Inorg. Chem. **2003**, *42*, 2759–2763

Inorganic Chemistry
Article

Localized versus Delocalized Bonding in the K_5Bi_4 Metallic Salt[†]

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Received November 6, 2002

The electronic structure of one member of the A_5Pn_4 family of metallic salts, K_5Bi_4, has been studied by means of first-principles density functional calculations. It is shown that the alkali and pnictide orbitals mix considerably providing for a large covalent bonding contribution to the stability of the compound. It is suggested that solids of the A_5Pn_4 family of compounds (A = K, Rb, Cs; Pn = As, Sb, Bi) should have better conductivity in the direction perpendicular to the plane of the tetrameric pnictide units and that the low-temperature transition in the antimonides is an order–disorder transition associated with one of the alkali positions.

1. Introduction

Solid-state reactions between alkali metals and post-transition elements have led to a plethora of new materials exhibiting an exceptional structural diversity.[1] The bonding, or more precisely, the relationship between the structure and number of electrons in most of these phases has been successfully rationalized in terms of chemical bonding schemes such as the Wade and octet rules.[1] Essentially, these schemes associate chemical stability with structural building blocks (clusters, networks, etc.) having an electronically closed shell configuration. Thus, a commonly accepted corollary is that these phases must be diamagnetic semiconductors (or insulators). Even if this aspect has not been systematically scrutinized, the conclusion seems to be essentially correct. With this situation in mind, an important recent development has been the preparation of several metallic compounds of this type.[2,3] Interesting problems from the viewpoint of the bonding description immediately emerge here.

One of the simplest cases is that of the A_5Pn_4 (A = K, Rb, Cs; Pn = As, Sb, Bi) compounds.[2f] Although there had been previous reports on these phases,[4] it was only recently that these salts were carefully studied and characterized.[2f] They exhibit metallic behavior (the bismuthides even become superconducting at low temperatures) and contain tetrameric Pn_4 units (see Figure 1). A first step in understanding the relationship between their stoichiometry, structure, and physical properties is to have a hint on the charge of the tetrameric pnictide units. As Gascoin and Sevov have discussed,[2f] both Pn_4^{4-} and Pn_4^{5-} are in principle equally likely. They have argued that the two descriptions should lead to different physical behaviors: temperature-dependent paramagnetism due to the spins localized in the tetrameric units in the second case but temperature-independent Pauli paramagnetism and metallic behavior in the first. Since all phases exhibit Pauli paramagnetism and metallic behavior, they concluded that the first alternative was the appropriate one. Of course, this does not imply that the "extra" electron is completely localized in the potassium network; it is probably somewhat delocalized along the structure and thus partially in the tetrameric units leading to a charge between 4− and 5−.

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(1) For recent reviews see: (a) Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 5178. (b) Corbett, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 670. (c) *Chemistry, Structure and Bonding of Zintl Phases and Ions*; Kauzlarich, S., Ed.; VCH Publishers: New York, 1996 and references therein.

(2) For some examples see the following references. (a) K_8In_{11}: Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1991**, *30*, 4875. (b) A_8Tl_{11} (A = K−Cs): Dong, Z.-C.; Corbett, J. D. *J. Cluster Sci.* **1995**, *6*, 187. (c) $K_{18}Tl_{20}Au_3$: Dong, Z.-C.; Corbett, J. D. *Inorg. Chem.* **1995**, *34*, 5042. (d) $K_{10}Tl_7$: Kaskel, S.; Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 778. (e) A_3Bi_2 (A = K, Rb, Cs): Gascoin, F.; Sevov, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 10251. (f) A_5Pn_4 (A = K, Rb, Cs; Pn = As, Sb, Bi): Gascoin, F.; Sevov, S. C. *Inorg. Chem.* **2001**, *40*, 5177.

