On the magnetism, thermal- and electrical transport of SrMoO₂N

D. Logvinovich,¹ J. Hejtmánek,² K. Knižek,² M. Maryško,² N. Homazava,³ P. Tomeš,²
R. Aguiar,⁴ S. G. Ebbinghaus,⁵ A. Reller,⁴ and A. Weidenkaff^{1,a)}

¹*Solid State Chemistry and Catalysis, EMPA, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland*

²*Institute of Physics, Academy Sciences of the Czech Republic, Cukrovarnická 10, CZ-15263, Prague 6, Czech Republic*

³*Analytical Chemistry, EMPA, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland*

⁴*Solid State Chemistry, University of Augsburg, D-80159 Augsburg, Germany*

⁵*Solid State Chemistry, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothers Strasse 2, D-06120 Halle (Saale), Germany*

(Received 25 July 2008; accepted 4 December 2008; published online 29 January 2009)

Physical properties of perovskite-type SrMoO₂N phases were studied in the temperature range of 3 K < *T* < 300 K. The oxynitride crystallizes in a cubic unit cell (space group *Pm3m*) as revealed by neutron and x-ray diffraction measurements. The polycrystalline material shows weakly temperature dependent electrical resistivity and low glasslike heat conductivity, both reflecting the unusual strength of the scattering processes in the charge carrier transport. Based on the positive Seebeck coefficient values, holes are identified as the dominating charge carriers in SrMoO₂N. Down to 150 K, the magnetic susceptibility is temperature independent and explained as enhanced Pauli paramagnetism ($\chi \sim 10^{-4}$ emu mol⁻¹ Oe⁻¹). The absolute value of its magnetic susceptibility is, however, half of that for SrMoO₃. Simultaneously, the lower Sommerfeld coefficient γ measured for the oxynitride confirms the lower density of states near the Fermi level for SrMoO₂N compared to SrMoO₃. At low temperature, both SrMoO₂N and SrMoO₃ show Curie paramagnetism superimposed to the temperature independent Pauli paramagnetism and an anomaly at *T* = 54 K. This anomaly is attributed to the presence of molecular oxygen in the material, while the Curie upturn is likely associated with a small amount of paramagnetic centers. © 2009 American Institute of Physics. [DOI: 10.1063/1.3067755]

I. INTRODUCTION

Partial substitution of oxygen by nitrogen offers an alternative to cationic substitution for altering physical properties of perovskites, ABO₃. Thus, substitution of oxygen by nitrogen in perovskite-type oxides with *d*⁰ configuration of the transition metal leads to an optical band gap reduction. The actual band gap value can be effectively tuned by varying the nitrogen content with cross substitution.¹ This makes perovskite-type oxynitrides (also be named nitride oxides) with the general formula ABO_{3-x}N_x, A = AE, RE, and B = Ti⁴⁺, Ta⁵⁺, Nb⁵⁺ prospective for optical^{2,3} and photocatalytic^{4,5} applications.

Since N³⁻ ions have a lower oxidation state than O²⁻ ions, partial substitution of oxygen with nitrogen in conducting oxide perovskites (with *d*^{*n*} configuration of the transition element) can be used to change the charge carrier concentration and consequently the electronic and magnetic properties of these materials.^{3,6,7}

Cubic perovskite SrMoO₃ (*d*²) exhibits high charge carrier density and optical transparency in the ultraviolet region.^{8,9} Therefore, this transparent oxide is a potential candidate for diverse applications, including solar cells.^{8,9} Partial substitution of oxygen in SrMoO₃ with nitrogen allows to generate mixed oxidation states of molybdenum and to explore new electronic and magnetic properties of the compounds.

