

LETTER TO THE EDITOR

Phase Transition and Spin-gap Behavior in a Layered Tetragonal Pnictide Oxide

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Spin-gap behavior has been observed for the first time in the layered tetragonal compound $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$. $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ shows a sharp discontinuity in magnetic susceptibility at 150 K, reminiscent of behavior observed in the spin–Peierls compound CuGeO_3 . $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ also shows a discontinuity in temperature-dependent resistivity at the magnetic transition and metallic behavior for all other temperatures, $5.7 \text{ m}\Omega \cdot \text{cm}$ at room temperature. Ti–Sb–Ti superexchange is proposed to be favored over Ti–O–Ti superexchange, based on the high-temperature magnetic susceptibility data and on the identity of the magnetic orbitals. © 1997 Academic Press

The realization of unusual magnetic ground states in spin-half systems, which remain disordered even at $T = 0$ due to quantum fluctuations, has been the subject of much research and excitement recently. These systems have a gap in the spin excitation spectra, and the low temperature magnetic susceptibility has an activated form. Such behavior can develop gradually as the temperature is lowered, as observed in “spin-ladder” materials (1) and in the quasi-2D material CaV_4O_9 (2). Such behavior can also arise through a finite-temperature phase transition, where the gap opens in the magnetic excitation spectra below the transition temperature. This behavior has so far been observed only in quasi-1D spin–Peierls materials (such as CuGeO_3 (3) and NaV_2O_5 (4, 5)). We report the first observation of a finite-temperature phase transition in the quasi-2D tetragonal material $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$, where the susceptibility drops precipitously below the transition and shows activated behavior at low temperatures. We discuss the unusual geometry of these new materials and offer qualitative arguments on the nature of superexchanges in them.

The $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$ ($\text{Pn} = \text{As}, \text{Sb}$) compounds belong to a small class of compounds known as pnictide oxides (6–11). The Ti-containing compounds attracted our interest since the formal oxidation state of Ti is +3, giving rise to a d^1 electronic configuration. The single crystal structure for $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ has been reported; it crystallizes in space group $I4/mmm$ (6). Samples were prepared by reacting stoichiometric amounts of Na_2O , Ti, and Sb powder in a sealed Ta tube, sealed under vacuum in a fused silica ampoule at 1000°C . The product is a gray-black powder that is air and water sensitive. All samples were handled in a nitrogen-filled drybox. The experimental X-ray powder diffraction profile of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ could be indexed and the lattice parameters, $a = 4.148(1) \text{ \AA}$ and $c = 16.594(1) \text{ \AA}$ (12), are in good agreement with those in the literature (6).

The structure of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ is shown in Fig. 1 (6). In brief, the structure is made up of $(\text{Ti}_2\text{O})_n^{4n+}$ planes that are “anti” to the CuO_2 layers in the superconducting cuprates. The Ti–O distances are $2.074(1) \text{ \AA}$ (Sb). The Ti–O–Ti angle is constrained by symmetry to be 180° . Two parallel sets of Ti–O–Ti chains can be discerned in each layer, and they intersect at each square planar oxygen atom. This could lead to Ti–O–Ti superexchange along each chain. Coupling between Ti atoms on perpendicular chains could be expected to be weak compared to the interactions along the chain, since any possible dp – pp – dp interaction would be destroyed. Each Ti atom also possesses four nearest neighbors at a distance of $2.933(1) \text{ \AA}$. The Ti \cdots Ti distances in the $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ compound are significantly longer than those in the Ti–Ti “dimer” of Ti_2O_3 (13, 14), indicating that direct Ti \cdots Ti interactions will be weak at best.