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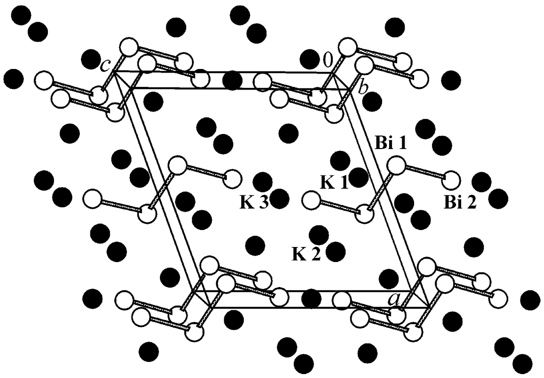

Figure 1. Crystal structure of K_5Bi_4 where the full (●) and empty (○) circles refer to the K and Bi atoms, respectively.

However, if we try to understand the properties of these and similar metallic salts, it is important to have a more in-depth picture of the electronic structure of the material so that we can ascertain how far the real situation lies from the two limiting ones. For instance, the extra electron can be heavily associated with the alkali metal network, and then, in general, the system will be a three-dimensional (3D) metal. But if it is mostly associated with the discrete nonalkali metal units, the physical behavior will critically depend on how these units see each other either directly or through the different alkali metal atoms. If there is a very small interaction, the system will be nonmetallic. Otherwise, it can be either a very isotropic or a low-dimensional metal depending on how the different units communicate. And indeed, low dimensional metals usually exhibit a rich low-temperature physics (usually associated with metal−metal and metal-semiconductor transitions) quite different from that of the 3D metals. Keeping this fact in mind may be pertinent for the A_5Pn_4 salts since the antimonides exhibit some kind of transition (at 110 K for K_5Sb_4 and 190 K for Rb_5Sb_4).[2f]

Semiempirical methods such as extended Hückel, which have been so useful in providing a simple but precise understanding of the electronic structure of many solids, can be less useful here. Both the strong Coulomb interactions and the uncertainty in the relative values of the parameters for the alkali and nonalkali elements may seriously affect the degree of mixing of their orbitals, a central issue here. Trying to contribute to an in-depth analysis of the electronic structure of this type of materials, we report here a first-principles density functional theory (DFT) study of the electronic structure of a representative member of this series of compounds, K_5Bi_4.

2. Computational Details

The calculations were carried out using a numerical atomic orbitals DFT[5,6] approach, which has been recently developed and designed for efficient calculations in large systems and implemented in the SIESTA code.[7−11] The use of atomic orbitals instead of plane waves greatly facilitates a chemical analysis of the results. We have used the local density approximation to DFT and, in particular, the functional of Perdew and Zunger.[12] Only the valence electrons are considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials[13] factorized in the Kleinman−Bylander form.[14] Nonlinear partial-core corrections to describe the exchange and correlation in the core region were included for Bi.[15] We have used a split-valence double-ζ basis set including polarization orbitals for all atoms, as obtained with an energy shift of 100 meV.[10] The integrals of the self-consistent terms of the Kohn−Sham Hamiltonian are obtained with the help of a regular real space grid in which the electron density is projected. The grid spacing is determined by the maximum kinetic energy of the plane waves that can be represented in that grid. In the present work, we used a cutoff of 150 Ry. The Brillouin zone (BZ) was sampled using a grid of $(2 \times 12 \times 4)$ k-points.[16] The Fermi surface was calculated using a grid of 726 k-points equally spaced on the irreducible wedge of the BZ. We have checked that the results are well converged with respect to the real space grid, the BZ sampling, and the range of the atomic orbitals.

3. Results and Discussion

The A_5Pn_4 compounds are isostructural, and as shown in Figure 1 for K_5Bi_4, the crystal structure is quite simple. It is built from tetrameric zigzag pnictide units (with two outer Bi−Bi distances of 3.046 Å and a central one of 2.998 Å) between which there are three different types of potassium atoms (K1, K2, and K3). The position for K3 is in fact refined as split around an inversion center with each position being 50% occupied for all A_5Pn_4 compounds except K_5Bi_4.[2f]