Mixed-valent molybdenum oxynitride perovskites are a rather poorly investigated group of materials. Until now, SrMoO_{2.6}N_{0.4} and SrMoO_{2.5}N_{0.5} (*x* = 0.4, 0.5) are the only reported powder and thin-film compositions.^{10–12} The magnetic measurements reveal Pauli paramagnetism ($\chi \sim 10^{-4}$ emu mol⁻¹ Oe⁻¹) at room temperature and a magnetic transition at *T* ~ 54 K. This anomaly is referred to an antiferromagnetic transition¹⁰ or to a spin-glass formation.¹¹

Recently, we succeeded in preparing CaMoO_{1.7}N_{1.3}, BaMo(O,N)₃,¹³ and SrMoO_{3-x}N_x (*x* > 1)¹⁴ compounds. Electronic properties of SrMoO_{3-x}N_x (*x* > 1) have been measured at temperatures of 340 K < *T* < 950 K.¹⁴ These novel materials showed low electrical conductivity (25–80 S cm⁻¹) and a positive Seebeck coefficient (15–30 μV K⁻¹), a value being about one order of magnitude higher than the reported one for SrMoO₃.¹⁵ To understand the influence of anionic substitution on the charge carriers subsystem, we compare in this work low temperature physical properties of the Mo oxynitride with those of the similarly prepared SrMoO₃.

II. EXPERIMENTAL

A quantity of 0.04 mol MoO₃ (JMC, Specpure) was dissolved in a minimal amount of NH₃ (aqueous, 25%) and precipitated with 100 ml of an aqueous solution of 0.4M. Sr(NO₃)₂ (Merck, >99%). The precipitate was washed with

^{a)}Electronic mail: anke.weidenkaff@empa.ch.

FIG. 1. XRD patterns confirming the phase purity of (a) SrMoO_4 after annealing at 1073 K for 4 h. Space group: $I4_1/a$. The reflections are assigned according to the pdf entry 85–0809; (b) SrMoO_3 ($Pm\bar{3}m$, pdf entry 81–0640) obtained by the reduction of SrMoO_4 ; (c) SrMoO_2N ($Pm\bar{3}m$) obtained by thermal ammonolysis of SrMoO_4 .

distilled water, dried, and annealed at 1073 K for 4 h to form phase pure well crystalline SrMoO_4 powder as confirmed by x-ray diffraction (XRD) [Fig. 1(a)].

SrMoO_3 was prepared by reduction of 1 g of freshly synthesized SrMoO_4 at $T=1373$ K with forming gas (5% H_2 /95% N_2 , 99.999% purity, Pangas). Under the gas flow of 300 ml/min, the reduction was completed in 5 h.

The thermal ammonolysis of SrMoO_4 was performed in a rotating cavity reactor described elsewhere.¹ A quantity of 2.25 g of the SrMoO_4 powder was ammonolyzed at $T=1073$ K for 11 h under ammonia (PanGas, >99.98%) with a gas flow of 150 ml/min. The synthesis temperature was reached with a heating rate of 10 K/min. After the reaction, the furnace was cooled down to room temperature with a cooling rate of 10 K/min under flowing ammonia.

The electrical transport measurements were performed on bars with dimensions of 1.65 mm $\times$ 5–10 mm $\times$ 1 mm. The bars were obtained by applying a uniaxial pressure of 10 bar followed by a cold isostatic pressing at 2000 bar. The bars of the oxynitride material were sintered at $T=1073$ K for 30 min under flowing ammonia. The bars of SrMoO_3 were sintered at $T=1373$ K for 4 h under flowing forming gas. The measured density of the obtained ceramics was about 75% of the theoretical density.

Structure and phase purity of the obtained oxynitrides were studied by XRD using a Phillips X'Pert PRO MPD Θ - Θ system equipped with an X'Celerator linear detector. The O/N content of the different samples was measured by

the hotgas-extraction method using a LECO TC500 analyzer. Silicon nitride and silicon oxide were used as calibration standards for nitrogen and oxygen, respectively.