The $(\text{Ti}_2\text{Sb}_2\text{O})_n^{2n-}$ layers are formed by the addition of Sb^{3-} anions above and below each square of Ti atoms in

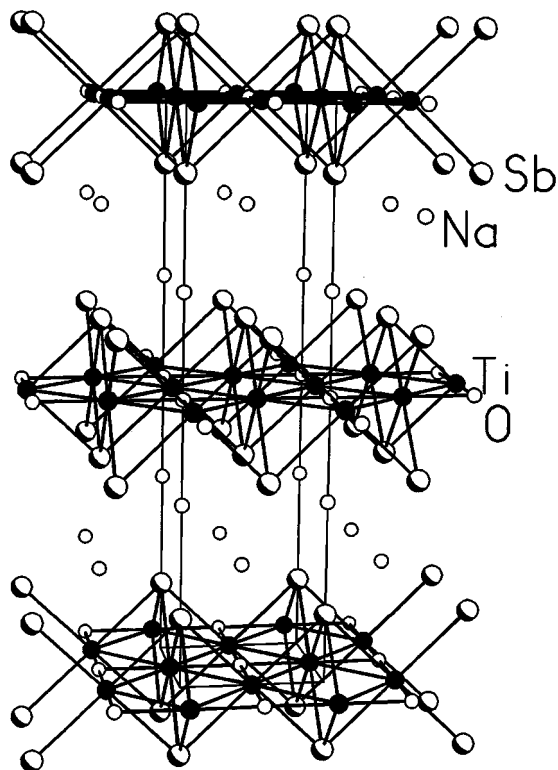


FIG. 1. The unit cell of $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$, viewed along (100).

the $(\text{Ti}_2\text{O})_n^{4n+}$ planes. Each pair of opposing Ti atoms is linked by two Sb atoms, 91.8° , resulting in the formation of $(\text{TiSb}_2)_n^{3n-}$ ribbons. If each ribbon is considered separately, this is the same geometry as is observed in the $(\text{CuO}_2)_n^{2n-}$ chains of CuGeO_3 (15). Thus, in these materials, Ti–Sb–Ti superexchange provides an alternative way to realize two independent sets of spin- $\frac{1}{2}$ chains. Another possible exchange pathway is through Sb which gives rise to the angle, 61° (Sb). To complete the structure, the $(\text{Ti}_2\text{Sb}_2\text{O})_n^{2n-}$ layers of this compound are separated by double layers of Na^+ cations, balancing charge.

Temperature-dependent magnetic susceptibility measurements were made on a Quantum Design SQUID magnetometer over the temperature range 5 to 300 K. Applied fields of 1000, 10,000, and 50,000 Oe were used. The temperature-dependent magnetic susceptibility data obtained for $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ are shown in Fig. 2. The molar susceptibility data are displayed as the open circles. Below 50 K, some weak Curie tailing is observed. It was accounted for by fitting the data from 5 to 80 K to $\chi = \chi_0 + C/T$, where $\chi_0 = 1.75 \times 10^{-4}$ emu/mol and $C = 6.43 \times 10^{-4}$. The μ_{eff} value calculated for this low temperature data is 0.0374 (1) μ_B . If all of the Ti atoms obeyed the Curie law, a spin-only moment of $2.447 \mu_B$ would be expected. Thus, whatever Curie behavior is present, intrinsic or not, accounts for only

1.5% of the Ti atoms in the sample. The value of χ_0 calculated from the Curie fit, 1.75×10^{-4} emu, is comparable in magnitude to the background assigned as the van Vleck contribution to the magnetic susceptibility in NaTiO_2 (16). A curve was calculated from these parameters and subtracted from the data, resulting in the open squares in Fig. 2. Examination of the susceptibility data reveals the presence of a sharp transition at $T_c = 114$ K, reminiscent of observations in the spin–Peierls compounds CuGeO_3 and NaV_2O_5 .

The solid line in Fig. 2 is a theoretical curve with a BCS-like gap expected from mean-field treatments (17) of the spin–Peierls problem: $\chi = (1/T)\exp[-\Delta(T)/T]$, where $\Delta(T) = \Delta_0[1 - (T/T_c)]^{1/2}$, with Δ_0 = gap energy = 400 K and $T_c = 114$ K. The value of Δ_0 represents the energy difference between the dimerized and undimerized states. Values of Δ_0 in spin–Peierls materials are commonly two to three times the T_c values (4, 5, 17) and this also is the case for $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$.

