstructures along the lines of high symmetry marked in Fig. 1 are shown in Figs. 2-6.

Fig. 1. First Brillouin zone of the hexagonal Bravais lattice.

As a function of position $\mathbf{r}$ the charge density $\rho_n(\mathbf{r})$ of the n th band is given by

$$\rho_n(\mathbf{r}) = 2e \sum_{\mathbf{k}}^{\text{BZ}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2, \quad (2)$$

where $\psi_{n\mathbf{k}}$ is the pseudowavefunction of this band corresponding to the wavevector $\mathbf{k}$ and where the summation extends over the entire Brillouin zone. Because of the flatness of the bands and of their pronounced grouping we were able in GaSe, Se and Te to obtain charge densities representative of entire bands or groups of bands by summing over 39 approximately weighted high symmetry $\mathbf{k}$ -points. Moreover, in SnSe₂ and in PbI₂ the Hamiltonian matrix was small enough to be diagonalized in a general $\mathbf{k}$ -point. In these cases it was possible, therefore, to evaluate the charge densities with sufficient accuracy by summing over three representative $\mathbf{k}$ -points contained in the irreducible wedge of the Brillouin zone. This method was first proposed by Baldereschi [16] and discussed in detail by Chadi and Cohen [17] who give the following coordinates for

Table 1. Cut-off energies and approximative numbers of plane waves included in the band calculations

	E_1 (Ryd)	E_2 (Ryd)	Numbers of plane waves for $ \mathbf{k} + \mathbf{K} ^2 \leq E_1$ $E_1 < \mathbf{k} + \mathbf{K} ^2 \leq E_2$	
SnSe ₂	3	6	45	150
PbI ₂	3	6	75	220
GaSe	5	10	250	750
Se	3	6	50	150
Te	3	6	60	180

Fig. 2. The band structure of SnSe_2 . Fig. 3. The band structure of PbI_2 .

the three representative k -points in the hexagonal structure: $k_1 = 1/9, 1/9, 1/4$; $k_2 = 2/9, 2/9, 1/4$ and $k_3 = 4/9, 1/9, 1/4$. The weighting factor for each of these points is $1/3$.

To discuss the bonding characteristics of the investigated semiconductors the results of the charge density calculations are reproduced in the form of contour maps. In GaSe these maps were obtained by evaluating the densities in 1200 points of the map plane. In all other cases they were evaluated in 2500 points. The densities indicated on the contours are measured in units of e/Ω , where Ω is

the unit cell volume. The planes and areas of the maps are depicted for each structure.

3. CHARGE DENSITIES

(a) SnSe_2 , PbI_2

SnSe_2 and PbI_2 crystallize in the CdI_2 type of layer structure whose unit cell (Fig. 7) contains one molecule. The main difference between the two compounds is that the anion of the first belongs to group VI, that of the second to group VII of the Periodic Table. The group IV cations of the two compounds therefore are quadri- and divalent re-

Fig. 4. The band structure of β -GaSe.

Fig. 5. The band structure of trigonal Se.

spectively. With 16 valence electrons per unit cell the 8 lowest bands are filled in SnSe_2 and the 18 valence electrons of PbI_2 are accommodated in 9 bands.

The filled bands in SnSe_2 are expected to correlate with the valence orbitals of the anions, the lowest two bands in Fig. 2 having s character and the bands 3–8 having p character. However, the corresponding (110) charge density contour maps (Figs. 8 and 9)

show that such a clearcut separation into anion s and p bands is not possible. Indeed, the spheroidal shape of the charge cloud around Se in Fig. 8 is misleading: the displacement of the density maximum with respect to the Se site indicates an appreciable p admixture to bands 1 and 2. Similarly the charge cloud corresponding to bands 3–8 (Fig. 9) is not centered on the anion site. Its central minimum which for pure p bands should in fact be a node, is

Fig. 6. The band structure of trigonal Te.