The neutron diffraction (ND) data were recorded at the high resolution powder diffractometer for thermal neutrons (HRPT) (Ref. 16) located at the Swiss Spallation Neutron Source (SINQ) of the Paul Scherrer Institut in Switzerland. The measurements were performed with a neutron wavelength $\lambda=1.494$ Å in the angular range of 10° – 150° with a step size of 0.05° . The background was fitted with a six-coefficients polynomial function. The peak shape was modeled using a Thompson–Cox–Hastings pseudo-Voigt profile function. Structure refinements were performed using FULLPROF.¹⁷

The microstructure of the samples has been studied with scanning electron microscopy (SEM) using a LEO JSM-6300 F electron microscope. The cationic compositions study was made by energy dispersive x-ray spectrometry (EDXS-Link Pentafet 5947, from Oxford Microanalysis group).

To check for possible magnetic impurities (Fe, Co, Ni) chemical analysis by inductively coupled plasma mass spectrometry was carried out. The measurements were performed with inductively coupled plasma quadrupole measurement system (ICP-QMS) ELAN 6000 instrument (Perkin Elmer/Sciex, Canada).

Low temperature physical properties measurements of SrMoO_3 and SrMoO_2N (see below) were performed in the temperature range $T=5$ –300 K using a Quantum Design physical property measurement system (PPMS). Magnetic susceptibility measurements were done by using a vibrating sample magnetometer (VSM) (Quantum Design PPMS) and a SQUID (superconducting quantum interference device) (Quantum Design magnetic property measurement system). The obtained values were corrected for diamagnetic contributions of the sample holder and the low temperature varnish, ionic core diamagnetism, and Van-Vleck paramagnetism.¹⁸ Field dependent isothermal magnetization measurements were performed at room and low temperatures.

III. RESULTS AND DISCUSSION

XRD measurements confirm phase purity of SrMoO_4 , SrMoO_3 and the oxynitride samples obtained after 11 h of ammonolysis at $T=1073$ K (Fig. 1). The cationic composition study reveals a Sr:Mo ratio of the oxide and oxynitride samples equal to 0.98(1):1.02(2). Thus, within the experimental error ($\sim 3\%$), the obtained ratio is identical with the nominal ratio 1:1. The lattice parameter, $a=3.9752(1)$ Å, refined from the XRD data of SrMoO_3 , is in perfect agreement with the previously reported value of 3.9751(3) Å.¹⁵ The O/N content measured for the oxynitride by hotgas extraction corresponds to the composition $\text{SrMoO}_{1.95(5)}\text{N}_{1.05(5)}$, i.e., within a 1σ -range integer values were found. The sample is therefore denoted as SrMoO_2N in the following. During the reaction of SrMoO_4 with ammonia, a significant microstructural reorganization occurs in the particles since the starting oxide and the oxynitride reveal different crystallographic structures and anionic compositions. Thus, the resulting ox-

FIG. 2. Microstructure of SrMoO_2N .

ynitride phases reveal a different particle size (larger surface area) compared to the starting compound. The physical properties of powder materials depend on the particle size, shape, and surface area, which have to be monitored carefully and taken into account for the interpretation of the measured data. Therefore, before performing physical and chemical properties measurements, the particle size of SrMoO_2N was determined. SEM investigations on SrMoO_2N reveal particles with an average diameter of $\sim 1 \mu\text{m}$ (Fig. 2), which are suitable for the bulk physical properties measurements.

Rietveld refinement of the SrMoO_2N powder neutron data was carried out in the space group $Pm\bar{3}m$. In the starting structural model, the Sr:Mo ratio was fixed to 1:1 (based on the cationic compositions study), and the O:N ratio was set to 2:1. Thermal displacement factors were refined isotropically for all atoms. In the next refinement steps, the occupancy factors for oxygen and nitrogen were refined with the anionic site constrained to be fully occupied. In succeeding runs, the occupancy factors of the anions were refined independently. Finally, the lattice and the profile parameters, $2\theta_0$, the background coefficients, the thermal displacement factors, and the anionic occupancies were refined together. Within the doubled standard deviation (2σ), no difference between the parameters obtained with the constrained and the unconstrained model were found. For this reason, in the final refinement, a complete occupation of the anionic sites was assumed and only the O/N ratio was refined. Refinements of the cationic occupancies gave no hints for the presence of the cationic vacancies. The statistics of the refinement and the visual inspection of the fit (Fig. 3) indicate that the model was chosen correctly. The refined O/N content corresponds to the composition $\text{SrMoO}_{1.89(2)}\text{N}_{1.11(2)}$, which is in a reasonable agreement with the result obtained by hotgas extraction.

