Crystal Chemistry and Electronic Structure of the
Metallic Ternary Nitride, SrTiN$_2$

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The crystal chemistry and electronic structure of the layered nitride SrTiN$_2$ have been studied by powder neutron diffraction (PND) and density functional methods, respectively. PND investigations at room temperature, 80 K, and 2 K show that the tetragonal KCoO$_2$ structure (space group P4/nmm (No. 129), a = 3.8823(1) Å, c = 7.7008(1) Å, V = 116.068(1) Å$^3$, Z = 2 at 298 K) is retained across the temperature range and confirm the structural model from previous room-temperature powder X-ray diffraction (PXD) studies. Furthermore, and importantly, PND data demonstrate that neither nitrogen nonstoichiometry nor substitution of O$^2$- for N$^{3-}$ within the anion sublattice is a plausible mechanism for hole generation. Density functional calculations show that strong covalent bonding occurs within the TiN$_2$ layers and that Sr–N interactions are pivotal in determining the band structure at the Fermi level. Calculations predict metallic and paramagnetic behavior for SrTiN$_2$. These findings are confirmed by experimental measurements.

Introduction

The solid state chemistry of nitrides has been developed significantly over the past few years. Among these compounds, ternary transition metal nitrides receive increasing attention because of their structural and physical properties.$^1$ In some of these structures, transition metal ions display unusual coordination to nitrogen that is rarely found elsewhere. Examples are the families of ternary phases $\text{A}_3\text{M}_5\text{N}_3$,$^4$–$^9$ ($\text{A}$ = alkaline earth; $\text{M}$ = Fe, Ga, Mn). Both contain $\text{M}_3\text{N}_5$ planar triangular units separated by alkaline earth cations. In addition to some unique structures, nitrides also adopt structural types seen in oxide and carbide chemistry. For instance, $\text{CaNiN}$ has the $\text{YCoC}$ structure containing chains of linear $\text{Ni}–\text{N}$ units$^{13}$ whereas $\text{Ba}_2\text{VN}_3$ crystallizes in the $\text{Rb}_2\text{TiO}_3$ structure containing chains of corner-sharing $[\text{VN}_3]^4$ tetrahedra.$^{14}$

Materials of stoichiometry $\text{ABX}_2$ are well-known in oxides and chalcogenides. The two-dimensional structural nature of many of these materials is intrinsic to their properties (e.g., batteries, electronic materials). Nitride examples, $\text{ABN}_2$, embrace both $\text{s}$-block metal–transition metal and mixed transition metal systems. In many cases, the observed structure types are also those found in chalcogenide chemistry. Most commonly, these nitrides are layered-type compounds and contain six-coordinate metals in either octahedral or trigonal prismatic geometry. The first metallic layered nitride discovered, $\text{LiMnO}_2$, adopts the $\text{P3}$ (Na$_0$CoO$_2$) structure.$^{15}$ It consists of a series of Mo$_2$N$_2$ layers along the $c$ direction between which are hexagonal layers of Li$^+$ cations. The coordination environment of the Mo atoms in the Mo$_2$N$_2$ layers is octahedral. A trigonal prismatic coordination of the alkaline metal atoms is adopted. Another structure type observed in $\text{AMN}_2$ nitrides is the $\alpha$-$\text{NaFeO}_2$ structure. This differs from the $\text{P3}$ structure type materials in the octahedral coordination of the A cations. $\text{CaNb}_2$ and $\text{CaTaN}_2$, two compounds that have been reported to exhibit a superconducting transition at $\approx$ 14 K and $\approx$ 8.2 K, respectively,$^{16}$–$^{18}$ adopt this

