Continuous metal-insulator transition of the antiferromagnetic perovskite NaOsO₃

Y. G. Shi,1,2 Y. F. Guo,1,2 S. Yu,3 M. Arai,1,2 A. A. Belik,1,2 A. Sato,5 K. Yamaura,2,3,* E. Takayama-Muromachi,1,2,3 H. F. Tian,5 H. X. Yang,6 J. Q. Li,1 T. Varga,7 J. F. Mitchell,7 and S. Okamoto8

1International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
2JST, Transformative Research-Project on Iron Pnictides (TRIP), 5 Sanbancho, chiyoda-ku, Tokyo 102-0075, Japan
3Superconducting Materials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
4Computational Materials Science Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
5Materials Analysis Station, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
6Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
7Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, USA
8Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

(Received 28 August 2009; published 23 October 2009; corrected 28 October 2009)

The perovskite NaOsO₃ shows a Curie-Weiss metallic nature at high temperature and suddenly goes into an antiferromagnetically insulating state at 410 K on cooling. Electronic specific heat at the low-temperature limit is absent, indicating that the band gap fully opens. In situ observation in electron microscopy undetected any lattice anomalies in the vicinity of the transition temperature. It is most likely that the antiferromagnetic correlation plays an essential role in the gap opening.

DOI: 10.1103/PhysRevB.80.161104
PACS number(s): 71.30.+h, 72.80.Ga

Metal-insulator transition (MIT) is a central topic of condensed-matter science for more than half a century, and it still attracts intense attentions because it underlies key principles of correlated electron science. Chronologically, a principal idea was proposed by Mott in 1940s and by Hubbard in 1960s, suggesting that strong Coulomb interaction in half filling opens a gap at the Fermi energy ($E_F$), turning the conducting state into an insulating state, regardless of the presence of magnetic correlations.1,2 Alternatively, Slater suggested in 1950s that antiferromagnetic (AF) order alone can open a gap in the half-filled state regardless of the magnitude of the Coulomb interaction.3 Experimentally, many numbers of conductors were found to show MIT, which seems to be well characterized in the above schemes.4 Regarding the AF correlation-induced MIT, most discoveries were attained on low-dimensional conductors and fairly few were on three-dimensional (3D) conductors. Generally, a 3D conductor causes only a small fraction of changes in its electronic structure through the AF ordering, resulting in robust conductivity such as found in Cr.5 In this context, the 3D conductors Cd₂Os₂O₇ (Refs. 6 and 7) and Ln₂Ir₂O₇ (Ref. 8) are outstanding because of those continuous AF MITs.

So-far studies on Cd₂Os₂O₇ suggested that the continuous MIT at 226 K can be characterized in terms of the AF correlation,6,7 although inherent magnetic frustration due to the pyrochlore lattice certainly complicates the MIT. The origin of the MIT of Ln₂Ir₂O₇ might include the magnetic frustration somewhat.8 It appears that the AF 3D MIT needs to be studied further. It is thus highly desirable to investigate an AF 3D MIT that is less relevant to the magnetic frustration.

We report a perovskite oxide showing a continuous MIT. The perovskite NaOsO₃ has the octahedral environment of Os⁵⁺O₂⁻ so that the electronic configuration is 5d⁵, suggesting that the 5g band is nearly half filling. NaOsO₃ shows a Curie-Weiss (CW) metallic nature and abruptly turns to an AF insulator at 410 K on cooling. It is notable that an AF 3D MIT appears on the perovskite lattice rather than the pyrochlore lattice. Because NaOsO₃ is expected to be less relevant to the magnetic frustration unlike the isoelectronic Cd₂Os₂O₇ and charge ordering is absent over the MIT of NaOsO₃, the perovskite is therefore significant to provide valuable opportunities to deepen our understanding of AF 3D MIT.

