

Electronic Structure of the Layered Compounds K[SnSb], K[SnAs] and Sr[Sn₂As₂]

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The electronic band structure, the density of states, and the electronic charge density distribution of K[SnAs], K[SnSb], and Sr[Sn₂As₂] are studied by means of self-consistent density-functional calculations in the local approximation. The valence bands and the conduction bands are separated by a band gap which in one case (Sr[Sn₂As₂]) is nearly zero. The fully occupied valence bands can be identified as *s*- and *p*-like bands of Sn, As, and Sb. These results indicate that the alkali and alkaline earth atoms form a cationic substructure. The Sn and As/Sb atoms form covalent and negatively charged layer structures. The correlations between the Zintl concept and the calculated band structures are discussed. © 1992 Academic Press, Inc.

I. Introduction

The crystal structures of K[SnAs], K[SnSb] (1, 2), and Sr[Sn₂As₂] (3) contain three-bonded Sn and As/Sb atoms which form puckered layers isostructural to elemental As/Sb but with alternating Group IV and V elements. In K[SnAs] and K[SnSb]

all the layers are separated by planes of K atoms, whereas in Sr[Sn₂As₂] the Sr atoms are localized between every second layer (Figs. 1 and 2). The structures can be interpreted in terms of the Zintl concept (4–7) assuming a charge transfer of the valence electrons of the alkali/alkaline earth atoms to the Sn atoms, thereby giving anionic substructures $\frac{2}{x}[\text{SnAs}]^-$ and $\frac{2}{x}[\text{SnSb}]^-$ in which the elements follow the octet rule.

The present work deals with the question of whether this simple model of formal

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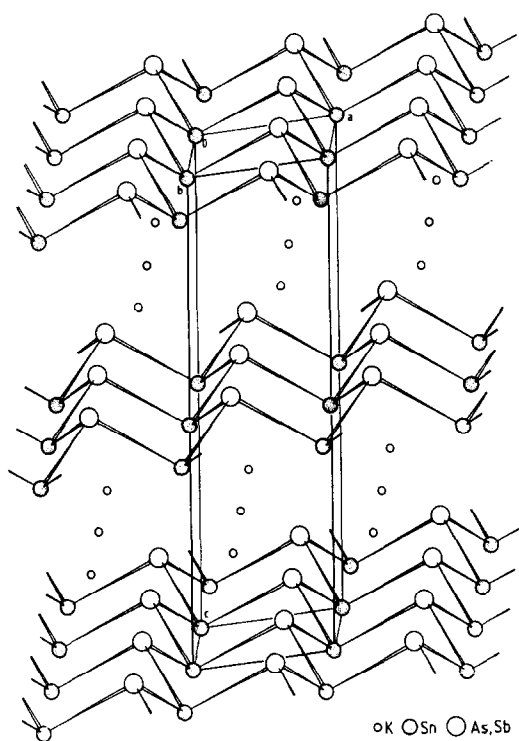


FIG. 1. Crystal structure of the isotopic Zintl phases K[SnSb] (K[SnAs]): hex.; $P6_3mc$; $a = 435.0, (410.2)$ pm; $c = 1342.1$ pm (1281.6 pm); $c/a = 3.0209, (3.1243)$; $Z = 2$.

charges (K^+ , Sn^{-1} , and As/Sb^0) is supported by detailed calculations of the charge distributions in these phases.

Different methods have been used to study the electronic structure of Zintl phases theoretically, ranging from complicated *ab initio* methods (8) to semiempirical extended Hückel calculations (9). Here we use the local density functional approximation (LDA) (10) together with the augmented spherical wave (ASW) method (11) for the numerical computations to obtain the self-consistent energy band structures and the partial density of states for K[SnSb], K[SnAs], and Sr[Sn₂As₂]. The LDA is parametrized according to Hedin and Lundquist (12), and the ASW method is a linearized band structure procedure similar to

Andersen's LMTO (13). We first outline those aspects of the ASW method from which the covalent and ionic contributions to the chemical bonds can be deduced (Section II). In Section III we show the results of our band structure calculations.