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structure as well as the strontium ternary nitrides SrMN$_2$ (M = Zr, Hf).$^{19}$ With the usual oxidation states of 3$-$ and 2$+$ for N and Sr, respectively, the formal d-electron count for the Zr and Hf in these latter compounds is d$^6$. The same electron count is obtained for the transition metal atoms in SrTiN$_2$, BaM$_2$N$_2$ (M = Zr, Hf), and BaZr$_1$-$x$Hf$_x$N$_2$,$^{1,2,22}$ compounds which are isotypic with KCoO$_2$. By contrast to the hexagonal-structured materials above, the transition metal atom is coordinated to five nitrogen atoms in a distorted square-based pyramidal geometry, forming layers of edge-sharing pyramids which stack along the c direction. The alkaline-earth atom A is situated between the group 4 atom–N layers and is also coordinated to five nitrogen atoms. The isoelectronic AMN$_2$ (A = Sr, Ba; M = Ti, Zr, Hf) compounds, irrespective of the crystallographic structures they adopt, exhibit magnetic properties which are not consistent with diamagnetic d$^0$ M species.$^{21-23}$ Whereas this may be rationalized in terms of binary impurities in M = Zr, Hf samples, the case of SrTiN$_2$ is seemingly less easily rationalized.

Here we report the structural elucidation of SrTiN$_2$ by variable temperature powder neutron diffraction. Using this technique we were able to identify potential mechanisms of hole doping, including nitride nonstoichiometry or partial substitution of isoelectronic O$^2$$^-$ in the anion sublattice. Electronic structure calculations were carried out to complement these experiments and to rationalize both the observed properties and the modes of bonding in these AMN$_2$ compounds.

**Experimental Section**

**Synthesis of Starting Materials.** The starting material Sr$_2$N was prepared by reaction of the molten alkaline earth metal–sodium alloy with dry nitrogen at 520 °C. The alloy was made by adding clean Sr metal to molten sodium in a stainless steel crucible at 250 °C in an argon-filled glovebox followed by reaction with nitrogen at 520 °C. Excess sodium was removed by heating under vacuum at 400 °C for 24 h. Full details of the preparation are given in ref 20. The reaction yielded crystalline samples of purple-black Sr$_2$N. The identity of Sr$_2$N was confirmed by powder X-ray diffraction (PXRD).

**Synthesis of SrTiN$_2$.** SrTiN$_2$ was prepared by the high-temperature solid-state reaction of Sr$_2$N and titanium nitride, TiN. Insonation was carried out at 1030 °C following the procedure in ref 20 with the exception that a 5 wt % excess of Sr$_2$N was added to minimize the likelihood of residual TiN in the ternary product. The resulting powder of SrTiN$_2$ was black and was analyzed by PXD using a Philips Xpert $\theta$-2$\theta$ diffractometer with Cu Ka radiation. PXD samples were prepared in a nitrogen-filled glovebox and data were collected using custom-designed sample holders. Powder data were compared to calculated patterns from previously Rietveld refined samples using POWDERCELL 2.3.$^{24}$ Cell parameters were refined by least-squares fitting. Samples were confirmed as major phase SrTiN$_2$ and contained minor phases of Sr and SrO as expected from the starting ratios and as observed previously. No TiN or other phases were detected within the limits of the instrument.

**Structure Refinement by Powder Neutron Diffraction (PND).** Time-of-flight (TOF) powder neutron diffraction (PND) data were collected for SrTiN$_2$ powder using a 2.2 g sample under using the high-intensity diffractometer POLARIS at the ISIS spallation source, Rutherford Appleton Laboratory. Diffraction data were collected using the He tube detector banks at 35° and 145° and the ZnS scintillator detector bank at 90°. Data were collected at 298 K, 80 K, and 2 K for a sample contained in an electron-beam-welded, 6-mm-diameter vanadium can with indium gasket. The nitride was pre-loaded and the can was sealed in a nitrogen-filled glovebox.