Crystal of NaOsO₃ grew up in a high-pressure apparatus that is capable of maintaining 6 GPa pressure during heating at 1700 °C for 2.5 h. The starting materials were Na₂O₂ (97%, Sigma-Aldrich) and OsO₂ (Os-84.0%, Alfa Aesar), and those were sealed in a Pt capsule at 15 mol % Na-rich stoichiometry with 0.1 mol of NaCl (99.99%, Rare Metallic Co.) per f.u. After the heating, the capsule was quenched in the press to ambient temperature before releasing the pressure. We prepared a polycrystalline sample as well by heating a mixture of Na₂OsO₄ and NaCl at 1700 °C for 2.5 h. The starting materials were Na₂OsO₄ (97%, Sigma-Aldrich) and NaCl (99.9%, Sigma-Aldrich) in a molar ratio of 1:2. The sample was annealed at 1200 °C for 10 h in the press without using NaCl. A photograph of a selected crystal is shown in Fig. 1(a). The samples were rinsed in water in a sonic bath for 2−3 min several times to remove residual ingredients, followed by

---

FIG. 1. (a) Photograph of a crystal of NaOsO₃ and (b) the Rietveld analysis of the synchrotron XRD profile for NaOsO₃. Cross markers and solid lines show the observed and calculated XRD profiles, respectively, and the difference is shown at the bottom. The positions of Bragg reflections are marked by ticks (lower ticks are for the impurity OsO₂). The inset is a structure view of NaOsO₃. (c) SAED pattern taken along [10−1] zone axis at room temperature.
drying in air at 140 °C for 10 min. The sample quality was checked by a powder x-ray diffraction (XRD) method using Cu Kα radiation in RINT 2200V, RIGAKU, confirming the absence of impurities. We should note that preliminary samples prepared without excess Na2O3O7 were found to contain nontrivial amount of Os2O5. The crystal structure of NaOsO3 was studied by a Rietveld method with powder synchrotron XRD data collected on the X-ray Operations and Research Beamline at the Advanced Photon Source, Argonne National Laboratory. The incident beam was monochromatized at λ=0.401 036 Å. The Rietveld analysis was carried out by the program Rietan-2000.

A selected crystal of NaOsO3 was examined in electron probe microanalysis (JXA-8500F, JEOL), finding the absence of contaminations such as Pt. The mean metal ratio at five points in the sole crystal was Na/Os=1.14(2), suggesting that a small amount of Na is possibly incorporated in the crystal. Crystals were studied by a selected area electron diffraction (SAED) method between room temperature and 600 K in a transmission electron microscope operated at 200 kV (Tecnai-F20, Philips Electron Optics). The electrical resistivity (ρ) of a selected crystal was measured by a van der Pauw method on the assumption that the charge transport of the crystal is isotropic in nature with a dc-gauge current of 0.1 mA between 2 and 330 K in Physical Properties Measurement System (PPMS), Quantum Design. Electrical contacts on the four corners of the crystal were prepared by gold wires and a silver paste. The limited size of the crystal did not allow us to estimate the actual degree of the charge transport anisotropy. ρ measurements between 300 and 550 K were conducted in a laboratory-made apparatus. The Hall coefficient (RH) was measured by rotating the crystal by 180° in a magnetic field of 50 kOe in PPMS between 25 and 400 K.

The specific heat (Cp) was measured by a time-relaxation method using the powder sample (compressed) in PPMS between 2 and 300 K. Differential scanning calorimetry (DSC) was conducted in DSC1 STAR® System, Mettler Toledo, between 300 and 440 K at heating rates of 0.5, 2, 5, 10, and 20 K/min. The magnetic susceptibility (χ) and the isothermal magnetization were measured using multiple single crystals randomly oriented in a sample holder (~20 pieces, 8.1 mg in total) in Magnetic Properties Measurement System, Quantum Design. The sample was cooled to 2 K without applying a magnetic field, and then warmed up to 300 K in a field of 50 kOe [zero-field cooling (ZFC)], followed by cooling to 2 K in the field [field cooling (FC)]. The measurement was again conducted between 300 and 600 K in an oven installed to the magnetometer.

