Phase transition and magnetic structure of pyrochlore oxide Cd$_2$Os$_2$O$_7$

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Abstract. The 5d transition metal oxide Cd$_2$Os$_2$O$_7$ having a pyrochlore lattice of Os atoms exhibits a metal-insulator transition with a magnetic ordering at $227 \text{ K}$, but the magnetic structure in the ordered state and the origin of the transition have not yet been specified. The commensurate magnetic reflection with the propagation vector $k = (0, 0, 0)$ was first observed in the resonant X-ray scattering using a high-quality single crystal. We also clarified the only one kind of magnetic moment via the synchrotron radiation-based Mössbauer effect. We propose that a strong spin-orbit interaction is notably apparent in the spin arrangement and the insulating mechanism in this compound.

1. Introduction
Metal-insulator (MI) transition is one of the most dramatic phenomena of electrons in a solid. The strong electron correlation causes a localized insulator with a first-order type Mott transition, which is often accompanied by a simple collinear-type antiferromagnetic order [1]. On the other hand, the Fermi surface nesting leads to a different type of insulator with a CDW or SDW transition, in which either a nonmagnetic singlet state or an incommensurate magnetic state is stabilized. Moreover, the other type of MI transition is theoretically expected, which is the Slater transition induced by the Brillouin zone folding due to a magnetic order [2]. The magnetic order associated with the Slater transition can be a commensurate or incommensurate antiferromagnetic order and is accompanied by no lattice distortion. Because electron correlations are not crucial, the transition should appear in weakly correlated electron systems.

The 5d transition metal oxide Cd$_2$Os$_2$O$_7$ with a pyrochlore lattice of Os atoms exhibits an MI transition at $T_{\text{MI}} = 226 \text{ K}$, accompanied by a magnetic ordering [3, 4]. The magnetic structure of the ordered state has not been determined, and the origin of the transition remains a mystery. A Slater mechanism and the formation of a SDW state were suggested in previous study [4, 5] but were questioned because of the lack of Fermi surface nesting in the calculated band structure [6, 7]. In this work, we investigated the MI transition of Cd$_2$Os$_2$O$_7$ by means of resonant X-ray scattering (RXS) and synchrotron radiation-based Mössbauer spectroscopy to unveil the magnetic ground state. These state-of-the-art techniques enable us to obtain element-selective signals from complex compounds [8, 9].
2. Experiments
A single crystal of Cd$_2$Os$_2$O$_7$ was synthesized from CdO and Os in a sealed quartz tube, which contained an appropriate amount of AgO for oxygen supply. The tube was placed in a furnace with a temperature gradient of 900-750 °C for a week. RXS experiments were carried out at the absorption edge of Os L3 ($E = 10.874$ keV) and Os L2 ($E = 12.387$ keV) using a six-circle diffractometer and an imaging plate at beamlines of SPring-8 BL19LXU and SPring-8 BL02B1, respectively [10, 11]. Synchrotron radiation-based Mössbauer spectroscopy was measured at 20 K in a beamline of SPring-8 BL09LXU, in which $^{185}$Os enriched powder samples of Cd$_2$Os$_2$O$_7$ and Os were used for the transmitter and the scatter on the velocity transducer, respectively [9]. The radiation at 36.332 keV was chosen by a high-resolution Si(111)-Si(400) monochromator to reduce the background, and the delayed emission was measured using a Si-APD detector.

3. Result and Discussions
Figure 1(a) shows the oscillation photograph on the imaging plate at the Os L2 edge at 100 K. The 00l ($l = 4n+2$) and 0kl ($k + l = 4n+2$) reflections, which violate the extinction rule of space group Fd-3m, are observed below $T_{MI}$. These forbidden reflections are not due to the lattice symmetry breaking but due to the magnetic or the anisotropic tensor susceptibility (ATS) scattering, as mentioned later.

Figure 1(b) shows the X-ray absorption spectra near the Os L3 edge and the energy dependence of the 006 reflection intensity at 10 K, which was obtained in the $\pi$-$\sigma'$ polarization channel at the azimuthal angle $\phi = -47^\circ$. Note that the 006 reflection peak has a maximum value strikingly at the Os L3 edge depicted by the dotted line, which is evidence of the resonant effect.