II. Theoretical Aspects

In the augmented spherical wave (ASW) method (11) used in the present work the

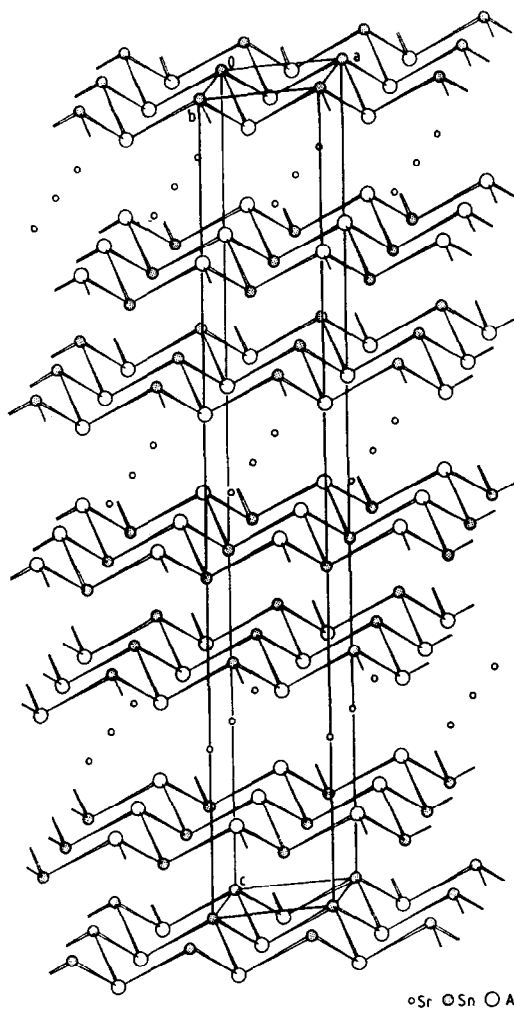


FIG. 2. Crystal structure of the Zintl phase Sr[Sn₂As₂]: hex.; $R3m$; $a = 420.4$ pm, $c = 2672.8$ pm, $c/a = 6.3578$.

crystal potential “seen” by the electrons is approximated by a spherical symmetric potential around each nucleus. The radii of the atomic spheres are chosen in such a way that the total volume of the (overlapping) spheres equals the total volume of the crystal. Usually the ratios of the radii of the spheres are chosen approximately like the ratios of the atomic covalent radii of the atoms.

The electronic charge density $-e \cdot \rho(\mathbf{r})$ of the compounds is calculated from the one-electron Bloch states $\psi_{\mathbf{k},n}(\mathbf{r})$

$$\rho(\mathbf{r}) = \sum_{\mathbf{k},n} |\psi_{\mathbf{k},n}(\mathbf{r})|^2, \quad (1)$$

where \mathbf{k} is the wave vector and n is the band index. The summation in Eq. (1) is performed over all occupied states.

Within the ASW method the $\psi_{\mathbf{k},n}(\mathbf{r})$ are expanded in basis functions φ . Each function φ is centered at one atom ν , and inside the corresponding atomic sphere the wave functions are expanded in spherical harmonics $Y_{l,m_l}(\widehat{\mathbf{r} - \mathbf{r}_\nu})$. We get basis functions,

$$\varphi_{\nu,l,m_l}(\mathbf{r} - \mathbf{r}_\nu) = h_l(|\mathbf{r} - \mathbf{r}_\nu|) Y_{l,m_l}(\widehat{\mathbf{r} - \mathbf{r}_\nu}) \quad (\text{inside sphere } \nu), \quad (2)$$

where the h_l are solutions of the radial Schrödinger equation that match continuously and differentiably to the spherical Hankel function of angular momentum l and energy -0.015 Ry. Function (2) is called the “head” of the basis function.

Outside the spheres the basis function φ_{ν,l,m_l} is a spherical wave for a free particle which consists of the spherical harmonic Y_{l,m_l} , a spherical Hankel function, and a constant.

Inside all other spheres in the crystal the basis function φ_{ν,l,m_l} is expanded in spherical harmonics $Y_{l',m_{l'}}(\widehat{\mathbf{r} - \mathbf{r}_{\nu'} - \mathbf{R}})$ centered at $\mathbf{r}_{\nu'} + \mathbf{R}$, where \mathbf{R} is a lattice vector and $\mathbf{r}_{\nu'}$ is the position of the atom ν' in the first unit-cell. In these spheres the solutions of the radial Schrödinger equation lead to radial functions $j_{l'}(|\mathbf{r} - \mathbf{r}_{\nu'} - \mathbf{R}|)$. Together with

KKR expansion coefficients $B_{l,m_l,l',m_{l'}}(\mathbf{r}_\nu - \mathbf{r}_{\nu'} - \mathbf{R})$ which guarantee that the basis functions are continuous (14), we get

$$\varphi_{\nu,l,m_l}(\mathbf{r} - \mathbf{r}_\nu) = \sum_{l',m_{l'}} B_{l,m_l,l',m_{l'}}(\mathbf{r}_\nu - \mathbf{r}_{\nu'} - \mathbf{R}) j_{l'}(|\mathbf{r} - \mathbf{r}_{\nu'} - \mathbf{R}|) Y_{l',m_{l'}}(\widehat{\mathbf{r} - \mathbf{r}_{\nu'} - \mathbf{R}}) \quad (3)$$

(inside all other spheres of the crystal). The $(l', m_{l'})$ dependent contributions to φ_{ν,l,m_l} are called the “tails” of the basis functions. In order to take into account the translation symmetry of the crystal we use the Bloch sums

$$\varphi_{\nu,l,m_l}^{(\mathbf{k})}(\mathbf{r} - \mathbf{r}_\nu) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \varphi_{\nu,l,m_l}(\mathbf{r} - \mathbf{r}_\nu - \mathbf{R}). \quad (4)$$

Finally the one-electron wave function $\psi_{\mathbf{k},n}$ is given by a linear combination of the functions (4),

$$\psi_{\mathbf{k},n}(\mathbf{r}) = \sum_{\nu,l,m_l} c_{\nu,l,m_l}^{(\mathbf{k},n)} \varphi_{\nu,l,m_l}^{(\mathbf{k})}(\mathbf{r}), \quad (5)$$

where the coefficients $c_{\nu,l,m_l}^{(\mathbf{k},n)}$ are determined by a variational procedure.