Above the transition, the susceptibility values drop gradually with temperature up to $T = 300$ K. The temperature dependence of the susceptibility does not agree with that of a nearest-neighbor Heisenberg chain-type interaction (18). This behavior is more like that observed in copper germanate. These results point toward Ti–Sb–Ti superexchange as the dominant mechanism. On the other hand, if Ti–O–Ti superexchange were the dominant mechanism, one would expect a closer agreement with the nearest-neighbor Heisenberg model (18). In a simple crystal field argument, placing the z axis along the O–Ti–O bond, the orbital where the d^1 electron is expected to reside is the d_{xy} . This suggests that Ti–Pn–Ti, rather than the Ti–O–Ti superexchange, is the most important.

The variable temperature electrical resistivity for $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ is shown in Fig. 3. The resistivity data were collected on a cold-pressed pellet from 300 to 15 K. A four-probe in-line method was used with an applied current 1.0 mA. The data correlate well with the magnetic susceptibility measurements. With decreasing temperature, the resistivity values fall from the room temperature value of $5.7 \text{ m}\Omega \cdot \text{cm}$. Between 120 and 100 K, the resistivity increases sharply, consistent with the opening of a gap and the concomitant localization of electrons. However, below the transition, the resistivity drops, reminiscent of metallic behavior. This temperature dependence of the resistivity is unlike a conventional spin–gap transition, where insulating behavior is expected below the transition. This suggests that there are changes in bonding that may contribute to a structural phase transition. This is the case for NaTiO_2 which shows a change from rhombohedral to monoclinic at the magnetic transition temperature of approximately 250 K (19). This behavior is most similar to that observed in charge or spin density wave materials. Temperature-dependent neutron diffraction experiments are under way to help elucidate the origin of the spin–gap behavior.

