Inorg. Chem. **1998,** *37,* 5807−5810

Concerning the Resistivity Anomaly in the Layered Pnictide Oxide $Na_2Ti_2Sb_2O$

Fabrizia Fabrizi de Biani

Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Diagonal 647,
08028 Barcelona, Spain

Pere Alemany*

Departament de Química-Física, Facultat de Química, Universitat de Barcelona, Diagonal 647,
08028 Barcelona, Spain

Enric Canadell*

Institut de Ciència de Materials de Barcelona (CSIC), Campus de la U.A.B., 08193 Bellaterra, Spain

Received June 22, 1998

The origin of the resistivity anomaly at 120 K in the layered pnictide oxide $Na_2Ti_2Sb_2O$ is discussed on the basis of tight-binding band structure calculations. The Fermi surface of this material is shown to result from the superposition of a two-dimensional and four pseudo-one-dimensional components. It is proposed that the resistivity anomaly is associated with a Fermi surface instability of these pseudo-one-dimensional portions leading to a periodic lattice distortion.

1. Introduction

Ternary or quaternary solids containing transition metal atoms and main group elements of the bottom part of the periodic table are interesting because of the very diffuse orbitals these main group elements possess. This feature can have unexpected consequences for their electronic structures. For instance, binary and ternary transition metal tellurides often exhibit structural and/or transport properties very different from those of the corresponding sulfides or selenides. Although much less explored than tellurides, antimony-containing solids of this class could also afford interesting new types of structures and physical properties. Recently, Kauzlarich et al.[1] have reported on the transport properties of the layered pnictide oxide $Na_2Ti_2Sb_2O$.[2] This phase shows metallic conductivity above 120 K, and at this temperature it exhibits a resistivity anomaly as well as a considerable decrease of the magnetic susceptibility. After the resistivity anomaly, however, $Na_2Ti_2Sb_2O$ keeps the metallic behavior.[1]

Since $Na_2Ti_2Sb_2O$ is a layered material, it could well be that the resistivity anomaly at 120 K originates from the kind of Fermi surface instabilities frequently found in low-dimensional metals.[3,4] To gain some insight on the transport properties of this interesting material we decided to study its electronic structure on the basis of the extended Hückel tight-binding method.[5] This method has so far given excellent results for many low-dimensional materials.[6] The atomic parameters and exponents employed in our calculations are summarized in Table 1. Our study strongly suggests that $Na_2Ti_2Sb_2O$ is a new material exhibiting the so-called hidden nesting,[7] which is most likely responsible for the resistivity anomaly at 120 K.

Table 1. Exponents and Parameters Used in the Calculations[a]

atom	orbital	H_{ii} (eV)	ζ_1	ζ_2	c_1[b]	c_2[b]
Ti	4s	−6.52	1.30			
	4p	−3.81	1.30			
	3d	−7.18	4.55	1.40	0.4206	0.7839
Sb	5s	−16.48	2.323			
	5p	−8.75	1.999			
O	2s	−31.60	2.275			
	2p	−14.80	2.275			

[a] A modified Wolfsberg−Helmholz formula (Ammeter, J.; Bürgi, H−B.; Thibeault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686) was used to calculate the off-diagonal H_{ij} values. [b] Contraction coefficients used in the double-ζ expansion.

---

(1) Axtell, E. A., III; Ozawa, T.; Kauzlarich, S.; Singh R. R. P. *J. Solid State Chem*. **1997**, *134*, 423.

(2) Adam, A.; Schuster, H.-U. *Z. Anorg. Allg. Chem*. **1990**, *584*, 150.

(3) (a) Wilson, J. A.; DiSalvo, F. J.; Mahajan, S. *Adv. Phys*. **1975**, *24*, 117. (b) *Electronic Properties of Inorganic Quasi-One-Dimensional Compounds*; Monceau, P., Ed.; Reidel: Dordrecht, 1985; Parts I and II. (c) *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures*; Rouxel, J., Ed.; Reidel: Dordrecht, 1986. (d) *Low-Dimensional Electronic Properties of Molybdenum Bronzes and Oxides*; Schlenker, C., Ed.; Kluwer: Dordrecht, 1989. (e) *Physics and Chemistry of Low-Dimensional Inorganic Conductors*; Greenblatt, M., Schlenker, C., Dumas, J., van Smaalen, S., Eds.; NATO-ASI Series B, Physics; Plenum: New York, 1996.