The bonding character can be analyzed from the value of partial charges and partial densities of states which are defined in the following way. The wave functions $\psi_{\mathbf{k},n}(\mathbf{r})$ are normalized over the unit cell,

$$\int_{\text{cell}} |\psi_{\mathbf{k},n}(\mathbf{r})|^2 = 1, \quad (6)$$

and within the normalization procedure the contribution outside the spheres is omitted. This is sometimes called the Wigner–Seitz or atomic sphere approximation. Then we see from Eqs. (2) and (3) that the integration in Eq. (6) can be separated into integrations over the atomic spheres ν , and according to the orthogonality of the spherical harmonics these integrations over the atomic spheres can be separated into integrations over the different angular momenta. To include the spin-degeneracy the resulting partial integrals $Q_{\nu,l}^{(\mathbf{k},n)}$ are normalized to 2,

$$2 = \sum_{\nu,l} Q_{\nu,l}^{(k,n)}. \quad (7)$$

For a detailed definition of $Q_{\nu,l}^{(k,n)}$ see Eq. (35) of Ref. (11). The total charge inside the sphere ν is given by

$$Q_{\nu} = \sum_{k,n} \sum_l^{\text{occ}} Q_{\nu,l}^{(k,n)}. \quad (8)$$

Next the density of states is considered. The total density of states $n(E)$ is equal to the number of electronic states per eV and per unit cell. Analogously to Eq. (7), $n(E)$ is separated into partial densities of states n_{ν} and $n_{\nu,l}$ with

$$n(E) = \sum_{\nu} n_{\nu}(E) = \sum_{\nu,l} n_{\nu,l}(E), \quad (9)$$

where $n_{\nu,l}(E)$ indicates the character of the band. For example, for an s -like band of ν the component $n_{\nu,l=0}(E)$ is the dominant contribution to $n(E)$.

The total electronic charge Q_{ν} , Eq. (8), is given by

$$Q_{\nu} = \int_{-\infty}^{E_F} n_{\nu}(E) dE. \quad (10)$$

The partial densities of states give some information about the bonding character. For those states which we describe by two-center two-electron bonds between ν and μ the corresponding partial densities of state $n_{\nu}(E)$ and $n_{\mu}(E)$ should have common maxima. For example, for a covalent bond between Sn and Sb in K[SnSb] the peaks in $n_{\text{Sn}}(E)$ and $n_{\text{Sb}}(E)$ must appear at the same energy values. However, it should be pointed out that the partial densities of states include both the "head" and the "tail" contribution. A small $n_{\nu}(E)$ resulting from the "tails" alone does not indicate the bonding mechanism.

A partial cationic substructure is indicated if the partial density of states $n_{\nu}(E)$ for the alkali or alkali earth atoms has its main contribution above the Fermi energy (15). This means in the molecular orbital picture

that the $4s$ level of K and the $5s$ level of Sr are unoccupied. It should be pointed out that an ionic bonding cannot necessarily be deduced from the partial charges Q_{ν} alone, because these quantities depend sensitively on the choice of the sphere radii.

III. Results and Discussion

Within the present investigation of the band structure of K[SnSb], K[SnAs], and Sr[Sn₂As₂] the following electrons are treated as band electrons,

K: $4s^1$; Sr: $5s^2$; Sn: $4d^{10}5s^25p^2$;

As: $4s^24p^3$; Sb: $5s^25p^3$.

It is found for all three compounds that the electronic states of the d electrons of Sn are far below the Fermi level and, as expected, the corresponding electronic bands do not contribute to the chemical bond. Even treating all d electrons as core electrons does not change the band structure significantly. In the following, only the electronic states above the $4d$ -like states of Sn are considered.

K[SnSb]

K[SnSb] and K[SnAs] crystallize in a hexagonal structure with two formula units in

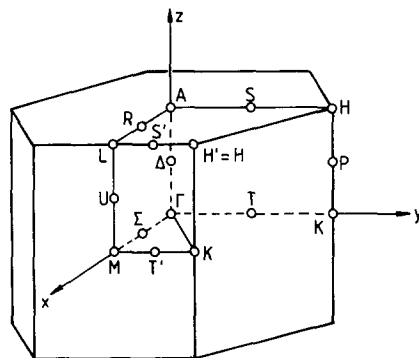


FIG. 3. Brillouin zone for the hexagonal Bravais lattice.