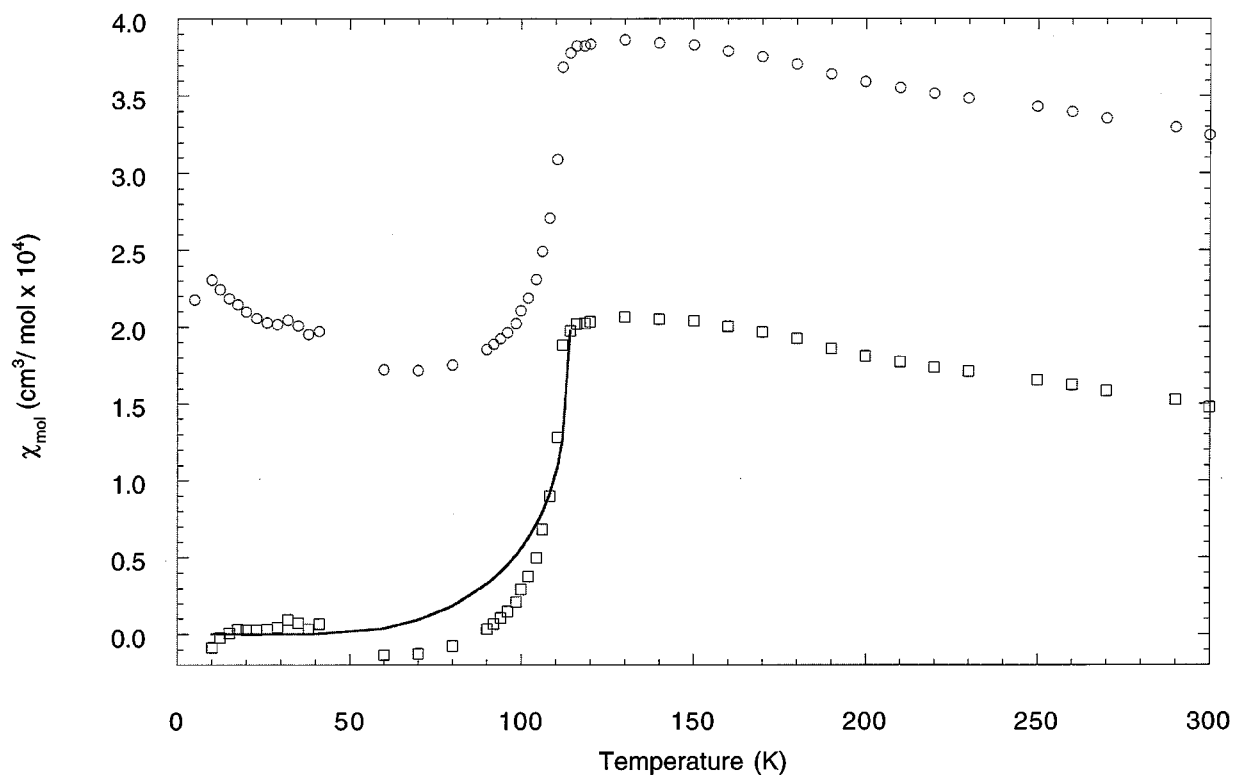


FIG. 2. The temperature-dependent molar magnetic susceptibility of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ at 1 T (open circles). The open square data points were generated by subtraction of the van Vleck and Curie contributions. The solid line represents activated behavior with a BCS-like gap.

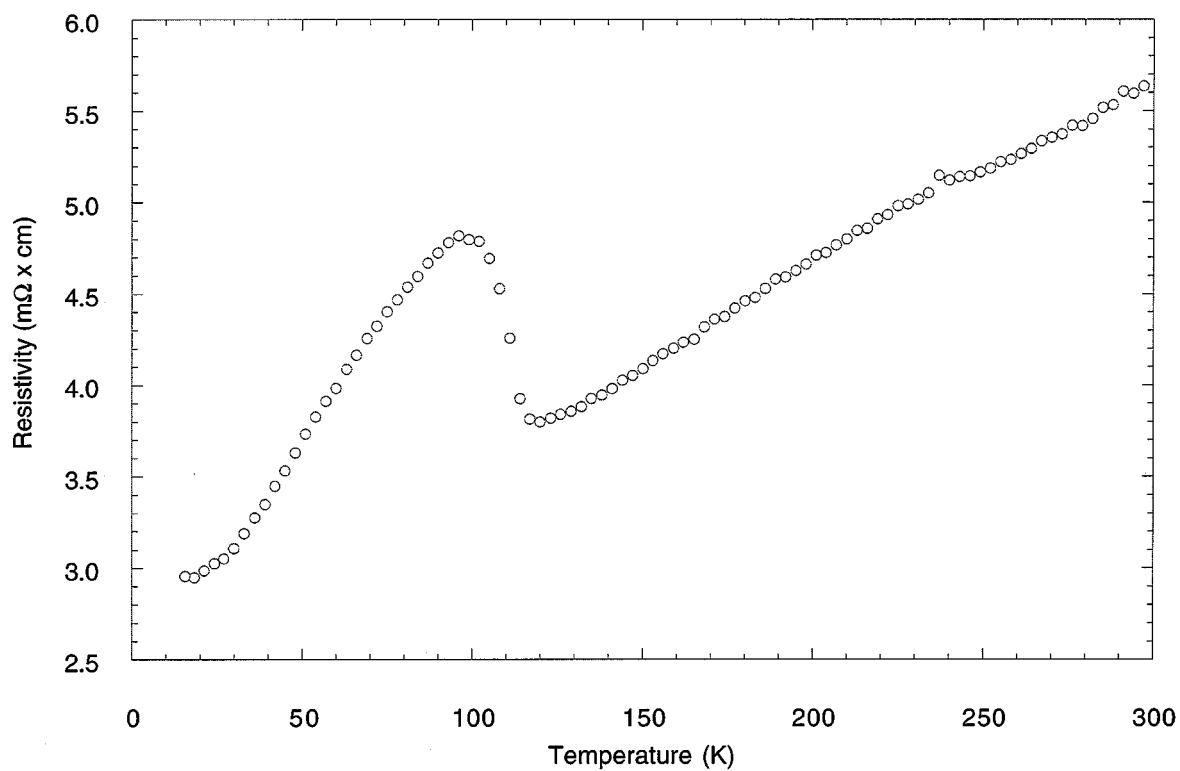


FIG. 3. Temperature-dependent resistivity of a cold-pressed pellet of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$.

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