Figure 4(a) shows the temperature dependence of resistivity measured for SrMoO_3 and SrMoO_2N . The resistivity of SrMoO_3 is significantly higher than the value reported in literature ($\sim 5 \mu\Omega \text{ cm}$) measured on the single crystal.¹⁹ This underlines that the limiting factor in the electrical transport is the grain-boundary scattering processes. However, despite of the approximately two orders higher resistivity, the synthesized polycrystalline SrMoO_3 ceramics show a metallic-like behavior of the electrical resistivity. Metallic-

FIG. 3. (Color online) Rietveld refinement plot of the ND data for SrMoO_2N . Space group: $Pm\bar{3}m$, $a=3.9835(1) \text{ \AA}$, $wR_p=0.0625$, $R_p=0.0469$, and $\chi^2=1.56$.

like nature of SrMoO_3 is also corroborated by its very low value of the Seebeck coefficient [Fig. 4(b)], which, unlike resistivity, is related to the bulk property of the material. The measured Seebeck values are close to the reported values^{15,20} and the Seebeck coefficient, despite the fact that it is very small, decreases continuously with temperature. This confirms that holelike carriers dominate the charge transport in SrMoO_3 . Figure 4(c) shows the temperature variation of thermal conductivity. The values of thermal conductivity are about three times lower than those reported in Ref. 20. This effect can be attributed to the lower density of our sample.

Measured magnetic susceptibility data reveal linear paramagnetic response. However, close inspection of magnetization curves at small fields unveiled that initial magnetic susceptibility is significantly higher than that at fields exceeding

FIG. 4. Temperature dependences of (a) resistivity; (b) Seebeck coefficient, and (c) heat conductivity of SrMoO_3 and SrMoO_2N .

FIG. 5. (Color online) Molar magnetic susceptibility of SrMoO_3 and SrMoO_2N measured with a SQUID magnetometer. The inset shows an expansion of the magnetic anomaly for SrMoO_3 when changing the magnetometer type from SQUID to VSM.

1 T. This feature was observed independently on temperature and field. Based on the ICP-QMS measurements, we attribute it to the presence of Ni and Fe traces (5–10 ppm) in our sample. Consequently, to minimize the role of this ferromagnetic impurity on the measured susceptibility, we adopted the conventional scenario, i.e., we applied sufficiently high field to saturate it. Accordingly, the zero field cooled and field cooled susceptibility measurements were performed under an applied field of 2 T.

As shown in Fig. 5, SrMoO_3 exhibits a temperature independent paramagnetism ($\chi \sim 1.8 \times 10^{-4} \text{ emu mol}^{-1} \text{ K}^{-1}$) between $T=100 \text{ K}$ and $T=300 \text{ K}$. This is consistent with the absolute value of magnetic susceptibility reported previously and explained as enhanced Pauli paramagnetism.¹¹ Below 100 K, the magnetic susceptibility slightly increases, according to a Curie behavior superposed to the temperature independent Pauli paramagnetism. Finally at $T \sim 54 \text{ K}$ a monotonous hyperbolic increase is interrupted by a weak anomaly (see below).