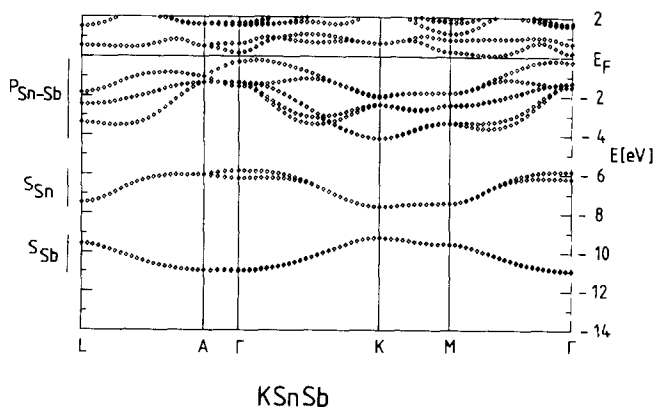


FIG. 4. Electronic band structure of the valence states of K[SnSb]. The Fermi energy E_F is the zero of the energy scale.

the unit cell, see Fig. 1. For K[SnSb] we have chosen the following radii of the atomic spheres $r_K = 211$ pm and $r_{Sn} = r_{Sb} = 182$ pm. Due to the atomic sphere approximation we are forced to include 12 empty spheres in this layer structure. They are located at the Wyckoff positions c and have radii $r_1 = 0.98$ pm and $r_2 = 0.77$ pm. The charge they collect is approximately $-0.1 e$ distributed over s and p functions.

The Brillouin zone of the hexagonal lattice is shown in Fig. 3, and the band structure of K[SnSb] is displayed in Fig. 4. We find that the occupied valence bands below the Fermi energy E_F (labeled s_{Sb} to p_{Sn-Sb} in Fig. 4) are separated by a small band gap of about 0.1 eV from the unoccupied conduction bands. Normally the local density approximation underestimates the value for the optical gap (16, 17) by a factor up to 2. In K[SnSb] the number of valence electrons per unit cell n_0 is equal to 20 and due to the band gap between the occupied and unoccupied states we find $n_0/2 = 10$ fully occupied valence energy bands. The character of these bands is considered next.

As pointed out in the previous section, the nature of the energy bands can be deduced from the partial densities of states

$n_{v,j}(E)$ which are shown for K[SnSb] in Fig. 5. We see that the two lowest lying valence bands labeled s_{Sb} in Fig. 4 (which are almost degenerated) correspond to the atomic $5s$ electrons of Sb, because the partial density of the $5s$ -like states $n_{Sb,s}$ (Fig. 5d) is the main contribution to $n(E)$ for these states. The two s_{Sb} -like bands are separated by an energy band gap of about 1.5 eV from the other valence bands, see Fig. 4. Both this energy separation and the dominance of $n_{Sb,s}$ indicate that the s electrons of Sb do not contribute significantly to the chemical bond in K[SnSb]. The same finding holds for the bands above the s_{Sb} -like bands, which are the two $5s$ -like bands of Sn, labeled s_{Sn} . Here the largest component to the partial density of states is $n_{Sn,s}(E)$, see Fig. 5c.

Above the s_{Sn} -like bands we find six bands labeled p_{Sn-Sb} . We see from Figs. 5c and 5d that within the energy range of these bands (-4.5 eV $\leq E \leq 0$ eV) both $n_{Sn,p}$ and $n_{Sb,p}$ contribute significantly to the total density of states. Furthermore the maxima of $n_{Sn,p}$ and $n_{Sb,p}$ are at the same energy values. This finding shows that the bonding mechanism corresponding to these energy bands can be described by strong covalent bonds between Sn and Sb. How-