(4) (a) Canadell, E.; Whangbo, M.-H. *Chem. Rev*. **1991**, *91*, 965. (b) Canadell, E.; Whangbo, M.-H. In *Physics and Chemistry of Low-Dimensional Inorganic Conductors*; Greenblatt, M., Schlenker, C., Dumas, J., van Smaalen, S., Eds.; NATO-ASI Series B, Physics; Plenum: New York, 1996; p 271. (c) Whangbo, M.-H.; Seo, D.-K.; Canadell, E. In *Physics and Chemistry of Low-Dimensional Inorganic Conductors*; Greenblatt, M., Schlenker, C., Dumas, J., van Smaalen, S., Eds.; NATO-ASI Series B, Physics; Plenum: New York, 1996; p 285.

(5) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc*. **1978**, *100*, 6093.

(6) Canadell, E.; Whangbo, M.-H. *Phys. Rev. B* **1991**, *43*, 1894 and references therein.

(7) (a) Whangbo, M.-H.; Canadell, E.; Foury, P.; Pouget, J. P. *Science* **1991**, *252*, 96. (b) Canadell, E.; Whangbo, M.-H. *Int. J. Mod. Phys. B* **1993**, *7*, 4005.

10.1021/ic980712e CCC: $15.00

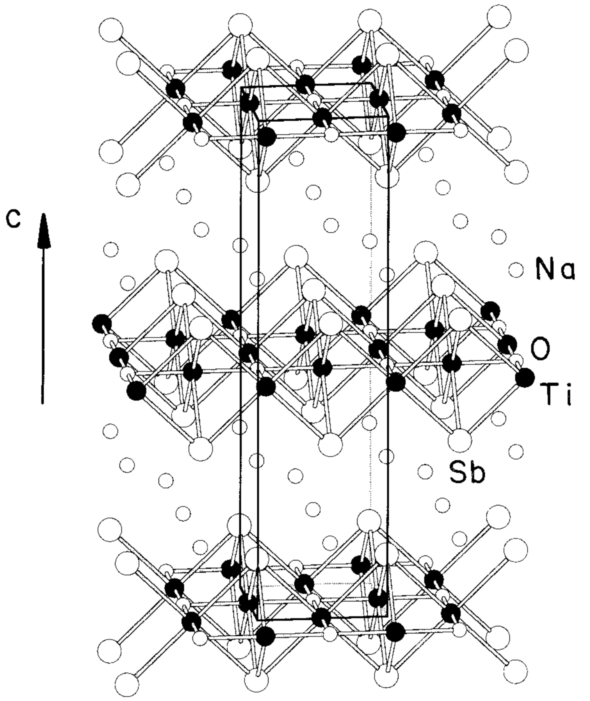


Figure 1. Crystal structure of $Na_2Ti_2Sb_2O$.