Unlike SrMoO_3 , the oxynitride SrMoO_2N shows semi-conductinglike behavior of its resistivity with temperature [Fig. 4(a)]. The thermal behavior of the electrical resistivity is reminiscent to that observed for glasses, i.e., systems with disorder on the atomic scale. Moreover, the absolute resistivity of SrMoO_2N is higher than that of SrMoO_3 . Based on the measured absolute Seebeck values, it can be deduced that holes are the predominating mobile charge carriers of SrMoO_2N [Fig. 4(b)]. The Seebeck values of SrMoO_2N are significantly higher than those of SrMoO_3 , pointing to the lower carrier concentration in SrMoO_2N .

The measured thermal conductivity value of SrMoO_2N is one order of magnitude smaller than that of SrMoO_3 . It also resembles the thermal conductivity of glasses, which corroborates with the presented behavior of the electrical resistivity [Fig. 4(c)].

The weak temperature dependence of the electrical resistivity together with the very low thermal conductivity of SrMoO_2N suggest that the mean free paths of both phonons and charge carriers are close to the interatomic distance. This can be caused by one or a combination of the following factors: (i) creation of the charge carrier traps (local defects,

scattering centers) due to the occupation of the same crystallographic site by atoms of different size, charge, and electronic level positions, (ii) dominating role of the charge carriers scattering on grain boundaries and within grains on microdomain boundaries, and (iii) bond length fluctuations in SrMoO_2N as suggested from its previous x-ray absorption near-edge spectroscopy study.¹⁴

SrMoO_2N oxynitride shows an analogous behavior as SrMoO_3 shows an analogous behavior with respect to a temperature independent paramagnetism down to $T=150 \text{ K}$, a low temperature upturn, and an anomaly at $T \sim 54 \text{ K}$. The temperature independent component is, however, smaller than that of SrMoO_3 and the low temperature increase and anomaly are enhanced. The magnetic data of SrMoO_2N can be fitted to the following equation:

$$\chi = \chi_{P+L} + \frac{C}{T - \Theta}, \quad (1)$$

where χ is the measured value of magnetic susceptibility (corrected for the sample holder, the varnish, and diamagnetic contributions), χ_{P+L} is the sum of the Pauli paramagnetic and Landau diamagnetic terms, C is the Curie constant, T is temperature, and Θ is the Weiss constant. The fit results in $\chi_{P+L} = 8.5 \times 10^{-5} \text{ emu mol}^{-1}$, $C = 3.310^{-5} \text{ emu mol}^{-1}$ and $\Theta = -63 \text{ K}$. The C value corresponds to the effective magnetic moment of $\mu_{\text{eff}} = 0.05 \mu_B$. The negative sign of Θ points to the antiferromagnetic interaction between the moments.

The temperature independent paramagnetic term χ_{P+L} can be expressed as

$$\chi_{P+L} = \mu_B N D_F \left(1 - \frac{1}{3} \left(\frac{m}{m^*} \right)^2 \right), \quad (2)$$

where D_F is density of states (DOS) at the Fermi level, N is the number of itinerant electrons per one mole of unit formula, m is the electron mass and m^* is the effective electron mass. Within the free electron approximation $m = m^*$, hence,

$$\chi_{P+L} \approx 0.7 \mu_B N D_F. \quad (3)$$

From this equation, the susceptibility related DOS at the Fermi level can be estimated. Its value for SrMoO_2N is equal to $D_F \sim 25 \text{ Ry}^{-1}/\text{f.u.}$, while that deduced for SrMoO_3 is significantly higher, i.e., $D_F \sim 55 \text{ Ry}^{-1}/\text{f.u.}$

Alternatively, the DOS at the Fermi level can be calculated from the Sommerfeld coefficient (γ), which is derived from the bulk-related heat capacity data. The specific heat data for polycrystalline SrMoO_2N are plotted as C_p/T versus T^2 (Fig. 6). Similar as for SrMoO_3 ,¹⁹ the data follow a straight line below 10 K. The sum of a linear term for the electronic (γT) and the lattice (βT^3) contributions is

$$C_p = \gamma T + \beta T^3, \quad (4)$$

where

$$\gamma = \frac{\pi^2}{3} K_B^2 N D_F, \quad (5)$$

FIG. 6. Temperature dependence of C_p/T ($2 \text{ K} < T < 13 \text{ K}$) measured on SrMoO_2N .

$$\beta = 12\pi^4 N k_B / 5 \Theta_D^3, \quad (6)$$

where k_B is the Boltzmann constant and Θ_D is the Debye temperature.