Fig. 7. The unit cell of the CdI_2 structure of SnSe_2 and PbI_2 . The large circles represent the anions, the small shaded ones the cations. Plane and area of the (110) density maps are indicated by hatching. The front face of the trigonal pyramid sitting on the basal plane of the cell is formed by the plane (304).

shifted away from the Se position, thus betraying an s contribution. The total charge resulting from all valence bands is somewhat more centered (Fig. 10). Since there are three equivalent planes (110), $(\bar{1}\bar{2}0)$ and $(\bar{2}10)$ at angles of 120° with respect to one another one readily recognizes that this charge derives to a large extent from an sp^3 hybridization on the Se atoms. Two of the tetrahedral legs of each

Fig. 8. The charge density in the (110) plane corresponding to the lowest two valence bands in SnSe_2 .

hybrid, i.e. the one pointing from Se to Sn and the one running along the c -axis are contained in the (110) plane of Fig. 10. The other two legs lie in the planes $(\bar{1}\bar{2}0)$ and $(\bar{2}10)$ respectively and the density saddle point between them gives rise to the lowest (32) of the three relative maxima which in Fig. 10 surround each Se. The highest one (42) among them appears between neighboring Sn and Se atoms and constitutes the covalent bond between them. The intermediate one (36) is formed by the lone-pair electrons. The three charges constituting the Sn-Se bonds formed by each Se are not completely balanced by the charge of the lone-pair. Each Se therefore carries a dipole pointing into the threefold SnSe_2 layer and although incomplete sp^3 hybridization might account for this polarization some d admixture probably contributes to it.

Fig. 9. The charge density in the (110) plane corresponding to bands 3-8 in SnSe_2 .

Fig. 11. The charge density in the (304) plane corresponding to band 3 in SnSe_2 .

Fig. 10. The charge density in the (110) plane corresponding to all eight valence bands in SnSe_2 .

As seen from Fig. 10 the valence bands also give rise to a small charge on the Sn sites. In order better to visualize the spatial distribution of this charge we have plotted in Figs. 11-13 contour maps corresponding to one link of the chain

contained in the (304) plane. The main contribution to the charge on the Sn sites comes from band 3. The symmetry of the corresponding contour map (Fig.

Fig. 12. The charge density in the (304) plane corresponding to bands 4-8 in SnSe_2 .

11) is indicative of s - d mixing on Sn. A similar but smaller contribution from bands 1 and 2 can be deduced by inspection from Fig. 8. Bands 4-8, finally, give rise to a mixed p and d charge (Fig. 12) so that the contributions from all eight valence bands (Fig. 13) add up to a total charge distribution around Sn which can be described as arising from a hybridization of the type d^2sp^3 .

In view of the small difference $\Delta x = 0.6$ between the electronegativities [18] of Sn and Se the covalent nature of the bonds in SnSe_2 , which is illustrated by the strong charge build-up between neighbouring atoms, is not surprising. The electronegativity difference $\Delta x = 0.95$ between divalent Pb and I is

Fig. 13. The charge density in the (304) plane corresponding to all eight valence bands in SnSe_2 .

Fig. 15. The charge density in the (304) plane corresponding to all nine valence bands in PbI_2 .

appreciably bigger and PbI_2 should therefore be considerably more ionic than SnSe_2 . This is confirmed by Figs. 14 and 15 in which the total charge densities of all 9 valence bands of PbI_2 are shown for the planes (110) and (304) respectively. Indeed, it follows from these figures that there is only a very small covalent charge build-up between neighbouring Pb and I atoms, both of them being surrounded by nearly spherical charge clouds. As would be expected from the divalency of Pb the charge around this atom has essentially *s* character. The charge around I, however, results from the superposition of an *s*-like charge (finite density at the I site) and of a *p*-like charge (shell around I).

It is of considerable interest to determine which bands contribute to the *s*-like charge on Pb. Thus, to explain the low ionization energy of the direct exciton in PbI_2 [19] Harbeke and Tosatti [20] have postulated this exciton to be "cationic", i.e. they suggested that the top of the valence band and the bottom of the conduction band both be formed by cation states. From Figs. 16 and 17 it follows that the charge corresponding to the highest valence band (band number 9) does indeed have appreciable *s*-character near Pb. The most intriguing feature of these figures, however, is that the deviations of the charges from spherical symmetry lead to charge accumulations *between* rather than on the shortest

Fig. 14. The charge density in the (110) plane corresponding to all nine valence bands in PbI_2 .