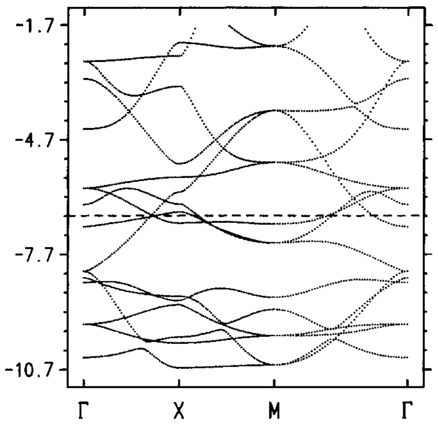
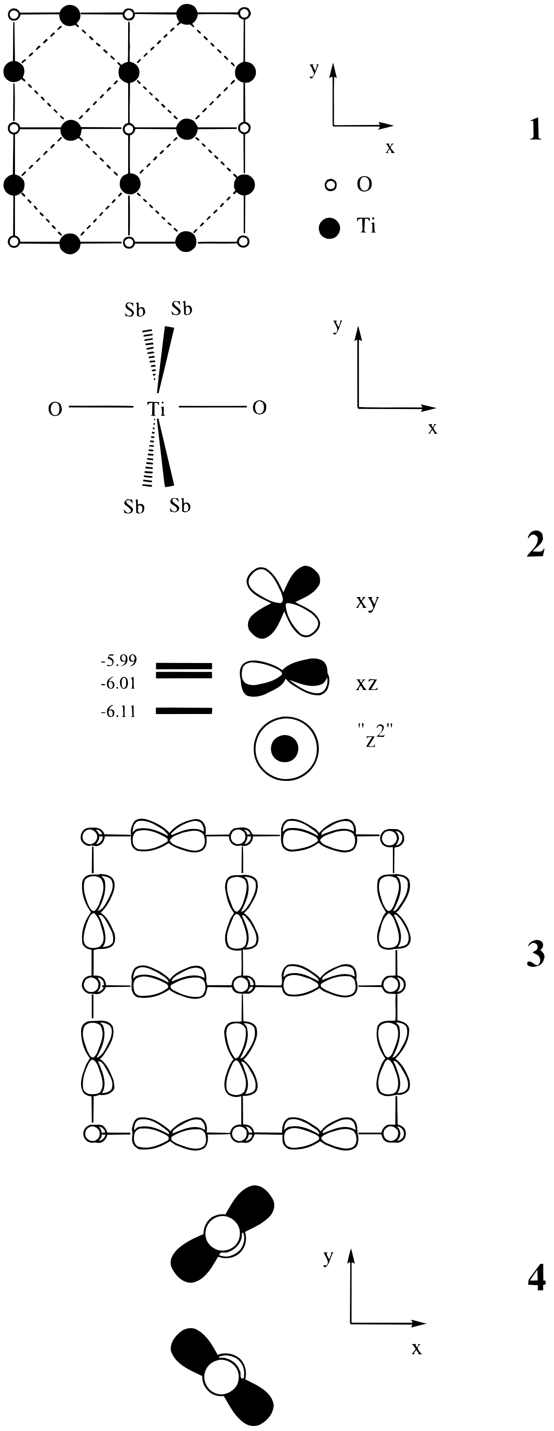


Figure 2. Calculated band structure for a $[Ti_2Sb_2O]^{2-}$ layer of $Na_2Ti_2Sb_2O$. The dashed line refers to the Fermi level. $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, and $M = (a^*/2, b^*/2)$. The energy scale is in eV.

2. Crystal Structure

The crystal structure of $Na_2Ti_2Sb_2O$ is built from $[Ti_2Sb_2O]^{2-}$ layers between which reside the sodium cations (see Figure 1).[2] In understanding the nature of the Fermi surface for this material, it is important to briefly describe these layers. They contain Ti_2O planes built from two orthogonal sets of parallel ...Ti−O−Ti−O... chains (**1**). These planes can be considered to be the "anti" layers of the CuO_2 planes found in the well-known high-T_c cuprates. All angles in this layer are either 90 or 180° and the Ti−O bond length is 2.074 Å. When two Sb atoms are symmetrically placed above and below the center of each of the Ti squares in **1** (see Chart 1) the complete Ti_2Sb_2O layer is formed (see Figure 1). The Ti−Sb−Ti bond angle is 91.8°. Important to notice for the following discussion is that each Ti atom is octahedrally coordinated to four Sb and two O atoms. In addition, as shown with dotted lines in **1**, every Ti atom makes four Ti···Ti short contacts along the diagonal directions. Although these contacts are clearly longer (2.933 Å) than those of normal Ti−Ti bonds, they are still short enough to allow for non negligible d-orbital interactions. For the time being let us consider that there is the strong possibility of extended ...Ti···Ti···Ti... interactions along the diagonal directions of the layer.