The calculated band structure and density of states (DOS) for K_5Bi_4 are reported in Figure 2a,b, respectively. All bands in Figure 2a are paired along $\Gamma \rightarrow Y$ and $\Gamma \rightarrow X$ because there are two formula units per repeat unit of the lattice which are related through a screw axis along b and a glide plane along a. Below the energy bands in Figure 2a, there are 4 pairs of bands mainly built from the s orbitals of Bi. As shown in Figure 2a, the Fermi level cuts two bands along the $\Gamma \rightarrow Y$ direction and one band along the $\Gamma \rightarrow Z$ direction. Since the first two bands exhibit a considerable dispersion (more that 1 eV), the system should be metallic, as reported by Gascoin and Sevov.[2f] The DOS diagram of Figure 2b shows that, as could be expected, the Bi contribution dominates in the filled energy bands. However, the important result of Figure 2b is that the K contribution is quite large. In fact, it is almost always around one-quarter that of the Bi atoms, this ratio being quite normal for heteroatomic bonding between atoms with such an electronegativity difference. Thus, there is very considerable mixing between the Bi and K orbitals so that the covalent contribution to the bonding in this phase must be quite important.

It is useful to look in more detail at both the DOS and band structure. Shown in Figure 2c is the contribution from

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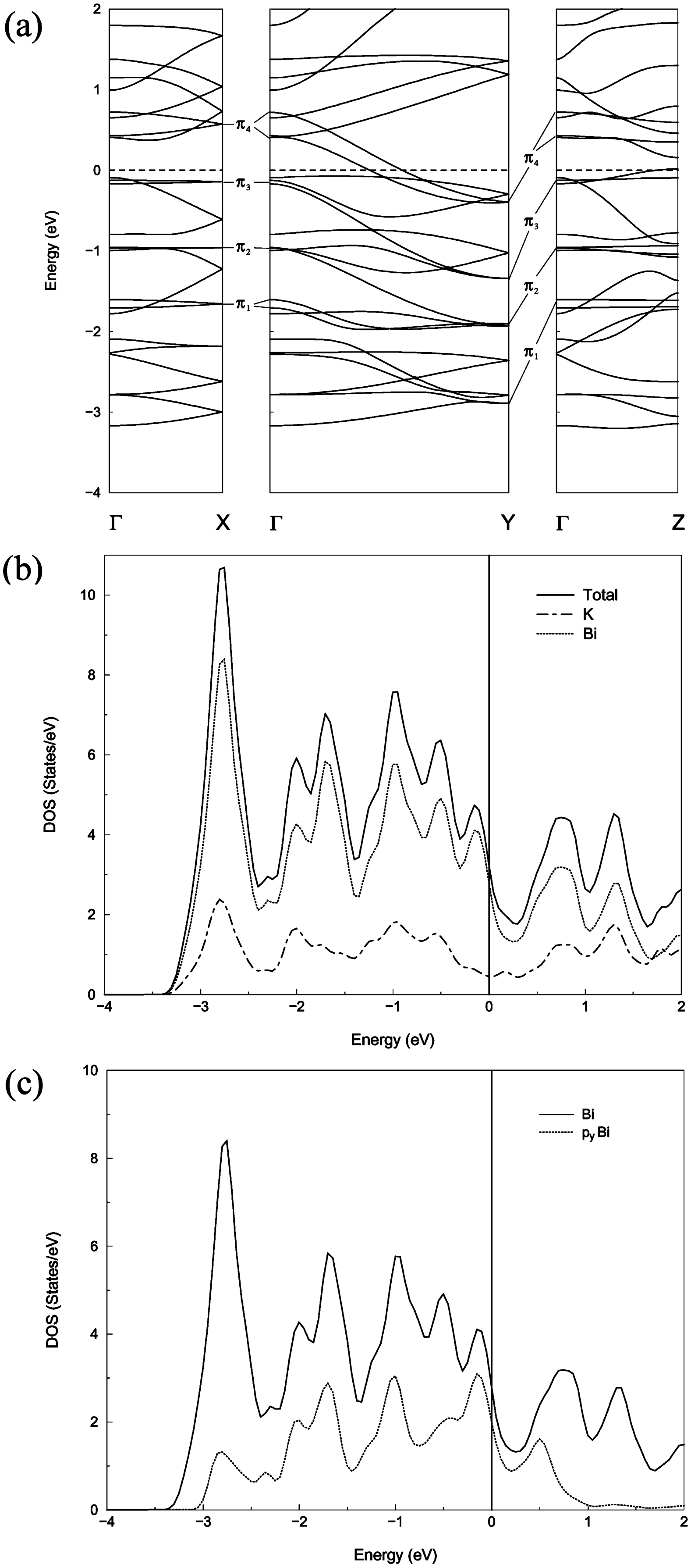
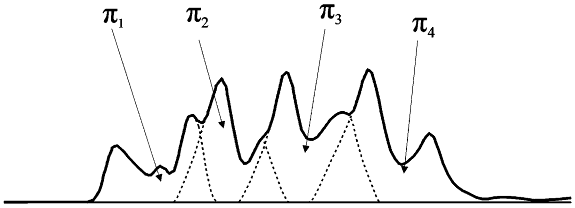