The ATS intensity, which is derived from the local atomic environment, of the 00l ($l = 4n + 2$) forbidden reflection at the azimuthal angle $\phi$ in the $\pi$-$\sigma'$ polarization channels are estimated using $I_{00l} = F^2\sin^6\alpha\cos^2\phi$, as shown by Dmitrienko [12]. Hence, the ATS contribution is negligible in the present experimental setting with $\phi = -45^\circ$ in the $\pi$-$\sigma'$ channel. Thus, the observed 006 reflection is not due to Thomson scattering and ATS scattering but due to magnetic scattering. The magnetic peak was not observed with a powder sample in the previous neutron experiment [13] and was detected for the first time in the present experiment. Considering that the commensurate magnetic reflections represent the violations of the extinction rules with the $d$-glide and without the face-centered symmetry operations, we conclude that a commensurate magnetic structure appears with the propagation vector $k = (0, 0, 0)$ below $T_{MI}$. The ATS intensity, which is derived from the local atomic environment, of the 00l ($l = 4n + 2$) forbidden reflection at the azimuthal angle $\phi$ in the $\pi$-$\sigma'$ polarization channels are estimated using $I_{00l} = F^2\sin^6\alpha\cos^2\phi$, as shown by Dmitrienko [12]. Hence, the ATS contribution is negligible in the present experimental setting with $\phi = -45^\circ$ in the $\pi$-$\sigma'$ channel. Thus, the observed 006 reflection is not due to Thomson scattering and ATS scattering but due to magnetic scattering. The magnetic peak was not observed with a powder sample in the previous neutron experiment [13] and was detected for the first time in the present experiment. Considering that the commensurate magnetic reflections represent the violations of the extinction rules with the $d$-glide and without the face-centered symmetry operations, we conclude that a commensurate magnetic structure appears with the propagation vector $k = (0, 0, 0)$ below $T_{MI}$.

Figure 2 shows the temperature dependence of the 006 magnetic reflection intensity in the $\pi$-$\sigma'$ channel at $\phi = -47^\circ$. The integrated intensity of the 006 reflection increases gradually below $T_{MI}=227$ K upon cooling, which can be fitted by a power law expression. The result reveals that this transition is the successive and the second-order type transition.

Figure 3 shows $^{185}$Os Mössbauer spectrum of Cd$_2$Os$_2$O$_7$ measured at 20 K for 96 hours. The spectrum is preliminary estimated at the Isomer shift $J.S. = 0.7$ mm/s relative to that of Os, the electric quadrupole splitting is $e^2Q = -6.2$ mm/s, and the internal magnetic field is $H_{int} = 28.8$ T. This single spectrum reveals that the unique magnetic moment inhabits the Os atom.

Here, we discuss the origin of the MI transition in this compound. Usually, the on-site Coulomb energy $U$ in 5d transition metal oxides is between 1-2 eV. Due to the hybridization of Os-5d and O-2p, the band width $W$ in Cd$_2$Os$_2$O$_7$ is 2 eV, which represents an intermediate coupling region with $U \sim W$. Considering these points, Mandrus et al. has suggested that the MI transition of this compound is the Slater transition, which is a continuous phase transition in the weak coupling region, instead of a Mott transition. [4] However, the present result of the spin arrangement with $k = (0, 0, 0)$ suggests that this transition is due to neither the Slater-type nor the SDW transitions accompanied by the band folding with the antiferromagnetic structure formation or the Fermi surface instability, respectively. Consequently, the band-gap formation of this compound is thought to arise from an unprecedented mechanism, that is presumably related to the unique spin arrangement within a primitive unit cell. Recently, Wan et al. provides a stabilization mechanism of the all-in/all-out spin arrangement in $R_2$Ir$_2$O$_7$, where the spin-orbit (SO) interaction plays an important role, from the LDA+U+SO band
Figure 1. (a) Oscillation photograph at the Os L2 edge at 100 K. Arrow shows the reflection, which is forbidden in $Fd-3m$. (b) X-ray absorption spectra near the Os L3 edge at room temperature and the energy dependence of the 006 reflection intensity in the $\pi$-$\sigma'$ polarization ($\phi = -47^\circ$) at 10 K.

Figure 2. Temperature dependence of the intensity of 006 magnetic reflection in the $\pi$-$\sigma'$ channel at $\phi = -47^\circ$, where the intensity is normalized by that at 10 K. The solid line represents the fitting by the power law expression for the second-order transition.

calculation (not yet experimentally confirmed) [14]. We also believe that the spin arrangement in the present compound is primarily related to the lattice symmetry and the SO interaction.

4. Summary

Pyrochlore oxide $\text{Cd}_2\text{Os}_2\text{O}_7$ exhibits the second-order type of metal-insulator transition at 227 K. The commensurate magnetic structure with the propagation vector $\mathbf{k} = (0, 0, 0)$ and the unique magnetic moment in the low-temperature phase was determined by the resonant X-ray scattering and the synchrotron-radiation based Mössbauer measurements. We propose that the feature of the 5d-electrons with the strong spin-orbit interaction notably emerges due to the spin arrangement and the insulating mechanism in this compound.
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