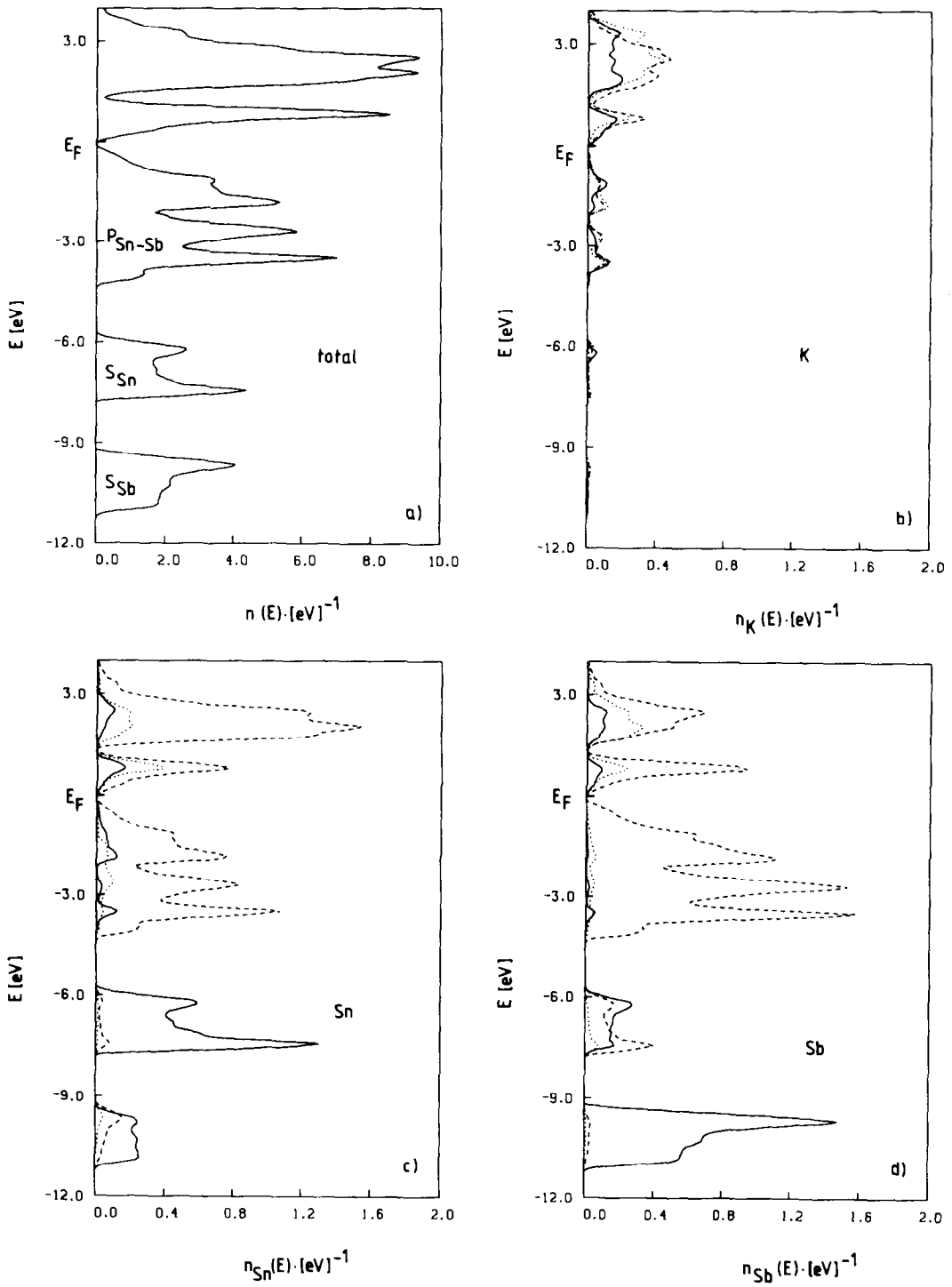


FIG. 5. Density of states as a function of E for the valence energy bands of $K[SnSb]$: (a) total density of state $n(E)$; (b-d) partial density of states $n_{\nu,l}(E)$, $l = 0$ (full line), $l = 1$ (broken line), $l = 2$ (dotted line) for $\nu = K$ (b), $\nu = Sn$ (c), and $\nu = Sb$ (d).

ever, there is no indication for a formal charge of -1 for Sn. We see that $n_{\text{Sb},p}(E)$ is larger than $n_{\text{Sn},p}$ and therefore the total charge at the Sb atoms is larger than the charge at Sn. Quantitatively we find for the partial charges $Q_{\text{Sn}} = 49.72$ compared to $Q_{\text{Sb}} = 51.06$. We conclude that Sb takes more valence charge than Sn.

Considering the partial density of states for the K sphere, we see from Fig. 5b that we find small contributions of $n_{\text{K},l}(E)$, $l = 0, 1, \text{ and } 2$, within the $p_{\text{Sn-Sb}}$ -like bands. As all three components $n_{\text{K},s}$, $n_{\text{K},p}$, and $n_{\text{K},d}$ are of equal size and because these contributions are small, we conclude that these are mainly "tail" contributions and do not indicate covalent or metallic bonds between K and Sn or Sb. That is, the occupation of the $4s$ -like states of K is low and the potassium substructure should have cationic character. However, the ionic character is much less pronounced than in a typical ionic crystal, because the band gap between the valence and conduction bands is distinctly smaller than in ionic crystals. In K[SnSb] the maxima of $n_{\text{K},s}(E)$ are between 0 and 3 eV above the p -like valence bands, whereas for a typical ionic crystal this energy distance is more than 5 eV. Therefore the actual charge distribution in K[SnSb] is best described by $\text{K}^{+\delta}[\text{SnSb}]^{-\delta}$, where δ should be smaller than the formal value $\delta = 1$. To get a quantitative value for δ the charge distribution has to be analyzed from three dimensional charge density plots. This analysis is planned using a full potential approach instead of the spherical symmetric approximation used in the present work.

K[SnAs]

K[SnAs] is isotypic to K[SnSb] and it is found that the band structure, the density of states, and partial density of states of K[SnAs] are very similar to those of K[SnSb]. No characteristic difference in

the electronic structure and therefore in the chemical bond is found between both compounds. Figure 6 shows the band structure for K[SnAs]. We see—besides the fact that As is replaced by Sb—the same sequence of energy bands as for K[SnSb], namely the s -like bands of Sn and As and the six occupied $p_{\text{Sn-As}}$ -like bands. These fully occupied valence bands are separated by a small band gap of about 0.1 eV from the conduction bands.