Fig. 16. The charge density in the (110) plane corresponding to the uppermost valence band in PbI_2 .

Fig. 17. The charge density in the (304) plane corresponding to the uppermost valence band in PbI_2 .

Fig. 19. The charge density in the (304) plane corresponding to band 3 in PbI_2 .

lines connecting neighbouring atoms. The charge on I for instance clearly results from an sp^3 hybridization, but compared to the sp^3 hybrid met on the anion in SnSe_2 , the one in Fig. 16 is inverted: The charge is predominantly distributed among the antibonding sites predicted for excited states by molecular orbital theory[21]. The antibonding character of the uppermost valence band is confirmed by the nodes appearing between neighbouring Pb and I atoms.

The bonding partner of band 9 is band 3 which lies 5 eV deeper and whose density contours in the planes (110) and (304) are reproduced in Figs. 18 and 19 respectively. It is obvious from Fig. 18 that the

charge maxima of the sp^3 hybrid around I now fall upon the bonding sites and that the nodes between neighbouring Pb and I have disappeared. Figure 19 is reminiscent of the (304) density map of band 3 in SnSe_2 , and once again indicates s - d mixing on the cation. This time, however, the s -character is considerably more pronounced.

A simple chemical argument would have predicted the valence s electrons of Pb to form lone pairs by occupying the (non-bonding) $5s$ states of Pb. It now becomes evident that these states combine with the valence orbitals of I to produce a bonding and an antibonding band. Since both bands are occupied their net effect on the cohesive energy in PbI_2 is negligible.

The group of closely spaced bands (4-8) lying between the bonding and antibonding bands discussed above has predominantly p character on I with but little s admixture (Fig. 20). A small covalent charge appears between neighbouring Pb and I atoms showing that PbI_2 has some covalent character. The lowest two valence bands (Fig. 21) are essentially Iodine s bands with a small p contribution accounting for the deviations from spherical symmetry.

Coming back to the problem of the cationic excitation we note that the lowest three conduction bands (Fig. 22) are indeed formed predominantly by cation p states. The relatively small contribution from the Iodine states has the typical antibonding sp^3 configuration already met in band 9. Schlüter and Schlüter[14] have shown that if spin-orbit coupling is neglected, two of the three conduction bands are degenerate at the A-point at which the direct transi-

Fig. 18. The charge density in the (110) plane corresponding to band 3 in PbI_2 .

Fig. 20. The charge density in the (110) plane corresponding to bands 4-8 in PbI_2 .

Fig. 22. The charge density in the (110) plane corresponding to the lowest three conduction bands in PbI_2 .

Fig. 21. The charge density in the (110) plane corresponding to the lowest two valence bands in PbI_2 .

Fig. 23. The charge density in the (110) plane corresponding to the conduction band minimum A_3^- in PbI_2 .

tion occurs. The density at A of the degenerate band A_3^- is shown in Fig. 23 for the plane (110). There are three such planes meeting along the parallel to c through each Pb and forming angles of 120° with respect to one another. One therefore recognizes that the states A_3^- produce a doughnut shaped charge on Pb which is typical of the combined p_x and p_y orbitals of this atom (x and y define the plane of the layers). The state A_2^- of the third conduction band gives rise to the p_z -like charge on Pb shown in Fig. 24.

Summing up the present findings one thus arrives at the conclusion that both the highest valence bands

and the lowest conduction bands are largely formed by cation states. Harbeke and Tosatti's [20] hypothesis of a cationic exciton therefore seems justified.

(b) *GaSe*

The charge densities of the valence bands in GaSe have already been discussed in some detail elsewhere [11]. However, because of a striking similarity between the electronic structures of GaSe and PbI_2 it is of interest to dwell upon this subject here. Indeed, in both these compounds the cations have more electrons than necessary for the saturation of

Fig. 24. The charge density in the (110) plane corresponding to the minimum A_2^- of the third conduction band in PbI_2 .

the anion valencies and like in PbI_2 we will find that the excess electrons in GaSe also occupy an antibonding rather than a nonbonding band.