The fitting to Eq. (4) results in $\gamma = 3.9 \text{ mJ mol}^{-1} \text{ K}^2$ and $\Theta_D = 320 \text{ K}$. The value of γ corresponds to the DOS of $D_F = 23 \text{ Ry}^{-1}/\text{f.u.}$, a value very close to that derived from the magnetic susceptibility and evidences the absence of strong electronic correlations in SrMoO_2N [(Sommerfeld–Wilson ratio $R_W \approx 1$ (Ref. 21)]. Let us note the literature value of γ for SrMoO_3 ($7.9 \text{ mJ mol}^{-1} \text{ K}^2$), which is higher than that of SrMoO_2N , and hence the DOS at the Fermi level of SrMoO_3 ($D_F \sim 45.0 \text{ Ry}^{-1}/\text{f.u.}$) is higher than that of SrMoO_2N . To conclude about the influence of the anionic substitution on the magnetic correlations of the $\text{SrMoO}_{3-x}\text{N}_x$ system, the Sommerfeld–Wilson ratio of SrMoO_2N should be compared with that of SrMoO_3 . From Eq. (3), we obtain the DOS of $55.0 \text{ Ry}^{-1}/\text{f.u.}$ for SrMoO_3 and, the Sommerfeld–Wilson ratio of SrMoO_3 is ~ 1.2 . Based on this analysis, SrMoO_3 does not exhibit strong electron correlations.

Lower DOS at E_F for SrMoO_2N is consistent with an expected increase in the formal Mo oxidation state, e.g., the removal of electrons from the itinerant t_{2g} states of Mo ions, when part of O^{2-} in SrMoO_3 is replaced with N^{3-} ,

Together with the anionic composition refined from the ND data, this points to the fact that an increase of the molybdenum oxidation state is the main charge compensating mechanism for partial substitution of O^{2-} with N^{3-} .

The anomaly measured at $T \sim 54 \text{ K}$ apparently cannot be associated with partial substitution of O^{2-} with N^{3-} as the same magnetic feature can be noted on the magnetic susceptibility curves of SrMoO_3 and Sr_2MoO_4 published previously.^{22,23} Although no explanations are given in Ref. 22, the authors of Ref. 23 have attributed the feature to molecular oxygen. It is known that residual oxygen presence in the sample and/or in the measurement chamber can significantly alter magnetic susceptibility data of weakly magnetic materials.²⁴

Bulk oxygen melts at $T = 54.4 \text{ K}$ and a paramagnetic γ -phase transforms into the antiferromagnetic β -phase at T

$= 43.8 \text{ K}$. Thus, a comparative magnetic measurement performed with another instrument is used to uncover the presence of molecular oxygen.

Magnetic susceptibility of the same sample was measured under the same experimental conditions additionally with a VSM PPMS option. From Fig. 5 (inset), it is clearly seen that the measurement with VSM gives a sufficiently expanded magnetic signal with two maxima at $T \sim 47$ and 54 K , respectively. We infer that the maximum at $T \sim 54 \text{ K}$ corresponds to the melting point of oxygen and the maximum at 47 K to the β - γ transformation of solid oxygen. Furthermore, we have verified that the measurement of an empty sample holder did not reveal any magnetic anomalies between $T = 40$ – 60 K . Thus, the measured signals result from the molecular oxygen in the samples and not in the holder. However, it is difficult to conclude where the molecular oxygen is located: on the measured samples surface, in pores between grains or within grains.