Chart 1



3. Electronic Structure

A. Band Structure and Fermi Surface. The calculated band structure for a $[Ti_2Sb_2O]^{2-}$ layer of $Na_2Ti_2Sb_2O$ is shown in Figure 2 (note that the unit cell of the layer is Ti_2Sb_2O). Six low-lying bands with strong Sb s-orbital and O character are not shown in Figure 2. The first six bands from the bottom of Figure 2 have mainly Sb orbital character and are full. Thus there is a total of twelve filled bands mainly O and Sb in character, in agreement with the formal oxidation states O^{2-} and Sb^{3-}. This leaves two electrons to fill the bottom of the

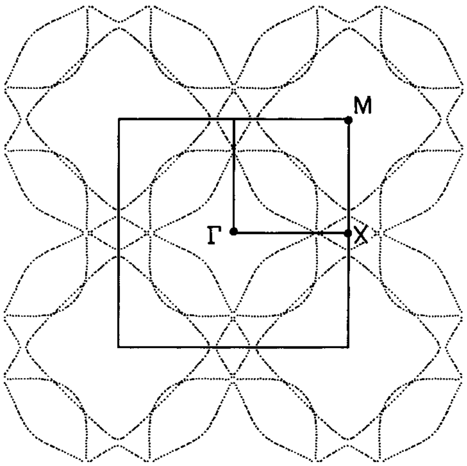


Figure 3. Calculated Fermi surface for a $[Ti_2Sb_2O]^{2-}$ layer of $Na_2Ti_2Sb_2O$.

Ti d-block bands so that the Ti atoms are formally d^1. These electrons partially fill a group of three bands, leading to the metallic behavior of $Na_2Ti_2Sb_2O$. These bands undergo several real and avoided crossings with other bands so that it is not easy to follow the nature of these bands all over the Brillouin zone. In such cases it is not useful to plot the individual contribution of each band to the Fermi surface but to project the different contributions on top of each other as shown in Figure 3.

Although at first sight the Fermi surface of Figure 3 can look complex, it is really quite simple. If the very weak gaps produced by band hybridization are neglected, the surface can be considered to result from the superposition of two hidden Fermi surfaces: (a) a closed Fermi surface with the shape of a square with rounded vertexes (see Figure 4a) and (b) a series of warped open Fermi surfaces perpendicular to the $(a + b)$ and $(-a + b)$ directions (see Figure 4b). According to this description, $Na_2Ti_2Sb_2O$ should be a two-dimensional (2D) metal because the Fermi surface contains both a 2D portion and two pairs of pseudo-one-dimensional (1D) portions along *orthogonal* directions. The existence of these superposed pseudo-1D portions strongly reminds the situation in several 2D molybdenum and tungsten oxides and bronzes where weakly hybridized pseudo-1D Fermi surfaces are responsible for the development of charge density wave (CDW) instabilities.[4a,b,7] Before considering the possible relationship between the pseudo-1D portions of the Fermi surface in $Na_2Ti_2Sb_2O$ and the resistivity anomaly at 120 K, we need to consider their structural and electronic origin. Let us note that we have verified that the shape of the Fermi surface of Figure 3 is stable with respect to reasonable changes in the exponents and parameters of Table 1.

B. Nature of the Partially Filled Bands. As shown in Figure 1, the Ti atoms of the layer are octahedrally coordinated by two O and four Sb atoms. The nonstrict orthogonality afforded by the presence of two different types of atoms leads only to a very small disruption of the degeneracy of the three t_{2g} levels (**2**). Note that in **2** the lowest t_{2g} orbital is represented as a z^2 orbital for simplicity. Although z^2 is the major component of this orbital, it also has some x^2-y^2 character so that it is really intermediate between a z^2 and a z^2-y^2 orbital. In the following we will refer to it as "z^2". In the context of the present discussion it should be noted that the "z^2" and *xy* orbitals are symmetric whereas *xz* is antisymmetric with respect to the plane of the layer. It must also be remarked that the antisymmetric t_{2g} orbital is *xz* for the Ti atoms of the ...O−Ti−O−Ti... chains along *x* but *yz* for the Ti atoms of the ...O−Ti−O−Ti... chains along *y*.