Sr[Sn₂As₂]

Sr[Sn₂As₂] also crystallizes in a hexagonal structure. However, there are differences in the crystal structures of Sr[Sn₂As₂] and K[SnAs], which can be seen from Fig. 1. In Sr[Sn₂As₂] the Sn and As atoms form double layers and the unit cell contains three formula units. The number of valence electrons per unit cell n_0 is 60 and we get 30 occupied valence bands in Sr[Sn₂As₂]. In Fig. 7 the band structure of Sr[Sn₂As₂] is displayed, but not all 30 energy bands are resolved. The density of states and partial density of states plots are given in Fig. 8. The sequence of the valence bands of Sr[Sn₂As₂] shows similarities to K[SnSb]. The six lowest lying valence bands are the s_{As} -like bands (see Fig. 8d), which are separated from the $5s$ -like bands of Sn by a band gap of about 1.5 eV. Above the s_{Sn} -like bands we find 18 fully occupied valence $p_{\text{Sn-As}}$ -like bands. We obtain a very small band gap at E_{F} between the $n_0/2$ valence and the conduction bands.

Comparing the band structure of K[SnAs] and Sr[Sn₂As₂] we find that the s_{Sn} -like and the $p_{\text{As-Sn}}$ -like valence bands show a larger dispersion in Sr[Sn₂As₂] than in K[SnAs]. It follows that the band gap between the s_{Sn} -like bands and the $p_{\text{As-Sn}}$ -like bands found for K[SnAs] disappears for Sr[Sn₂As₂], see Fig. 8a. The broadening of the energy ranges of the s_{Sn} and $p_{\text{As-Sn}}$ energy bands in Sr[Sn₂As₂] compared to

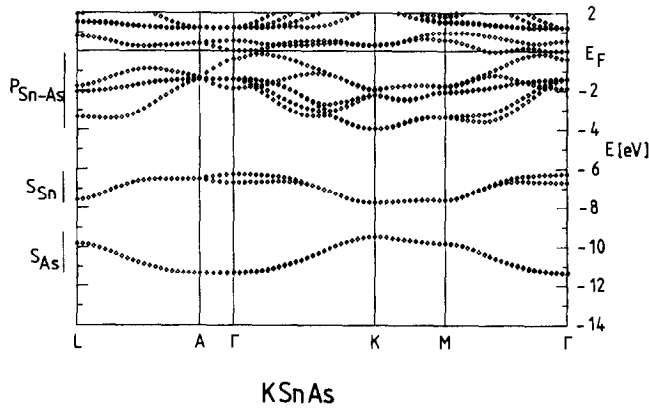


FIG. 6. Electronic band structure of the valence states of K[SnAs].

K[SnAs] is studied in more detail. From the analysis of the wave functions it follows that this effect is mainly caused by the different role of Sn in the bonding mechanism of both compounds. In K[SnAs] the coordination of Sn consists of three Sb and three K of the cationic substructure, whereas in Sr[Sn₂As₂] Sn is neighbored by three As and three Sn of the second anionic layer, see Fig. 2. The resulting differences in the bonding of the Sn atoms in both compounds is most pronounced for states at the top of the s_{Sn} -like bands of Sn.

In K[SnAs] these states are not pure s states of Sn anymore, but these states form covalent s -like bonds between Sn and As. For Sr[Sn₂As₂] the wave function amplitudes (the coefficients c in Eq. (5)) of these states at the neighboring As atoms are smaller than in the case of K[SnAs], and furthermore these states have additional amplitudes at the neighboring Sn atoms of the second layer of Sn/As. Therefore the additional interlayer covalent bonds between the Sn atoms seem to cause the increase of the dispersion of the energy bands in Sr[Sn₂As₂] compared to K[SnAs].

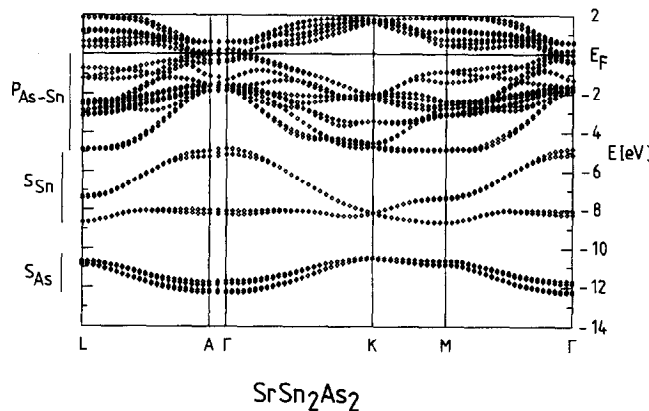


FIG. 7. Electronic band structure of the valence states of Sr[Sn₂As₂].