Figure 2. Calculated band structure (a), density of states (b), and contribution of the p_y orbitals of Bi to the density of states (c) for K_5Bi_4. In (a) Γ = (0, 0, 0), X = (1/2, 0, 0), Y = (0, 1/2, 0), and Z = (0, 0, 1/2) in units of the monoclinic reciprocal lattice vectors.

Scheme 1



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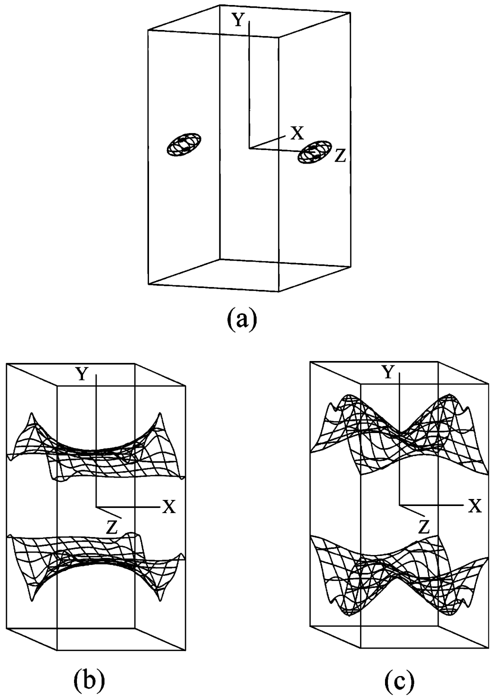
the Bi p_y orbitals to the DOS. Since our coordinate axis is such that the planar tetrameric units lie in the *xz* plane, this contribution is that of the π-type orbitals of the tetrameric units. As sketched in Scheme 1, this contribution is really the superposition of four typical one-dimensional (1D) DOS components (i.e., with maxima at the borders and a minimum nearly in the middle)[17] centered around 0.2, −0.75, −1.5, and −2.5 eV. Coming back to the band structure of Figure 2a, it can be seen that these energy values correspond to the middle of the dispersive bands along the $\Gamma \rightarrow Y$ direction. Even if several avoided crossings can make it difficult to recognize, these bands originate from four sets of two bands pairing at the Y point (in fact, this is clearly visible for the bands noted as π_4 in Figure 2a). Careful analysis of the band orbitals shows that, as suggested by the results of Figure 2c, these four pairs of bands have as the major components the four well-known π-type levels (π_1 to π_4) of the zigzag tetrameric units,[18] respectively. These bands acquire dispersion mostly through the bonding mixing of the higher lying s and p orbitals of potassium (the shortest Bi···Bi contact along *b* is 5.54 Å). In order to help trace back these four pairs of bands in Figure 2a, we have added the labels π_1−π_4 for some special points. It is clear that the π_4-based bands are approximately half-filled and the π_1-, π_2-, and π_3-based ones are full, as it would correspond for a formal charge of 5− for the tetrameric units. Such an occupation of the π-type levels of the tetrameric unit harmonizes with the fact that although the Bi−Bi bonds are not so different (2.998 vs 3.046 (×2) Å), the central one is definitely shorter. The remaining five pairs of filled bands plus the four lower ones (not shown in Figure 2a) correspond to the nine σ-type levels (Bi−Bi bonds and Bi lone pairs) of the tetrameric units. Many of these bands show quite large dispersion along the three directions of the reciprocal lattice, a consequence of the strong participation of the K orbitals in these filled bands as shown in Figure 2b (only along *c* there is a short Bi···Bi contact of 4.388 Å, all other contacts are longer than 5.5 Å). Thus, although every one of the pairs of bands in Figure 2a can be clearly traced back to one of the levels of a tetrameric Bi_4^{5-} unit, it would be impossible to understand the details of the electronic structure without realizing that the K atoms are far from just providing electrons to satisfy the electronic requirements of the more electronegative Bi atoms and a mostly Coulombic-type force keeping together the K_5Bi_4 network. They are indeed part of a 3D network with a large covalent bonding component. The fact that a detailed analysis of the band structure validates both this conclusion and the formal description of the tetrameric pnictide units as Pn_4^{5-} (i.e., formally possessing all the electrons of the system) illustrates the essential bonding ambiguity, with strong consequences for the transport properties, of these and similar systems.