Rietveld refinements were performed using the general structure analysis system (GSAS) through the EXPGUI interface.$^{25,26}$ Our starting model was taken as the previously published PXD structure of SrTiN$_2$ in tetragonal space group P4/nmm (No. 129) using cell parameters refined by least-squares fitting of indexed PXD data ($a = 3.880(2)$ Å, $c = 7.705(3)$ Å).$^{20}$ Peak shape was modeled using TOF profile function 3 (a convolution of back-to-back exponentials with a pseudo-Voigt function). Background was handled with function 6 (modeling high and low Q contributions) with up to 7 refined coefficients for each bank. Initially, data from the backscattering detector bank were refined in isolation until a stable refinement and reliable model were achieved. Strontium oxide (SrO) and strontium metal ($\alpha$ and $\beta$ phases) were simultaneously refined as impurity phases (final phase fractions: SrTiN$_2$ 70 wt %, SrO 6 wt %, $\beta$-Sr 19 wt %, $\alpha$-Sr 5 wt %). With PXD data, no titanium-containing phases were observed as impurities in the profiles. Final cycles included profile and background parameters, strain broadening parameters, scale factor and phase fractions, cell parameters, atomic positions, and anisotropic temperature factors. Weak reflections in the low-temperature data, corresponding to the cryostat, were excluded from the refinement.

Considering the observed properties of AMN$_2$ compounds we considered various mechanisms for hole generation within SrTiN$_2$ over the course of the refinement. Initially we evaluated nitrogen nonstoichiometry as a means to achieve this by varying both independently and collectively the occupancy of the Sr (N1) and N (N2) sites. At 80 and 2 K, the occupancies of both N sites remained at unity, however they were varied. At 298 K, both occupancies refined to values very slightly below unity (0.99(1)), but these were not considered to be statistically significant and in final cycles were fixed at full occupancy without affecting the quality of fit. Considering replacement of nominal N$^-$ by O$^-$ as an alternative route to hole-doping led to N occupancies above unity and negative occupancies of oxygen at all temperatures. We observed this result whether O was introduced to either or both of the N sites. Our final model is thus one commensurate with the fully stoichiometric nitride, SrTiN$_2$, irrespective of data collection temperature.

**Computational Procedure.** Self-consistent ab initio band structure calculations were performed on SrTiN$_2$ with the scalar relativistic tight-binding linear muffin-tin orbital (LMTO) method in the atomic spheres approximation including the combined correction.$^{27}$ Exchange and correlation were treated using the Perdew-Wang 1991 (PW91) functional.$^{28}$ Double-zeta valence basis sets were employed. The all-electron pseudopotential of a Sr atom was included in the valence basis set. We used the FMK v2001 code.$^{29}$

in the local density approximation using the von Barth–Hedin local exchange correlation potential.28 Within the LMTO formalism interatomic spaces are filled with interstitial spheres. The optimal positions and radii of these additional “empty spheres” (ESs) were determined by the procedure described in ref 29. Three nonsymmetry-related ESs with 0.55 Å ≤ ReS ≤ 0.65 Å were introduced for the calculations on SrTiN2. The full LMTO basis set consisted of 5s, 5p, 4d, and 4f functions for Sr spheres, 4s, 4p, and 3d for Ti spheres, 2s, 2p, and 3d functions for N spheres, and s and p functions for ES. The eigenvalue problem was solved using the tetrahedron method.30 Charge self-consistency and the average formalism interatomic spaces are filled with interstitial spheres. The full LMTO basis set consisted of 5s, 5p, 4d, and 4f functions for Sr spheres, 4s, 4p, and 3d for Ti spheres, 2s, 2p, and 3d functions for N spheres, and s and p functions for ES. The eigenvalue problem was solved using the following minimal basis set obtained from the Lo¨wdin downfolding technique: Sr 5s, 4d; Ti 4s, 4p, 3d; N 2s, 2p and interstitial 1s. The k space integration was performed using the tetrahedron method.30 Charge self-consistency and the average properties were obtained from 84 irreducible k points. A measure of the magnitude of the bonding was obtained by computing the crystal orbital Hamiltonian populations (COHPs) which are the Hamitonian population weighted density of states (DOSs).31 As recommended,32 a reduced basis set (in which all ES LMTOs have been downfolded) was used for the COHP calculations. Bands, DOS, and COHP curves are shifted so that Fa lies at 0 eV.

**Magnetic and Conductivity Measurements.** Variable-temperature magnetic measurements were performed on powder samples (ca. 0.3 g) of SrTiN2 using a Quantum Design MPMS-XL 5 SQUID magnetometer. Samples were loaded in a nitrogen-filled glovebox. Data were collected between 4 and 300 K, under a field of 1 × 104 Oe. Measurements were taken at 1-K intervals between 4 and 30 K and 5-K intervals between 30 and 300 K with sufficient pauses built in to allow for thermal equilibrium. Data were corrected for core diamagnetism33 and the diamagnetic contribution of the sample holders (gelatine capsules).

Conductivity measurements were performed in a nitrogen-filled glovebox on compressed pellets of SrTiN2 samples (typical dimensions: thickness ca. 2.5 mm and diameter ca. 8 mm, measured by micrometer) using a simple four-point approach. Sintering these pellets under nitrogen was problematic and not especially satisfactory in accordance with many other materials of this type. Pellets gave resistance readings of approximately 100 Ω and corresponding conductivity, σ = 4 × 10⁻¹ Ω⁻¹ cm⁻¹ at 293 K.34

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**Table 1. Crystallographic Data for SrTiN2**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Sr (2c) (1/4b, 1/4z)</th>
<th>Ti (2c) (1/4b, 1/4z)</th>
<th>N (1b) (1/4, 1/4, 1/2)</th>
<th>N1 (2b) (3/4, 1/4, 1/2)</th>
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<td>298</td>
<td>0.83691(16)</td>
<td>0.83689(9)</td>
<td>0.83682(9)</td>
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<tr>
<td>100 × U11 = Uα2</td>
<td>0.608(2)</td>
<td>0.24(2)</td>
<td>0.23(2)</td>
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</tr>
<tr>
<td>100 × U33 = Aβ2</td>
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<td>0.25(3)</td>
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<tr>
<td>100 × U11 = Uα2</td>
<td>0.41(1)</td>
<td>0.30(2)</td>
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<tr>
<td>100 × U33 = Aβ2</td>
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<tr>
<td>100 × U11 = Uα2</td>
<td>0.43(1)</td>
<td>0.27(1)</td>
<td>0.26(1)</td>
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<tr>
<td>100 × U33 = Aβ2</td>
<td>1.24(1)</td>
<td>0.72(2)</td>
<td>0.70(2)</td>
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</table>

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**Table 2. Final Atomic Parameters for SrTiN2**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Sr (2c) (1/4b, 1/4z)</th>
<th>Ti (2c) (1/4b, 1/4z)</th>
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<td>0.34(4)</td>
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<td>1.24(1)</td>
<td>0.72(2)</td>
<td>0.70(2)</td>
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**Results and Discussion**

**Crystal structure.** Crystallographic parameters for the PND refinements are shown in Table 1. Final atomic parameters from the structure refinements are described in Table 2. Representative observed, calculated, and difference profile plots for the refinements are shown in Figure 1. The refined structure of SrTiN2 at room temperature (298 K) is very similar to that obtained from powder X-ray data.20 The structure is described in detail in the earlier reference. Following a nominally ionic model, this essentially consists of [TiN2]²⁻ planes of edge-linked TiN5 square-based pyramids with Sr2⁺ cations situated between the pyramid apexes. Ti–N pyramids point alternately up and down relative to the c-axis (Figure 2). This structure is retained at lower temperatures with an approximately linear decrease in lattice parameters and cell volume with temperature. Whereas the strontium (2c) position remains effectively unaltered with temperature and the N(1) (2b) position is fixed by symmetry, both the Ti (2c) and N(2) (2c) positions change significantly outside standard deviations between 298 and 2 K. The thermal parameters of the metals approach an isotropic environment at lower temperature whereas N1 and N2 thermal profiles remain elongated and compressed, respectively, along the c direction. Importantly, the neutron data establish that the nitride undergoes no structural phase transition between 298 and 2 K, has the stoichiometric composition SrTiN2, and displays no reflections at low-temperature representative of magnetic ordering. In
light of these results and magnetic measurements performed on these samples (see below), it would appear that the unusual drop in susceptibility seen in some previous samples at ca. 40 K (but not in samples measured here) is not, therefore, an intrinsic property of the (stoichiometric) ternary nitride.23

Table 3. Interatomic Distances and Angles in SrTiN$_2$ at Different Temperatures (K)

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</thead>
<tbody>
<tr>
<td>298</td>
<td>3.2403(4) × 4</td>
<td>2.6109(4) × 1, 2.7470(1) × 4</td>
<td>2.0522(4) × 4</td>
<td>1.8274(9) × 1</td>
<td>3.8823(1) × 4, 3.7209(6) × 4</td>
<td>50.125 (6) × 4, 73.61(1) × 2</td>
<td>113.23(2) × 8, 63.11(1) × 8, 143.197(5) × 4</td>
<td>92.07(2) × 4, 89.925(1) × 4</td>
<td>83.92(1) × 4, 142.02 (4) × 2</td>
<td>108.99(2) × 4</td>
</tr>
<tr>
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<td>1.8261(14) × 1</td>
<td>3.8784(1) × 4, 3.7175(10) × 4</td>
<td>50.127 (9) × 4, 73.60(2) × 2</td>
<td>113.33(4) × 8, 63.21(2) × 8, 143.195(8) × 4</td>
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<td>83.85(2) × 4, 141.79(7) × 2</td>
<td>109.10 (3) × 4</td>
</tr>
<tr>
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<td>2.6012(6) × 1, 2.7424(1) × 4</td>
<td>2.0515(4) × 4</td>
<td>1.8254(13) × 1</td>
<td>3.8762(1) × 4, 3.7161(9) × 4</td>
<td>50.132 (9) × 4, 73.62(2) × 2</td>
<td>113.37(3) × 8, 63.24(2) × 8, 143.191(7) × 4</td>
<td>91.92(3) × 4, 89.936 (2) × 4</td>
<td>83.83(2) × 4, 141.72 (6)</td>
<td>109.14(3) × 4</td>
</tr>
</tbody>
</table>

Figure 1. Observed, calculated, and difference (OCD) profile plot for the Rietveld refinement of powder neutron diffraction data for SrTiN$_2$ at (a) 298 K, (b) 80 K, and (c) 2 K. Crosses represent observed data, the solid line is the calculated profile, and tick marks are the positions of main and impurity phase reflections. The refined phases are SrTiN$_2$ (bottom) through SrO and $\beta$-Sr to $\alpha$-Sr (top). The difference profile is plotted below. Data represented are from detectors at 2θ = 90°.

Figure 2. Perspective representation of the structure of SrTiN$_2$.  

Table 3. Interatomic Distances and Angles in SrTiN$_2$ at Different Temperatures (K)
ues are typical for group 2 and transition metals in ternary nitrides. Again, this serves to emphasize the $\pi$ contribution to the Ti–N bond (Ti appearing “over-bonded”) as we depart from an ionic model. Calculations also generate a low valence for Sr (appearing “under-bonded”) that is comparable to values seen in binary and ternary nitrides alike.\textsuperscript{36} Note that the valence sum for Sr is less than 2 even including the four longer Sr–N(1) interactions within its coordination sphere. The other distance of note is the Ti–Ti interaction of ca. 3.05 Å that is invariant with temperature. Although much smaller than equivalent distances in other ternary titanium nitrides, this separation remains significantly larger than those observed in both Ti metal and metallic binary titanium nitrides.\textsuperscript{37–39} This has a profound effect on the electronic structure of SrTiN$_2$ as compared to Ti metal and Ti–N compounds as discussed below.

**Electronic Structure and Properties.** With the usual oxidation states of 3– and 2+ for N and Sr, respectively, TiN$_2$ layers present a –2 charge and the formal d-electron count for the Ti atoms is d$^0$. As an ionic interaction between the Sr cations and the Ti–N layers can be assumed, and the occurrence of any metal–metal interaction is unlikely given the refined Ti–Ti distances (3.053 Å vs 2.90 Å in $\alpha$-Ti metal),\textsuperscript{37} diamagnetic properties consistent with the d$^0$ electron count for the Ti atoms might be envisioned. As a first approach, first principle calculations were carried out without taking into account the spin polarization. The resulting total and projected DOS, and COHPs for several atomic contacts are depicted in Figures 4 and 5, respectively. Bands localized between ca. –4 and

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Coordination environment of (a) Sr and (b) Ti to N in SrTiN$_2$ at 298 K.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{(a) Total DOS of SrTiN$_2$. (b) N(1) (plain) and N(2) (dotted) projected DOS. (c) Sr (plain) and Ti (dotted) projected DOS.}
\end{figure}

\textsuperscript{(37)} Clark, H. J. Metals 1949, 1, 588.
\textsuperscript{(38)} Schmitz-Pranghe, N.; Dunner, P. Z. Metallik. 1968, 59, 377.
-2 eV are both centered on Ti and nitrogen atoms, whereas bands that lie in the vicinity of -11 eV present a major nitrogen character. These bands strongly contribute to the Ti–N bonds (Figure 5). Ti–N COHP curves suggest a stronger bond between the transition metal atom and the apical nitrogen atom of the TiN5 pyramid N(2) than with N(1). An integrated COHP (ICOHP) of -3.67 eV is computed for the Ti–N(2) bond. This suggests some π-bonding as foreseen by the Ti–N(2) separation. Compared to the Ti–N(2) ICOHP, the value of -1.50 eV for the Ti–N(1) contacts is rather weak, even for a σ-bond. In fact N(1) atoms are coordinated to four Ti atoms which form a plane that does not contain the N(1) atom. Leaving a nonbonding lone pair on N(1), three atomic orbitals occupied by three electrons must be taken into account to assume the four Ti–N(1) bonds. Therefore, these four contacts cannot be associated to four two-electron bonds, and a delocalized bonding scheme with the transition metal atoms around the N(1) atoms has to be considered. One important feature of the DOS curves is the significant contribution of the Sr atoms to the occupied bands. Such a contribution is unexpected in the case of an ionic interaction between the TiN2 layers and the alkaline earth metal. Sr–N(2) COHPs indicate that significant interactions occur between the alkaline-earth metal and the nearest neighbor atoms, N(2), that form a square-based pyramid. Given the sum of the covalent radii of Sr and N (2.67 Å) (40) and the separation of Sr and N(2) (2.611 Å), a consistent interaction can be foreseen between the apex of the N(2)5 pyramid and the central Sr atom. An ICOHP of -1.22 eV is computed for this contact. COHP between Sr and basal N(2) separated at 2.747 Å is also significant, especially in the range [-2, 0] eV. ICOHP for this contact is equal to -0.95 eV. Considering the π character of the Ti–N(2) bond, N(2) atoms formally present a sp2 hybridization. Rotation axes of the hybrid orbitals that describe the lone pair localized on the N(2) notably point toward a direction that is close to the Sr atoms. Therefore, a π-type interaction occurs as shown by the COHP calculations. Of the alkaline earth metal orbitals, the dxy is that mainly involved in this interaction. As shown by the band structure of SrTiN2 (Figure 6), some of the occupied bands that lie just below the Fermi level present an important Sr dxy character. These bands derive also mainly from the orbitals that describe the lone pairs on the N(2) atoms and the one localized on

\[(40)\text{Emsley, J. The Elements; Oxford University Press: New York, 1989.}\]
Figure 8. Plot of magnetic susceptibility of SrTiN$_2$ as a function of temperature.

N(1). This latter pair is oriented along the c axis, perpendicular to the TiN$_2$ layers. The Ti–Ti distances suggest reduced metal–metal interaction within the nts compared to Ti metal (3.053 Å vs ca. 2.90 Å and 2.87 Å in α-Ti and β-Ti, respectively). 37,38 COHP calculations and an ICCHP value close to zero indicate that negligible Ti–Ti bonding occurs.

It the I→Z direction of the Brillouin zone, flat bands lie in the vicinity of the Fermi level. Only two of the four bands approach full occupation. Such a band structure suggests that a high spin configuration should be more stable. A more stable electronic structure by –0.15 eV is computed for a SrTiN$_2$ unit cell within the spin-polarized formalism. Figure 7 shows the band plots for the α and β spins. The major consequence of the spin-polarization occurs in the I→Z direction. In other directions of the Brillouin zone, few modifications are noteworthy and analyses of the spin-polarized DOS and COHP curves reveal no significant differences with the previous calculations (without spin-polarization). For example, the sum of the α and β ICCHP for Ti–N(1), Ti–N(2), and the two Sr–N(2) contacts are equal to those computed without spin polarization. Thus, remarks and conclusions on the bonding mode in this compound remain unchanged. Spin-polarization is stronger on N(1) and weaker on N(2), Ti, and Sr (0.73 e$^-$, 0.31 e$^-$, 0.22 e$^-$, and 0.07 e$^-$ in the atomic sphere, respectively). This is in agreement with the nature of the bands that are the more disturbed in the I→Z direction, i.e. that describe the lone pairs localized on N(1) and N(2).

The calculated electronic structure of the ternary nitride thus predicts that SrTiN$_2$ should be a three-dimensional metal. A similar strong interaction between Sr and N atoms in the nitride Sr$_2$NiN$_2$ is at the origin of the metallic behavior of this compound. 41 As in SrTiN$_2$, the strontium ion in this compound also lies within a square pyramid of nitrogens. One can note that the three-dimensional properties foreseen for the title compound and those measured for the layered nitride LiMoN$_2$ do not have the same origin. 42,43 In the latter compound these properties do not result from interlayer coupling through the Li ions but arise from the pronounced direct N–N bonding.

Theoretical calculations predict that SrTiN$_2$ should be nondiamagnetic. Magnetic measurements support this prediction, with variable temperature measurements on samples prepared with excess Sr$_2$N (to reduce possible Ti(N) impurities) showing predominantly temperature-independent susceptibility profiles. A plot of the susceptibility as a function of temperature is shown in Figure 8. The susceptibility is essentially temperature-independent between 100 and 300 K. An acceptable fit to the susceptibility was obtained by modeling the behavior as a mixture of Curie-like and temperature-independent contributions, $\chi_T = \chi_0 + C/T$. This yields a $C_0$ value of $1.08(2) \times 10^{-5}$ emu g$^{-1}$ K and $\chi_0 = 4.47(1) \times 10^{-6}$ emu g$^{-1}$. The susceptibility profile is typical of that seen for Pauli paramagnetic, metallic, ternary transition metal nitrides. The small value of $C_0$ would equate to a moment of 0.06 μ$_B$ per Ti. Equally this value might originate from low levels of paramagnetic impurity below detection limits. This contribution could derive from steel components (or their oxides) (e.g., from reaction vessels) or from transition metal impurity in the TiN starting material. The moment would correspond, for example, to 0.06% Fe$^{2+}$ (assuming S = 2). The magnitude and sign of $\chi_0$ compare favorably with 3D metallic ternary nitrides such as LiMoN$_2$ 15 and Na$_x$Ta$_3$N$_5$. 44 Unlike the layered ternary nitride CaTaN$_3$, 15 which is two-dimensional in nature, we see no evidence of a superconducting transition above 4 K. Given the nature of the samples, the measured conductivity values represent at best an upper limit estimate. Nevertheless, it is evident that given also the physical appearance and magnetic behavior of the material, SrTiN$_2$ can be


described as having the properties of a (semi-)metal, commensurate with its electronic band structure.

**Conclusion**

The ternary layered nitride SrTiN$_2$ has been synthesized and its structure was elucidated by variable-temperature time-of-flight powder neutron diffraction. Structural investigations demonstrate that the material retains the KCoO$_2$ structure across the temperature range studied (2–298 K), that the nitride is stoichiometric in nitrogen, and that there is no evidence of magnetic ordering at low temperature. First-principle calculations were carried out to study the electronic structure of SrTiN$_2$. Strong covalent interactions occur within the TiN$_2$ layers. A strong interaction between the alkaline-earth metal and nitrogen atoms of the nets has been observed and this interaction is at the origin of an unexpected three-dimensional metallic-like band structure for this compound. A strong spin-polarization for SrTiN$_2$ is computed and paramagnetic behavior should be therefore intrinsic to the material. Experimental measurements support the predicted electronic properties, revealing SrTiN$_2$ to be a stoichiometric, three-dimensional metallic nitride.

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