Finally, we summarize the three following possible explanations of Curie paramagnetism measured below 50 K : (i) it is related to intrinsic property of the material and can be concerned with the presence of electronic defects (such as Mo'_{Mo}) as it found before for the $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ system,²⁵ (ii) the presence a paramagnetic impurity phase which cannot be detected neither by x-ray nor ND, or (iii) paramagnetism of γ oxygen, confined in pores of the measured material.

Thus, lower magnetic susceptibility confirms that the DOS at E_F is lowered in SrMoO_2N with respect to SrMoO_3 while the more pronounced low temperature features indicate (in coherence with difficult synthesis of SrMoO_2N) the higher concentration of localized magnetic moments.

IV. CONCLUSIONS

Low temperature physical properties of the cubic perovskite polycrystalline phases, SrMoO_2N and SrMoO_3 , have been measured in the temperature range of $5 \text{ K} < T < 300 \text{ K}$. These materials are p -type conductors as deduced from the Seebeck coefficient measurements. Both compounds show paramagnetism dominated by the temperature independent Pauli term. Smaller Pauli susceptibility and Sommerfeld coefficient values for the oxynitride confirm independently lower DOS near Fermi level compared to that of SrMoO_3 . This corroborates with the higher valence of Mo in SrMoO_2N . The similar anionic compositions, refined from the ND data and deduced from hotgas extraction, point to the fact that the increase of the molybdenum oxidation state is the main charge compensating mechanism for partial substitution of O^{2-} with N^{3-} . Comparison of the DOS values derived from the magnetic susceptibility and heat capacity measurements allows to rule out the presence of strong electronic correlations in SrMoO_2N .

In contrast to SrMoO_3 , the oxynitride sample reveals a low thermal conductivity and semiconductinglike electrical resistivity, which point toward short mean free path for phonons and charge carriers and/or low charge carrier mobility in that compound.

Since the electrical resistivity measurements were performed on bars of pressed and sintered powders and not on

single crystals, the obtained resistivity values are to be corrected concerning the remaining porosity. Nevertheless, the metallic-like behavior of SrMoO_3 is verified by comparing our data with data measured on a SrMoO_3 monocrystal.¹⁹ The semiconducting behavior of SrMoO_2N is in accordance with its higher Seebeck coefficient, compared to that of SrMoO_3 and the possibility of $\text{Mo}(\text{O},\text{N})_6$ octahedra distortion.¹⁴ Thus, the obtained temperature dependence of the electrical resistivity for SrMoO_3 and SrMoO_2N seems to be correct. The electrical transport properties, the enhanced Seebeck coefficient, as well as the lower thermal conductivity of SrMoO_2N compared to SrMoO_3 , makes the oxynitride an interesting candidate as potential thermoelectric material.

Complex magnetic measurements and data analysis reveal that molecular oxygen presence in the measured materials is likely responsible for the magnetic anomaly observed at $T \sim 54$ K, contrary to previously suggested intrinsic anti-ferromagnetic or spin-glass transitions. It is also likely that paramagnetic oxygen contributes to the observed increase of the magnetic susceptibility at low temperatures. SrMoO_2N monocrystals would be required to verify this statement.

ACKNOWLEDGMENTS

The authors acknowledge the German Science Foundation (Grant No. DFG-SPP 1136) for the financial support as well as Dr. Denis Sheptyakov (SINQ) for the technical assistance. This work is partly based on the experiments performed at the Swiss Spallation Neutron Source SINQ, Paul Scherrer Institute, Villigen, Switzerland.

¹D. Logvinovich, A. Borger, M. Dobeli, S. G. Ebbinghaus, A. Reller, and A. Weidenkaff, *Prog. Solid State Chem.* **35**, 281 (2007).

²M. Jansen and H. P. Letschert, *Nature (London)* **404**, 980 (2000).