(a)

(b) (c)

Figure 3. Calculated Fermi surfaces for K_5Bi_4 where X = (1/2, 0, 0), Y = (0, 1/2, 0), and Z = (0, 0, 1/2) in units of the monoclinic reciprocal lattice vectors. Note that in (a) the image has been rotated around *b** with respect those in (b) and (c).

As shown in Figure 2a, two bands (i.e., the two π_4-based ones) cross the Fermi level along the $\Gamma \rightarrow Y$ direction and one (i.e., one of the two π_3-based ones) along the $\Gamma \rightarrow Z$ direction. Thus, the Fermi surface has three components. The π_3 band leads to small closed hole pockets around the Z point (see Figure 3a). In contrast, the π_4 bands lead to open but very corrugated sheets (Figure 3b,c). Despite the small closed hole pockets and the very corrugated open sheets, which strictly speaking will make them 3D metals, the conductivity should be much better along the *b**-direction. Thus, K_5Bi_4 can be considered as quite anisotropic and thus a low-dimensional metal. In view of the crystal structures reported by Gascoin and Sevov,[2f] these conclusions should also apply for the other members of the A_5Pn_4 family of compounds (A = K, Rb, Cs; Pn = As, Sb, Bi). However, the low-temperature transition exhibited by the antimonides should not find its origin in this low-dimensionality. The two open components of the Fermi surface are too much corrugated and do not exhibit the nesting features typical of many low-dimensional metals.[17] If the K contribution to the bonding would have been smaller, the open Fermi surfaces would have been much flatter and these compounds would have been really pseudo-1D metals. The low-temperature behavior could have been quite different. However, note that, by having smaller K contributions, our analysis suggests that

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the band dispersion would also decrease and eventually the metallic character could disappear. This illustrates the decisive influence of the K atoms on the transport properties of these compounds and, more generally, of the less electronegative atoms on the properties of the so-called metallic Zintl phases.[3] Although the transport properties are due to the very small subset of levels near the Fermi level, which are obviously not those responsible for the structure of the system, it is however the structure which imposes the strength of the interactions leading to the band dispersion around the Fermi level. The strong involvement of the alkali atoms in the 3D network of these phases ultimately leads to the delocalization of the electron of the π_4 level of the tetrameric units, to the open but strongly corrugated and non-nested major components of the Fermi surface, and thus, it is responsible for the stable metallic behavior of the phases.

Finally, let us note that analysis of the different K contributions to the DOS shows that the K3 atoms have the larger weight in the region of the Fermi level (i.e., the contribution of one of the K3 atoms is more than twice that of one of the K1 or K2 atoms) so that the transport properties must be quite sensitive to the actual location of the K3 atoms (and consequently, of the A3 atoms in other phases of this family). Since, except for K_5Bi_4, the A3 positions were found to be split in two positions 50% occupied,[2f] and given the impossibility of a Fermi surface nesting scenario, the low-temperature transition observed in the antimonides is most likely due to an order−disorder transition associated with the A3 atoms and not to an instability of the Fermi surface.

Acknowledgment. This work was supported by DGI-Spain (Project BFM2000-1312-C02-01) and Generalitat de Catalunya (Project 2001 SGR 333) and by grants of computer time from the CESCA-CEPBA. We thank P. Ordejón, J. L. Mozos (deceased), G. Tobias, and P. Alemany for useful advice and discussions.

IC026156C