The unit cell of β -GaSe is shown in Fig. 25 where the part of the (110) plane covered by the charge density maps is hatched. Since the cell extends over

Fig. 25. The unit cell of β -GaSe. The large circles represent the anions, the small shaded ones the cations. Plane and area of the density maps are indicated by hatching.

Table 2. Symmetrized combinations of atomic orbitals at the Γ -point for a single layer of GaSe (space group D_{3h}). The $4s$ and $4p$ orbitals involved are centered at the positions 5, 6, 7 and 8 marked in the insert. The Γ -point symmetries of the space group D_{6h} of β -GaSe are also indicated

Atomic positions	D_{3h}	Single layer combinations	D_{6h}
Γ_1^+	$s^6 + s^7$ $s^5 + s^8$ $p_z^6 - p_z^7$ $p_z^5 - p_z^8$	Γ_1^+, Γ_4^-
	Γ_2^-	$s^6 - s^7$ $s^5 - s^8$ $p_z^6 + p_z^7$ $p_z^5 + p_z^8$	Γ_2^-, Γ_3^+
	Γ_3^+	$p_x^6 + p_x^7$ $p_y^6 + p_y^7$ $p_x^5 + p_x^8$ $p_y^5 + p_y^8$	Γ_3^+, Γ_6^-
	Γ_3^-	$p_x^6 - p_x^7$ $p_y^6 - p_y^7$ $p_x^5 - p_x^8$ $p_y^5 - p_y^8$	Γ_3^-, Γ_6^+

two layers the number of bands in Fig. 4 is twice that reported by Bassani and Pastori[22] in their tightbinding calculations for a single layer. The one-layer (space group D_{3h}) and two-layer (space group D_{6h}) representations for the Γ -point are listed in Table 2. In order to allow a direct comparison between the present charge density results and the symmetrized combinations of atomic orbitals proposed in Ref. [22] and listed in Table 2 we have added up the densities of corresponding band pairs. We therefore do not differentiate between states which are bonding and antibonding with respect to the interlayer interaction. Because this interaction is considerably smaller than the intralayer one—the first is measured by the splitting of the valence band pair Γ_1^+, Γ_4^- the second by that Γ_4^-, Γ_2^- across the gap—the information lost in this manner is very small.

From the spatial distribution of their total charge density one readily deduces that the lowest band pairs Γ_1^+, Γ_4^- and Γ_3^+, Γ_2^- are formed by the $4s$ states of the four Se atoms in the unit cell. They are obviously nonbonding and the electrons occupying them behave like core electrons. Like band 3 in PbI_2 the next higher band pair Γ_1^+, Γ_4^- already contains cation states, i.e. a mixture of the $4s$ and $4p_z$ ($z \parallel c$) states of Ga in which the s character dominates (Fig. 26). Since the p_z orbitals are added with opposite signs (see Table 2) a strong charge build-up results which constitutes a Ga-Ga bond. A small mixed s, p_z contribution on the Se atoms is also present and

Fig. 26. The charge density in the (110) plane corresponding to the intermediate band pair Γ_1^+, Γ_4^- in GaSe.

Fig. 27. The charge density in the (110) plane corresponding to the highest filled band pair Γ_3^+, Γ_2^- in GaSe.

gives rise to a weak antibonding configuration between the Se and the Ga atoms. The next bandpair Γ_3^+, Γ_2^- which lies about 2 eV higher is still constituted by s and p_z orbitals, the latter now having the same signs. This pair (Fig. 27) is the complement of that Γ_1^+, Γ_4^- : between the Ga atoms it has strong antibonding character and between neighbouring Ga and Se atoms it is weakly bonding. It is this antibonding bandpair which like band 9 in PbI_2 accommodates the excess cation electrons. The uppermost among the filled bandpairs Γ_1^+, Γ_4^- is formed predominantly by the $4p_z$ orbitals of the Ga and Se atoms (Fig. 28) and establishes a second Ga-Ga bond. With what was said above one is therefore tempted, in the chemist's language, to describe the total Ga-Ga interaction as the result of a superposition of σ $4s$ bonding, σ^* $4s$ antibonding and σ $4p_z$ bonding states. The paradox of this description illustrates the difficulties encountered by a too narrow interpretation of the bond picture: in spite of the concentration of charge between the Ga atoms the wavefunctions extend over the whole unit cell and the mutual orthogonality of the filled Γ_1^+, Γ_4^- pairs is of course warranted by the p_z charges which in the higher pair occur on the Se atoms.