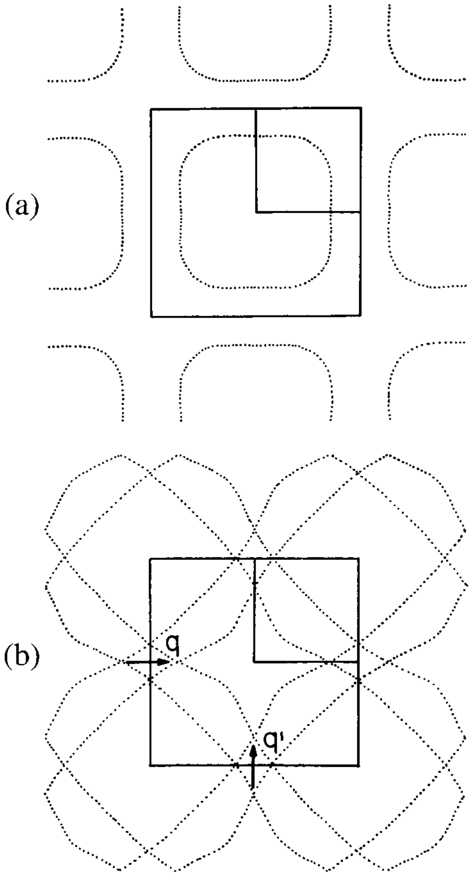


Figure 4. Decomposition of the Fermi surface of Figure 3 in (a) a 2D contribution, (b) pseudo-1D contributions perpendicular to the $(a + b)$ and $(-a + b)$ directions.

As shown in **3**, these *xz*/*yz* orbitals form a 2D series of orbitals which can interact both through the O *z*-orbitals and through the Sb mainly p-orbitals. Our calculations show that the dispersion of the corresponding bands is dictated not only by these types of interactions but also by some direct metal−metal interaction. The lowest of the two bands based on the *xz*/*yz* orbitals crosses the Fermi level and leads to the closed component of the Fermi surface shown in Figure 4a. However, despite the different coupling mechanisms, the band has a strong memory of the fact that the two ...Ti(*xz*)−O(*z*)−Ti(*xz*)−O(*z*)... and ...Ti(*yz*)−O(*z*)−Ti(*yz*)−O(*z*)... sets of orbitals run along orthogonal directions and leads to the "square with rounded vertexes" portion of the Fermi surface shown in Figures 3 and 4a. This is due to the nature of *both* the lattice and the t_{2g} orbital.

As noted, the "z^2" and *xy* orbitals are both symmetric with respect to the plane of the layer so that they can hybridize leading to a pair of orbitals as shown in **4**. Of course, these orbitals are very well suited to interact along the "Ti chains" running along the diagonal directions of the layer and, consequently, to lead to 1D bands. Since there are two Ti atoms per unit cell and thus two pairs of orbitals **4**, the Fermi surface should contain four pairs of approximately parallel (1D) lines, two of them being perpendicular to the $(a + b)$ direction and the other two being perpendicular to the $(-a + b)$ direction. The different 1D systems should have very weak direct interaction. The parallel sets of d-orbitals do not interact because they make very weak δ-type interactions. The perpendicular sets of d-orbitals almost do not interact because of the local orthogonality of the d-orbitals. They interact, however, through the Sb p-orbitals, which slightly couple both the parallel and perpendicular sets of orbitals. This leads to both the warping of all the lines and the splitting of the sets of two nearest "parallel" lines in the Fermi surface. This coupling is, however, weak enough to preserve the 1D character of the associated portion of the Fermi surface as shown in Figures 3 and 4b. Thus, it is clear that the two sets of pairs of warped lines in Figures 3 and 4b are associated with the two pairs of orbitals **4** making metal−metal interactions along the diagonal directions of the layers slightly coupled through the Sb atoms.