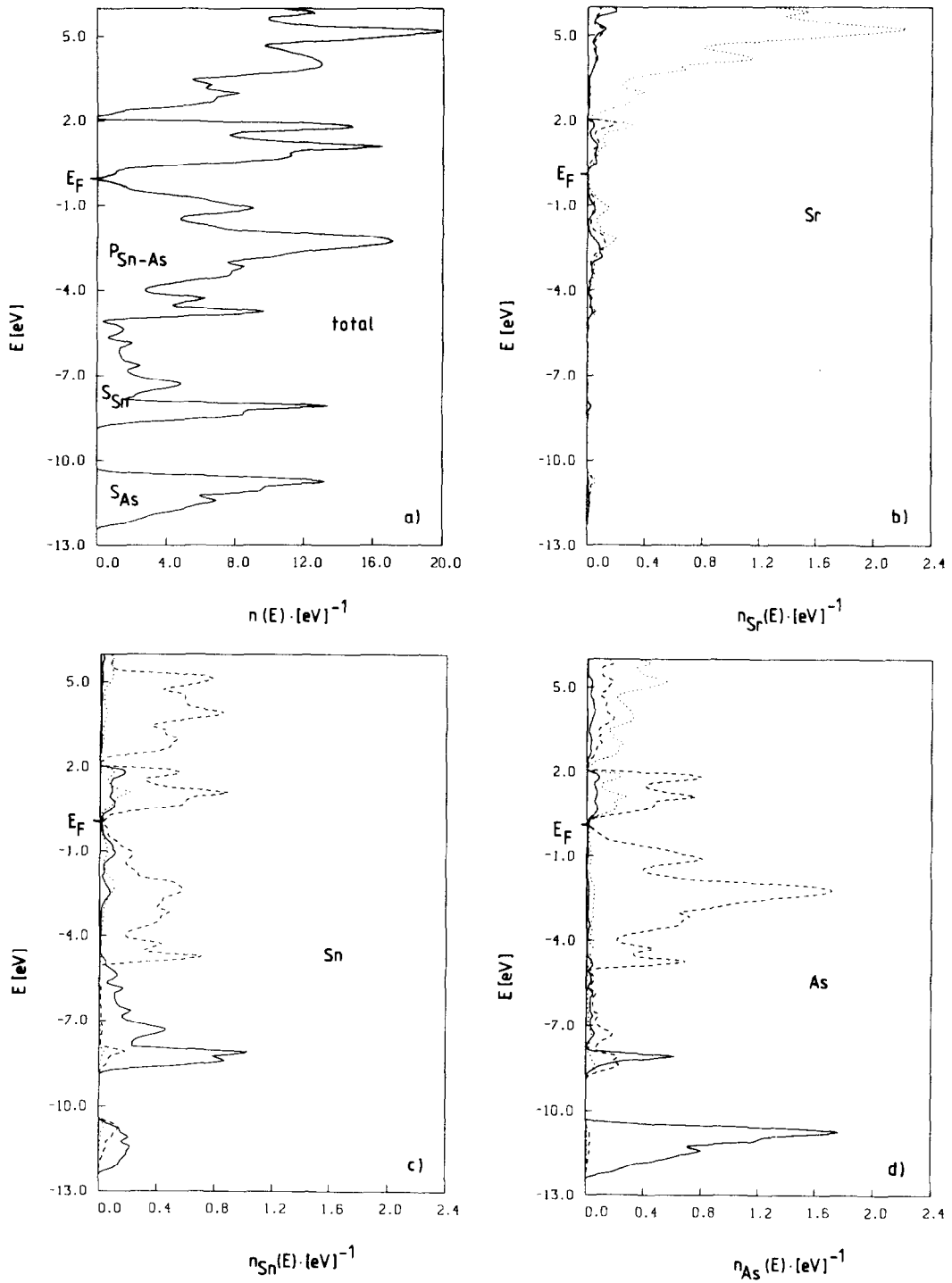


FIG. 8. Density of states as a function of E for the valence energy bands of $\text{Sr}[\text{Sn}_2\text{As}_2]$: (a) total density of state $n(E)$; (b–d) partial density of states $n_{\nu,l}(E)$, $l = 0$ (full line), $l = 1$ (broken line), $l = 2$ (dotted line) for $\nu = \text{Sr}$ (b), $\nu = \text{Sn}$ (c), and $\nu = \text{As}$ (d).

That is the overlap of the s_{Sn} -like bands with the $p_{\text{Sn-As}}$ -like bands follows from interlayer interaction.

Comparison with NaTl and Gray As

Finally we want to compare the results for K[SnSb] and K[SnAs] with those found for NaTl (18), which is the prototype of the B32-type Zintl phases, and with those found for gray arsenic (19), which has the same layer structure as the $\frac{1}{2}$ [SnAs] layers in K[SnAs].

In NaTl there are $n_0 = 8$ valence electrons per unit cell (two formula units NaTl in the unit cell). Three valence electron bands are fully occupied. The 4th valence band is almost fully occupied (occupancy 1.96 electrons (18)) and the 5th band is nearly empty (occupancy 0.04 electrons). It follows that the density of states shows a sharp minimum at the Fermi level E_F . Furthermore, the partial density of states of Na is distinctly smaller than expected for covalent bonded sodium. Therefore in both cases, NaTl and the compounds considered here, we find two common properties: a charge transfer from the alkali/alkaline earth substructure to the more electronegative elements and, additionally,

$n_0/2$ (almost) fully occupied valence bands separated from the $(n_0/2 + 1)$ th energy band by (nearly) a band gap.

In gray arsenic there are six As atoms in a hexagonal unit cell. We get $n_0 = 30$ valence electrons per unit cell. The band structure of arsenic is shown in Fig. 9. There are 14 fully occupied valence bands and 3 partly filled valence bands. It follows that there is no band gap between the occupied and unoccupied electronic states, see also (19). We think that this metallic character is due to interlayer interaction of the As atoms similar to those discussed above for Sr[Sn₂As₂]. In As the bond distance between interlayer As atoms is equal to $R_{\text{inter}} = 313.7$ pm compared to $R_{\text{intra}} = 250.6$ pm. In a computer experiment we have left R_{intra} constant and have increased R_{inter} up to 467.8 pm in order to reduce the interlayer interaction. The resulting band structure is shown in Fig. 10. Using $R_{\text{inter}} = 467.8$ pm we find a band gap between the 6th and 7th band separating the occupied and unoccupied p -like states. Therefore the layer structure forms for large interlayer distances saturated bonds. The occupied and unoccupied p -like band states of As are separated, and the bonding mech-

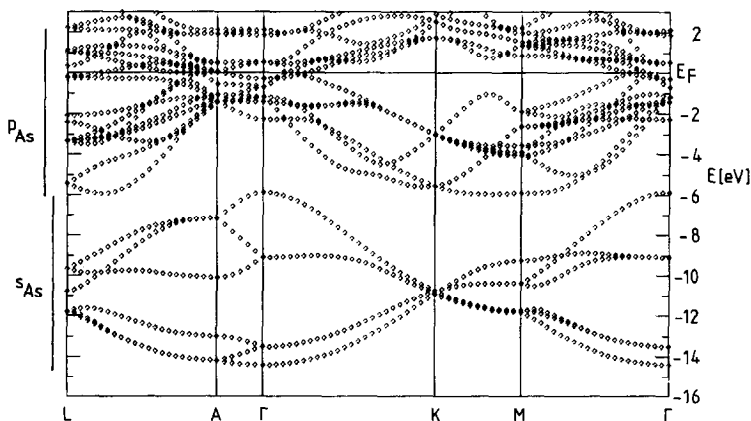


FIG. 9. Electronic band structure of gray arsenic using the hexagonal unit cell. The six low lying bands labeled s_{As} are the s -like bands. Above these bands we find the p -like bands (p_{As}).

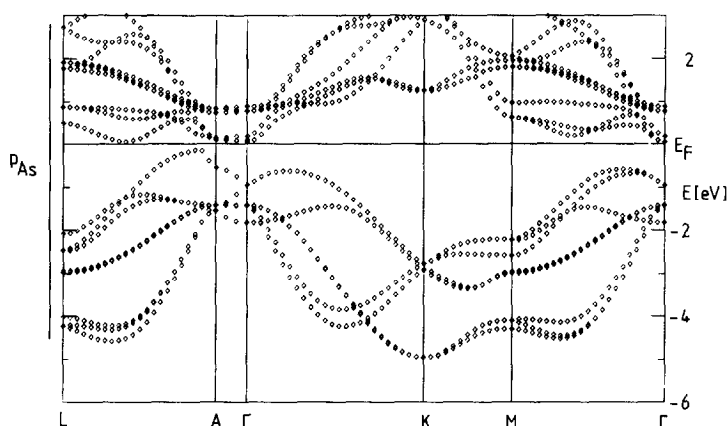


FIG. 10. Electronic band structure of the p -like bands (see Fig. 9) of a hypothetical As structure with an increased interlayer distance up to 467.8 pm, instead of the experimental value of 313.7 pm.

anism is similar to the bonding mechanism in $\frac{2}{3}$ [SnAs] and $\frac{2}{3}$ [SnSb] layers studied here.

IV. Conclusions

Using the Zintl concept to interpret the chemical bonds in K[SnAs], K[SnSb], and Sr[Sn₂As₂], the arrangement of the atoms in these compounds suggests that the almost free valence electrons of K/Sr are transferred to the Sn/As or Sn/Sb substructures to form saturated covalent bonds between Sn and As or Sn and Sb according to the octet rule. If this picture is correct, we expect distinct nonmetal or semimetal behavior for these compounds concerning properties like conductivity, magnetic susceptibility, or NMR data. The band structure results support these assumptions. First, the electronic valence states in the compounds are fully occupied energy bands separated by a small energy gap from the unoccupied energy bands. Second, a charge transfer is indicated by the finding that the partial density of states of Sn and As or Sn and Sb are exclusively the dominant contributions; the partial density of state for K or Sr gives only a minor

contribution to the total density of states. Third, the $8 - N$ rule in the molecular orbital picture seems to correspond to the finding that there is a band gap between the $n_0/2$ and $(n_0/2 + 1)$ th energy band, where n_0 is the number of valence electrons per unit cell.

Acknowledgments

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