Figure 1(b) shows the synchrotron XRD pattern with the analysis result.10 A structure model with the space group Pnma, which is often observed for perovskite oxides, was found to reasonably fit to the pattern. The R factors and the difference curve in Fig. 1(b) indicate the high quality of the solution. The overall structure view is shown in Fig. 1(b). Based on the result, we investigated the local coordination of Os. We found that it is fairly isotropic: variation of the six bond distances between Os and O is smaller than 0.4% of the longest 1.946(1) Å bond, and the O-Os-O angles are 90.7°, 89.9°, and 90.1°, being fairly close to the right angle. Besides, in order to alternatively confirm the solution quality, the bond valence sum of the atoms in the cell was calculated,11,12 4.92(Os), in reasonable agreement with the formal valence of Os and 1.40(Na), which is fairly obtained.

We also studied the perovskite lattice by a SAED method and found that all diffraction spots at room temperature are distributed in accord with the Pnma model; in short the 2a0p × 2a0p × 2ap (ap: primitive cell constant) order was clearly confirmed. The superstructure is due to the cooperative rotation and tilting of the OsO6 octahedra as in the GdFeO3-type perovskite.13 Additional superstructure neither commensurate nor incommensurate was detected at room temperature. A selected SAED pattern is shown in Fig. 1(c). Besides, we carried out in situ heating in the microscope to test the appearance of a possible lattice anomaly over the MIT. However, no visible changes were detected to 600 K, excluding a major structure change and strong lattice-electron coupling in the vicinity of the MIT temperature. However, a possibility of structural distortions in local without symmetry change still remains, being investigated in future studies.

Figure 2(a) shows the temperature dependence of ρ of the single crystal NaOsO3. The higher-temperature part shows a slightly positive slope around the resistivity of 1~2×10−4 Ω cm, being consistent with an expected character for a metallic oxide. ρ suddenly jumps up at 410 K on cooling and continuously rises to 2 K over six orders of magnitude. It is notable that the warming and the cooling curves follow the same trace within an experimental accuracy, suggesting that the MIT is the second-order phase transition. The DSC confirmed the order of the transition (see the inset to Fig. 2), as the heat-flow-peak temperatures in cooling and heating are identical. The DSC measurements were repeated at different rates to extrapolate the result for 0 K/min, finding no shifts in the peak onsets and the peak positions.

In Fig. 2(b), the Hall number (e/RH) steadily decreases with temperature decreasing beyond five orders of magni-
We found that the spontaneous magnetization is fairly small, 0.005 $\mu_B$/Os at 5 K; this corresponds to only 0.17% of the expected moment for $S=3/2$, indicating that the transition is weakly ferromagnetic (FM).

In order to further analyze the magnetic properties, we applied the CW law to the paramagnetic part (>410 K), as shown in the inset to Fig. 3(a). The analytical formula was $\chi(T)=N_A \mu_{eff}^2 / 3 \pi (T-\Theta_W)$, where $N_A$ is the Avogadro’s constant and $\Theta_W$ is the Weiss temperature. The effective Bohr magneton ($\mu_{eff}$) was estimated to be 2.71 $\mu_B$, being 70% of the expected moment for $S=3/2$. $\Theta_W$ was −1949 K, suggesting that AF interactions are strong and dominant in the spin system if the CW analysis provides a valid indication. The overall magnetic data including the CW analysis results thus suggest that NaOsO$_3$ undergoes an AF transition at 410 K accompanying the weak magnetization most likely due to the Dzyaloshinsky-Moriya interaction generated by the broken inversion symmetry.

We studied the electronic structure of NaOsO$_3$ using the local-density approximation (LDA) (Ref. 14) of density-functional theory. We used the WIEN2K package, which is based on a full-potential augmented-plane-wave method. Experimental lattice parameters and atomic coordinates were used with the atomic radii of 2.0, 1.8, and 1.7 a.u. for Na, Os, and O, respectively. The cutoff wave number $k$ in the irreducible Brillouin zone was set to $R K=7$, where $R$ is the smallest atomic radius. The integration over Brillouin zone was performed by a tetrahedron method with 144 k points in the irreducible Brillouin zone (IBZ). For spin-polarized calculations, the convergence was checked with finer integration mesh points up to 468 k points in the IBZ.