Between the partners of the highest pair Γ_1^+, Γ_4^- lie two pairs Γ_5^-, Γ_6^+ and Γ_5^+, Γ_6^- of doubly degenerate bands which according to Table 2 are formed by the

Fig. 28. The charge density in the (110) plane corresponding to the highest filled band pair Γ_1^+, Γ_4^- in GaSe.

Fig. 29. The charge density in the (110) plane corresponding to the two band pairs Γ_5^- , Γ_6^+ and Γ_5^+ , Γ_6^- in GaSe.

$4p_x$ and $4p_y$ orbitals of the Se and Ga atoms. As seen from Fig. 29 in which the corresponding (110) density is plotted the Se orbitals predominate. Moreover, the accumulation of charge between the Ga and Se atoms indicates that these four bands are responsible for the covalent component of the Ga-Se bond. It follows from Fig. 30 in which the total charge density of all valence bands is reproduced that the Ga-Se bond also has an ionic component, the electrons favouring the Se orbitals. From the total density Schlüter [11] has evaluated the effective charge on Se to be $0.4 e$. This value has since been confirmed by Sapre and Mande [23] who, from measurements of the chemical shift of X-ray K -absorption discontinuities have obtained effective Se charges varying between 0.4 and $0.5 e$.

(c) Se, Te

The trigonal structure of Se and Te (Fig. 31a) is characterized by spiral chains each atom having two nearest neighbours (Se: $d_1 = 2.37 \text{ \AA}$, Te: $d_1 = 2.88 \text{ \AA}$) in the chain and four more next nearest neighbours at somewhat longer distances (Se: $d_2 = 3.43 \text{ \AA}$, Te:

Fig. 30. The total (110) charge density of all valence bands in GaSe.

Fig. 31. The structure of (a) trigonal and (b) cubic Se and Te. Plane and area of the density maps are indicated by hatching.

$d_2 = 3.45 \text{ \AA}$) in adjacent chains. The bonding leading to this characteristic 8- N type of coordination has long since been interpreted as being essentially due to the interaction of p orbitals (see, e.g. Ref. 7). An interpretation along the same line but involving s - p hybridization was given by Tutihasi and Chen [24].

There are three atoms per unit cell and one recognizes from Figs. 5 and 6 that the bands in Se and Te are grouped in triplets. Each of the contour

maps shown in Figs. 32-35 contains the total density of one of these triplets. The area covered by the maps is indicated by hatching in Fig. 31a. Clearly, the lowest triplet (Fig. 32) contains the 4s and 5s orbitals of Se and Te respectively. The next three triplets, two of which lie below the gap, are essentially formed by the p orbitals. The deepest lying one among them has predominantly bonding p_x and p_y character* and produces considerable covalent charges between neighbouring pairs of Se and Te atoms (Fig. 33). An additional charge accumulation near the lower right corner of the maps points away from the chain in the direction of the neighbouring chain. This charge together with the two covalent charges in the bond sites are nearly trigonally disposed in the x, y plane and have been described in

*The coordinates x and y define the plane of the contour maps and the orbitals p_x and p_y referred to are those on the atom in the upper left corner. Since the Se and Te chains are not planar it is the p_x and p_z orbitals which in the atom near the upper right corner participate in the intrachain bonding. In the atom near the lower left corner the contributing orbitals are p_x and p_z .

Fig. 32. The charge densities corresponding to the lowest band triplet in Se and Te.

Fig. 33. The charge densities corresponding to the intermediate band triplet in Se and Te.

Fig. 34. The charge densities corresponding to the highest filled band triplet in Se and Te.

Fig. 35. The charge densities corresponding to the lowest conduction band triplet in Se and Te.

Ref. [24] as resulting from sp^2 hybridization. However, it should be noted that the charge densities have rather low values at the centers of the Se and Te atoms and the s character of the bonds is therefore smaller than indicated by Tutihasi and Chen[24]. This is confirmed by the photoemission data on Se reported by Shevchik *et al.*[25] and by those on Te reported by Pollak *et al.*[26], which show that the s and p valence bands of these elements are well separated energetically (see also Figs. 5 and 6). Since we have already met some evidence for p - d mixing in SnSe , we propose that the near trigonal symmetry of the charges around Se and Te is at least in part the result of a hybridization of the type dp^2 .

The next higher band triplet—it contains the uppermost valence band—is nonbonding[27]. This is readily seen from Fig. 34 in which the corresponding charge densities are reproduced and which shows that this triplet consists essentially of those p orbitals which are not involved in the intra-chain bonding. Among them is the p_z orbital of the atom at the upper left corner. Because the x,y plane is a nodal surface of this orbital, it does not contribute to the mapped densities.

The lobes of the non-bonding p orbitals of next-nearest neighbours are seen to approach each other rather closely in the x,y plane. Their mutual repulsion is responsible for the opening-up of the bond angles beyond 90° and since the charge density reaches higher values in Se than in Te the Se bond angle is somewhat larger (103.0°) than that in Te (101.8°). We add that according to Schlüter and Joannopoulos[28] this second nearest neighbour interaction critically affects the dispersion of the uppermost filled triplet. Repulsion of the nonbonding orbitals—on nearest neighbours this time—is also responsible for the fact that the chain links in Se and Te are not coplanar but spiral around the c -axis. Indeed, by housing the nonbonding electrons suc-

Fig. 36. The change with structure of the charge density of the bonding p triplet in Te. The bottom diagram corresponds to the actually observed trigonal modification and the top diagram to the cubic modification.

Fig. 37. The change with structure of the charge density of the non-bonding p triplet in Te.

Fig. 38. The change with structure of the charge density corresponding to the antibonding p triplet (conduction band) in Te.

cessively in ... p_x, p_y, p_z, p_x ... orbitals the repulsive interaction is minimized.

The last p band triplet (Fig. 35) lies above the gap and comprises the conduction band. It has obviously antibonding character: Nodes separate the nearest neighbour atoms from each other and squeeze the charge out of the bonding into the antibonding sites which are similarly disposed around the Se and Te as they were around the I in PbI_2 . The trend towards delocalisation of the conduction electrons is clearly visible.

A comparison of Figs. 31a and b shows that the trigonal structure of Se and Te is closely related to the simple cubic lattice of the heaviest of the group VI elements, Po. By reducing the bond angle

to 90° and by adjusting the interatomic distance we have simulated on the computer a transition from trigonal to cubic Te and followed the charge densities through this transition. The results obtained in this way for the three p band triplets are shown in Figs. 36–38, and in Fig. 39 the densities corresponding to the sum over all three triplets are given. The most striking feature of these figures is that they indicate more even spreading in each triplet of the electronic charge in the unit cell as the structure becomes increasingly cubic. This delocalization of the electrons is of course expected since cubic Te, like Po, should be metallic. In fact the bands in cubic Te overlap and the gap disappears. The distinction between the three triplets is therefore artificial and it

Fig. 39. The change with structure of the total charge density corresponding to the three p triplets in Te (including the antibonding one).

is surprising that in spite of this the corresponding charge density maps begin to resemble each other. In the cubic form the Fermi level cuts across the bands leaving some of the original nonbonding states empty and filling some of the antibonding ones. The total charge density corresponding to four p electrons per atom should of course have cubic symmetry. The theoretical results are consistent with this because, as seen from the uppermost map in Fig. 39, the density corresponding to all three triplets (six p electrons) has this symmetry and the density of the antibonding triplet (Fig. 38, top) very

nearly has it. By filling up some antibonding states and emptying some bonding ones cubic symmetry should be obtained.

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