4. Fermi Surface and Resistivity Anomaly

When a piece of a Fermi surface can be superposed on another piece by a vector q, the Fermi surface is said to be nested by this vector.[3a,4a] A metal with a nested Fermi surface is susceptible toward a charge density wave (CDW) instability that introduces an additional periodicity of the electronic density distribution and ultimately leads to a periodic lattice distortion. The CDW formation removes the nested portions of the Fermi surface. Since the lattice distortion associated with a CDW induces lattice strain, the lattice vibration most likely to couple with the CDW instability of a nested Fermi surface is that leading to a maximum electronic energy stabilization, i.e., the one whose wave vector provides a maximum possible nesting.

The Fermi surface of Figure 3 exhibits a certain number of flat portions (for instance, the opposite sides of the squares centered at M or, to a lesser extent, those of the rounded squares centered at Γ) which are nested and, in principle, could lead to some kind of periodic lattice distortion. However, if we look for the vector associated with the maximum possible nesting, we must turn to the pseudo 1D components of Figure 4b. As noted there, the vector q along a^* (or equivalently q' along b^*) allows the nesting of a large part of the hidden pseudo 1D Fermi surface. Except for the small portions of the more irregularly warped region, most of the Fermi surface of Figure 4b is nested. Thus there is a strong driving force toward a CDW instability with wave vector $q \approx 0.27a^*$ (or equivalently $q' \approx 0.27b^*$).[8] The periodic lattice distortion associated with this instability could well be one in which the position of the Ti atoms of one set of parallel ...O−Ti−O−Ti−O... chains is modulated with a wave vector q—the modulation being in phase for all parallel chains—whereas the position of the Ti atoms of the perpendicular ...O−Ti−O−Ti−O... chains remains unaltered. Of course the Sb atoms will also follow a little bit this modulation. After the CDW-induced lattice distortion, the closed Fermi surface of Figure 4a as well as the pockets around the non nested regions of Figure 4b will remain. Thus, the system should keep the metallic character after the periodic lattice distortion, as experimentally found. We thus suggest that this CDW instability is at the origin of the resistivity anomaly at 120 K. As a way to test our proposal, X-ray diffuse scattering measurements in order to look for superlattice reflections at approximately $0.27a^*$ (or $0.27b^*$) would be very interesting.

As noted above, the Fermi surface of Figure 3 has also large flat portions associated with the squares around the M point. The nesting vectors in that case, which occur along the $(a + b)$ and $(-a + b)$ directions, are different from those associated with the hidden nesting mechanism. Thus, if the lattice distortion associated with the hidden nesting mechanism induces too much strain, the system could choose to undergo this second type of CDW induced lattice distortion.[9] Since only the squares around M would be destroyed by the modulation, the system should also hold in that case the metallic character after the anomaly. To carry out X-ray diffuse scattering measurements would be the more direct way to distinguish between the two scenarios. Nevertheless we believe that the hidden nesting mechanism is more likely.

Acknowledgment. This work was supported by the DGES-Spain Projects PB96-0859 and PB95-0848-C02-01, by Generalitat de Catalunya (1997 SGR 24) and by the Training and Mobility of Researchers Program, Access to Large Installations, under Contract ERBFMGECT950062 "Access to supercomputing facilities for european researchers" established between the European Community and CESCA−CEPBA. We are grateful to an anonymous referee for his comments concerning the possible computational dependence of the Fermi surface.

IC980712E

---

(8) Note that the exact value of the q vector depends on the relative position of the *xz*/*yz* band with respect to the other bands. In other words, the *xz*/*yz* band acts like an electron reservoir and the modulus of the q vector can depend on computational details. Model calculations suggest that, within the context of the present study, this dependence is not very important for reasonable changes in the exponents and parameters. Nevertheless, other computational techniques could lead to different answers concerning the positioning of this band.

(9) Note that this second mechanism could also be likely if the coupling between the 1D sets of interactions through the Sb p-orbitals was slightly underestimated in our calculations. In that case, the warping near Γ would increase (see the avoided crossing between two bands, one Ti-based and the other Sb-based, not far from Γ along the Γ → M direction and near the Fermi level) so that the nesting associated with the q and q' vectors will deteriorate and the hidden nesting mechanism will become less likely.