³R. Aguiar, D. Logvinovich, A. Weidenkaff, A. Rachel, A. Reller, and S. G. Ebbinghaus, *Dyes Pigm.* **76**, 70 (2008).

- ⁴A. Kasahara, K. Nukumizu, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen, *J. Phys. Chem. B* **107**, 791 (2003).
- ⁵R. Aguiar, Y. Lee, K. Domen, A. Kalytta, D. Logvinovich, A. Weidenkaff, A. Reller, and S. G. Ebbinghaus, *Ceramic Materials Research Trends* (Nova Science, New York, 2007), pp. 107–133.
- ⁶P. Antoine, R. Marchand, Y. Laurent, C. Michel, and B. Raveau, *Mater. Res. Bull.* **23**, 953 (1988).
- ⁷P. Antoine, R. Assabaa, P. L'Haridon, R. Marchand, Y. Laurent, C. Michel, and B. Raveau, *Mater. Sci. Eng., B* **5**, 43 (1989).
- ⁸H. Mizoguchi, K. Fukumi, N. Kitamura, T. Takeuchi, J. Hayakawa, H. Yamanaka, H. Yanagi, H. Hosono, and H. Kawazoe, *J. Appl. Phys.* **85**, 6502 (1999).
- ⁹H. Mizoguchi, N. Kitamura, K. Fukumi, T. Mihara, J. Nishii, M. Nakamura, N. Kikuchi, H. Hosono, and H. Kawazoe, *J. Appl. Phys.* **87**, 4617 (2000).
- ¹⁰G. Liu, X. Zhao, and H. A. Eick, *J. Alloys Compd.* **187**, 145 (1992).
- ¹¹I. D. Fawcett, K. V. Ramanujachary, and M. Greenblatt, *Mater. Res. Bull.* **32**, 1565 (1997).
- ¹²I. C. Lekshmi, A. Gayen, and M. S. Hegde, *Mater. Res. Bull.* **40**, 93 (2005).
- ¹³D. Logvinovich, M. H. Aguirre, J. Hejtmanek, R. Aguiar, S. G. Ebbinghaus, A. Reller, and A. Weidenkaff, *J. Solid State Chem.* **181**, 2243 (2008).
- ¹⁴D. Logvinovich, R. Aguiar, R. Robert, M. Trottmann, S. G. Ebbinghaus, A. Reller, and A. Weidenkaff, *J. Solid State Chem.* **180**, 2649 (2007).
- ¹⁵L. H. Brixner, *J. Inorg. Nucl. Chem.* **14**, 225 (1960).
- ¹⁶P. Fischer, G. Frey, M. Koch, M. Konnecke, V. Pomjakushin, J. Schefer, R. Thut, N. Schlumpf, R. Burge, and U. Greuter, *Physica B* **276–278**, 146 (2000).
- ¹⁷J. Rodriguez-Carvajal, *Physica B* **192**, 55 (1993).
- ¹⁸J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Clarendon, Oxford, 1932).
- ¹⁹I. Nagai, N. Shirakawa, S. Ikeda, R. Iwasaki, H. Nishimura, and M. Kosaka, *Appl. Phys. Lett.* **87**, 024105 (2005).
- ²⁰T. Maekawa, K. Kurosaki, H. Muta, M. Uno, and S. Yamanaka, *J. Alloys Compd.* **390**, 314 (2005).
- ²¹K. G. Wilson, *Rev. Mod. Phys.* **47**, 773 (1975).
- ²²S. I. Ikeda and N. Shirakawa, *Physica C* **341–348**, 785 (2000).
- ²³N. Shirakawa and S. I. Ikeda, *Physica C* **364–365**, 309 (2001).
- ²⁴F. Beuneu, P. Vajda, and O. J. Zogal, *Phys. Rev. Lett.* **83**, 761 (1999).
- ²⁵I. H. Inoue, O. Goto, H. Makino, N. E. Hussey, and M. Ishikawa, *Phys. Rev. B* **58**, 4372 (1998).