The DOS is plotted in Fig. 4(a). The Os $t_{2g}$ bands distribute between ~2.5 and 1 eV, being wider than those for Cd$_2$Os$_3$O$_7$, because frustration is absent in NaOsO$_3$. Reflecting the nominal configuration of Os$^{5+}$ with 5$d^3$, the calculated $E_F$ lies near the center of Os $t_{2g}$ bands and the total DOS shows the broad peak around $E_F$. Since the half-filled $t_{2g}$ bands suggest instability of the nonmagnetic phase, we examined possible magnetic solutions within LDA. However, any stable solutions with FM or AF spin alignments were found. Besides, we further performed LDA calculations with spin-orbit (SO) coupling since they may affect qualitatively the electronic structure, as intensively discussed for...
the $5d$ oxide Sr$_2$IrO$_4$. Figure 4(b) shows the total DOS with SO coupling. As is common with Cd$_2$Os$_2$O$_7$, the SO coupling indeed modifies the $t_{2g}$-band structure. However, $E_F$ still locates at the vicinity of the broad peak with an almost comparable DOS, suggesting that the SO coupling plays an insignificant role in the gap opening in NaOsO$_3$ unlike what was found for Sr$_2$IrO$_4$. Stable magnetic solutions with the SO coupling were unattained.

Afterward, we somehow obtained a stable magnetic solution by introducing a local coulomb interaction $U$ as the Hubbard term in the LDA+$U$ approximation. At a moderate $U$ of 1 eV, a stable AF solution appeared with a small but finite energy gap as shown in Fig. 4(c), while attempts with FM spin alignments never resulted in a corresponding solution qualitatively and quantitatively. Thus, the results suggest that the AF correlation is highly significant to open the gap in NaOsO$_3$. It is also suggested that there was a picture with a single on-site $U$ alone ($U=W$, where $W$ is the bandwidth) is too simple to account for the MIT of NaOsO$_3$.

The MIT of NaOsO$_3$ seems to be characterized by the degree of magnitude of AF correlation, as discussed in Ref. 19. The theoretical study using dynamical mean-field technique suggested that a gapped state in a half-filled electronic structure appears at the strong limit of the AF correlations, while a Mott transition is caused by the strong Coulomb repulsion regardless of the strength of magnetic correlations. In fact, magnetically weak materials such as V$_2$O$_3$ and much magnetic materials such as NiS$_2$,Se$_2$ show different MIT features. Regarding NaOsO$_3$, the MIT coincides with the AF transition; NaOsO$_3$ is thus close to the strong magnetic limit of the 3D MIT. We believe that such a paramagnetic metal to AF insulator transition at finite temperature is of second order as we observed. Further discussion is left for future work.

On the other hand, a charge-order model was intensively discussed for the 3d perovskite LnNiO$_3$ (Refs. 20 and 21): the MIT features are however readily distinguishable from what we found for NaOsO$_3$. For instance, SmNiO$_3$ shows a large temperature gap between the MIT at 400 K and a subsequent magnetic transition at 220 K. In addition, the magnetic transition in SmNiO$_3$ is coupled with lattice alteration probably due to ordering between the $t_{2g}$ and $e_g$ orbitals, while such a strong electron-lattice coupling is absent in NaOsO$_3$. It is thus reasonable to exclude the charge-order model from the framework of the MIT of NaOsO$_3$.

In summary, the perovskite NaOsO$_3$ shows a dramatic MIT at 410 K. The MIT nature is far different from what we observed for LnNiO$_3$ since it is associated with the magnetic ordering and is less relevant to the lattice anomaly. Furthermore, it is possibly different from the MIT nature of the isoelectrical Cd$_2$Os$_2$O$_7$ because the degree of magnetic frustration is highly reduced and the SO coupling is insignificant. The first-principles calculation suggests that the intense AF correlation (with small $U$) is the principal origin of the MIT of NaOsO$_3$. If the picture is true, NaOsO$_3$ is a “Slater insulator” in three dimensions, which can work at room temperature. Further studies toward the nature of the MIT and possible practical applications are in progress.

We thank D. Mandrus for valuable discussion, T. Kolodiaznyi for the $R_{HH}$ measurement, and K. Kosuda for the EPMA. The use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. This research was supported in part by the WPI Initiative on Materials Nanoarchitectonics from MEXT, Japan and the Grants-in-Aid for Scientific Research (Grant No. 20360012) from JSPS. S.O. is supported by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy.