Inorg. Chem. **2005**, *44*, 1644–1646

Inorganic Chemistry
Communication

Electronic Structure of the K_3Bi_2 Metallic Phase

Pere Alemany,[*,†] Miquel Llunell,[†] and Enric Canadell[*,‡]

Departament de Química Física and Centre de Recerca en Química Teòrica (CeRQT), Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain, and Institut de Ciència de Materials de Barcelona (CSIC), Campus de la Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

Received December 15, 2004

The electronic structure of K_3Bi_2 is discussed on the basis of first-principles DFT calculations. It is shown that the dimers are formally $(Bi_2)^{3-}$, even though this might seem to be in contradiction with the metallic character of the salt. The apparent puzzle is explained by the sizable participation of the K levels in the bonding.

A large number of phases result from the solid-state reaction of post-transition elements with alkali or alkali-earth metals.[1] Many of them obey traditional electron counting rules, which basically associate chemical stability with the existence of a closed-shell electronic configuration for the anionic clusters or networks in the structure, thus suggesting that these phases should be insulators or semiconductors. However, an increasing number of these phases have been found to exhibit metallic properties, either because of the existence of an excess/deficit of electrons according to these rules or because the stability of some of the structural fragments is related to an odd number of electrons. $K_{10}Tl_7$,[2a] $Ba_5In_4Bi_5$,[2b] and K_5Bi_4,[2c] respectively, are examples of the three categories.

From the conceptual viewpoint, one of the more challenging problems concerning these phases is to have an idea of the relationship between the crystal structure, the formal electron count, *and* the transport properties of the materials. Here, one must remember that the transport properties are dictated by a small subset of energy levels, i.e., those near the Fermi level. The presence of an odd number of electrons does not guarantee metallic behavior because the electrons can remain localized. For instance, whereas both $K_{10}Tl_7$[2a] and $Na_9K_{16}Tl_{18}Cd_3$[3] are phases with an excess number of electrons, the first is metallic whereas the second is not. Thus, it is important to examine a representative set of phases in order to develop some understanding of the problem. As an extension of our work along this line on K_5Bi_4[4] and $Ba_5In_4Bi_5$,[2b] we report here on the electronic structure of K_3Bi_2, an example of the A_3Bi_2 (A = K, Rb, Cs) metallic phases.[5]

The calculations reported in this work were carried out using a numerical atomic orbitals density functional theory (DFT)[6] approach, recently developed and designed for efficient calculations in large systems and implemented in the SIESTA code.[7−9] We employed the generalized gradient approximation to DFT and, in particular, the functional of Perdew, Burke, and Ernzerhof.[10] Only the valence electrons were considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials[11] factorized in the Kleinman−Bylander form.[12] We used a split-valence double-ζ basis set including polarization orbitals for all atoms, as obtained with an energy shift of 100 meV.[13] The integrals of the self-consistent terms of the Kohn−Sham Hamiltonian were obtained with the help of a regular real space grid onto which the electron density was projected. The grid spacing was determined by the maximum kinetic energy of the plane waves that could be represented in that grid. In the present work, we used a cutoff of 150 Ry. The Brillouin zone was sampled using a grid of $(6 \times 6 \times 6)$ k points.[14] Except when otherwise stated, the experimental crystal structure[5,15] was used in the calculations.

---

[*] To whom correspondence should be addressed. E-mail: alemany@qf.ub.es (P.A.); canadell@icmab.es (E.C.).

[†] Universitat de Barcelona.

[‡] Campus de la Universitat Autònoma de Barcelona.

(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) Kauzlarich, S., Ed. *Chemistry, Structure and Bonding of Zintl Phases and Ions*; VCH Publishers: New York, 1996, and references therein.

(2) (a) Kaskel, S.; Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 778. (b) Cho, A.; Sevov, S. C.; Tobías, G.; Canadell, E.; Ponou, S.; Fässler, T. *Chem. Eur. J.* **2004**, *10*, 3615. (c) Gascoin, F.; Sevov, S. C. *Inorg. Chem.* **2001**, *40*, 5177.

(3) Huang, D. P.; Corbett, J. D. *Inorg. Chem.* **1999**, *38*, 316.

(4) Rodríguez-Fortea, A.; Canadell, E. *Inorg. Chem.* **2003**, *42*, 2759.

(5) Gascoin, F.; Sevov, S. *J. Am. Chem. Soc.* **2000**, *122*, 10251.

(6) (a) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, 864. (b) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, 1133.

(7) Soler, J. M.; Artacho, E.; Gale, J. D.; García, A.; Junquera, J.; Ordejón, P.; Sánchez-Portal, D. *J. Phys.: Condens. Matter.* **2002**, *14*, 2745.

(8) http://www.uam.es/siesta/ (accessed Aug 2004).

(9) For reviews on applications of the SIESTA approach, see: (a) Ordejón, P. *Phys. Status Solidi (b)* **2000**, *217*, 335−356. (b) Sánchez-Portal, D.; Ordejón, P.; Canadell, E. *Struct. Bonding* **2004**, *113*, 103.

(10) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(11) Trouiller, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993.

(12) Kleinman, L.; Bylander, D. M. *Phys. Rev. Lett.* **1982**, *48*, 1425.

(13) Artacho, E.; Sánchez-Portal, D.; Ordejón, P.; García, A.; Soler, J. M. *Phys. Status Solidi B* **1999**, *215*, 809.

(14) Monkhorst, H. J.; Park, J. D. *Phys. Rev. B* **1976**, *13*, 5188.

(15) The *a* value reported in ref 5 is incorrect. The correct value is 9.361 Å. We thank Prof. S. Sevov for communication of this fact.

10.1021/ic048239u CCC: $30.25

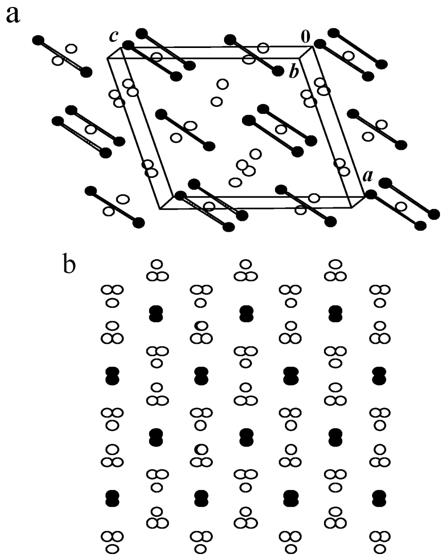

Figure 1. (a) Crystal structure of K_3Bi_2. (b) View along the [−1 0 1] direction showing the K_3Bi_2 structure as a pseudohexagonal packing of ···Bi−Bi···Bi−Bi··· chains.

The crystal structure K_3Bi_2 is very simple and contains dimeric Bi_2 units surrounded by K atoms (see Figure 1a). However, these Bi_2 units are less isolated than it might appear at first view; two of them are separated along the direction of the Bi−Bi bonds (3.014 Å) by a distance of 4.420 Å, certainly long but nonnegligible, leading to chains of Bi_2 dimers. As shown in Figure 1b, the structure can also be seen as a quasihexagonal packing of these ···Bi−Bi···Bi−Bi··· chains surrounded by K atoms. In our recent work on the closely related K_5Bi_4,[4] we found that the four π-type orbitals of the Bi_4 units lead to pseudo-one-dimensional (1D) bands along the direction perpendicular to the plane of these units despite having Bi−Bi contacts along this direction longer than 5.5 Å. The interactions are mediated through the K atoms. Thus, we anticipated that K_3Bi_2 could well be a new pseudo-1D metal species and thus exhibit an interesting physics, an additional motivation for our study.

The first step in correlating stoichiometry, structure, and transport properties is to guess the charge of the Bi_2 dimers. As discussed by Gascoin and Sevov,[5] once the absence of protons in the structure is confirmed, one can imagine two different situations. First, the dimers are $(Bi_2)^{3-}$ units immersed in a sea of K^+ cations. Second, the dimers are $(Bi_2)^{2-}$ units, and an extra electron must be delocalized though the potassium subnetwork. As pointed out by these authors, these two views lead to different descriptions of the physical behavior of A_3Bi_2 salts: temperature-dependent paramagnetism due to the unpaired electrons localized in the dimers in the first case, but temperature-independent Pauli paramagnetism and metallic behavior in the second. Because of the Pauli paramagnetism and metallic behavior exhibited by the A_3Bi_2 phases, they concluded that the latter alternative was the appropriate one.

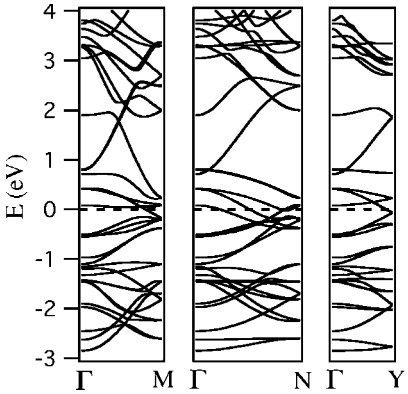

Figure 2. Calculated band structure for K_3Bi_2, where the dashed line indicates the Fermi level. Γ = (0, 0, 0), Y = (0, 0.5, 0), M = (−0.5, 0, 0.5) and N = (0.5, 0, 0.5) in units of the monoclinic reciprocal lattice vectors.

As a check for our computational approach, we first optimized the structure. The calculated Bi−Bi bond length is 3.037 Å, i.e., 0.7% larger than the experimental value, and the cell constants are within 1.5−2.5% of the experimental values. In addition, we considered possible nonmetallic states and found a ferromagnetic state 0.3 eV above the metallic state but no antiferromagnetic state. All of these results are in excellent agreement with the experimental information.[5,15]

The calculated band structure along three representative lines in reciprocal space are shown in Figure 2. The Γ → M, Γ → N, and Γ → Y lines describe the interactions along the directions ($c - a$), ($a + c$), and b, respectively. Several bands cut the Fermi level, in agreement with the metallic character of the salt. However, the situation is considerably more complex than in K_5Bi_4. Here, several bands overlap near the Fermi level, making the orbital analysis considerably more involved. Bands cross the Fermi level in all directions, which means that, in contrast to our initial expectations, K_3Bi_2 is a stable three-dimensional metal.

Although a chemical analysis of the band structure of Figure 2 is possible, in cases such as this, it is preferable to consider the density of states (DOS). In the present case, the analysis can be made transparent by using a Cartesian system of axes in which x and y lie on the ab plane in such a way that y runs along the Bi−Bi bond direction and x runs perpendicular to it. The z axis is perpendicular to the ab plane. The calculated DOS as well as the partial contributions of the Bi p_x, p_y, and p_z orbitals are shown in Figure 3. On the basis of these projections and consideration of the wave vectors at some special points, the Bi contribution to the DOS can be easily analyzed in terms of the different orbitals of a Bi_2 unit (see Figure 4). The contributions of the $1\sigma_g^+$ and $1\sigma_u^+$ levels are found at energies lower than those shown in Figure 3. The peak between −3 and −1 eV is the superposition of three contributions, that of the $2\sigma_g^+$ level (red curve) and those of the two π_u bonding levels (blue and green curves). The peak between −1 and 0.5 eV contains two contributions originating from the two π_g antibonding levels. These levels are partially filled. The contribution of the antibonding $2\sigma_u^+$ level (upper red curve) is very broad and occurs above the Fermi level. Integration of each contribution allows for the determination of the formal occupation of the different levels and thus the formal charge of the diatomic unit. For a $(Bi_2)^{n-}$ unit, formally 75%, 87%, and 100% of the π levels are filled for $n = 2$, 3, and 4, respectively.

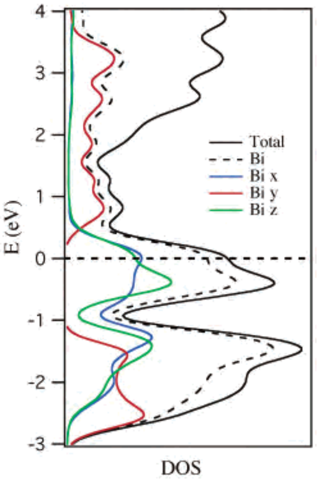

Figure 3. Density of states for K_3Bi_2 (black line). The partial contributions of Bi (broken line) and the Bi p_x (blue line), Bi p_y (red line), and Bi p_z (green line) orbitals are also shown.

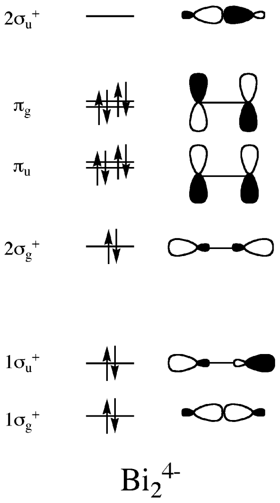

Figure 4. Qualitative orbital diagram for a $(Bi_2)^{4-}$ unit.

Integration of the x and z contributions of Figure 3 gives 88% occupation, showing that the diatomic units are clearly $(Bi_2)^{3-}$ units even though the system is metallic. As discussed in ref 5, the Bi−Bi distance is intermediate between those of typical single and double Bi−Bi bonds, in harmony with the $(Bi_2)^{3-}$ formal description.

As shown in the case of K_5Bi_4, the key to understanding this apparent paradox is the notable participation of the K levels around the Fermi level (in fact, in large parts of the filled portion of the DOS). That potassium is not just providing electrons to the bismuth dimers, with some kind of Coulombic force keeping together the K_3Bi_2 structure, is clear from the participation of the K levels in the filled part of the DOS. (Recall that, in DFT approaches using localized basis sets such as the present one, the total DOS is simply the addition of those of the different atomic contributions.) To obtain a somewhat more precise idea of this involvement, we carried out a Mulliken population analysis and found that the valence electron population of a K atom (the difference among the two types of K atoms is practically nil) is 0.85e, i.e., the charge is +0.15. This value is notably smaller than that calculated adopting exactly the same computational details for typical ionic salts of K (for instance, +0.64 for KF). Bearing in mind the possible shortcuts of Mulliken analysis, we also determined these values using the Voronoi Deformation Density (VDD)[16] and Hirshfeld (H)[17] approaches. The K charge in K_3Bi_2 is +0.04 (VDD) and +0.02 (H), whereas in KF, it is +0.32 (VDD) and +0.35 (H). These values are all quite clear in showing a significant mixing of the potassium and bismuth orbitals in the present compound.

We emphasize that, by writing $(Bi_2)^{3-}$, we do not imply that the dimers are discrete units with an unpaired electron, as we are counting not electrons actually transferred but rather the number of occupied orbitals mainly centered on the dimers.[18] As shown in Figure 2, the bands in the region around the Fermi level have the π_g dimer orbitals as the major component, *but* the K orbitals mix into them, providing a link between neighboring dimers and leading to the spread of the orbitals into bands. This mixing decreases the *true* charge of the dimers because part of the *formal* 3− charge is shared with the K atoms. Yet, the formal description is pertinent because it grasps the main features of the electronic structure of the material.

The levels responsible for conduction are based on the two π_g orbitals of the $(Bi_2)^{3-}$ units. The band structure of Figure 2 does not show the existence of one-dimensional bands along the chain direction (i.e., $\Gamma \rightarrow M$). The bands that could lead to direct Bi−Bi interactions along this direction are those based on the $2\sigma_g^+$ level, which, in fact, do interact but are far below the Fermi level. As for K_5Bi_4,[4] it is because of the mixing with K orbitals that the different units *see* each other, leading to the delocalization and hence to the metallic properties of the salt. The difference from the case of K_5Bi_4, which showed a quite pronounced low-dimensional character,[4] lies in the fact that the elementary bismuth units now have two orthogonal π-type levels partially filled that communicate through the K atoms, thus leading to a typical three-dimensional metal. Despite the sizable mixing of the alkali and post-transition metal atom orbitals that leads to the metallic character of both systems, it is clear that the nature of the partially filled levels of the post-transition metal units is extremely important in determining the nature of the bands at the Fermi level and thus the transport properties of these phases.

Acknowledgment. We are greatly indebted with Professors J. D. Corbett and S. Sevov for their insightful comments. This work was supported by DGI-Spain (Projects BFM2003-03372-C03 and BQU2002-04033-C02-02) and Generalitat de Catalunya (Projects 2001 SGR 333 and 2001 SGR 00044). Part of the computations were carried out using the facilities of CESCA-CEPBA.

IC048239U

---

(16) Fonseca Guerra, C.; Handgraaf, J.-W.; Baerends, E. J.; Bickelhaupt, F. M. *J. Comput. Chem.* **2004**, *25*, 189.
(17) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129.
(18) Nesper, R. *Prog. Solid State Chem.* **1990**, *20*, 1−45.