Anomalous magnetic phase in an undistorted pyrochlore oxide Cd$_2$Os$_2$O$_7$ induced by geometrical frustration

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We report on the muon spin rotation/relaxation study of a pyrochlore oxide, Cd$_2$Os$_2$O$_7$, which exhibits a metal-insulator (MI) transition at $T_{\text{MI}} \simeq 225$ K without structural phase transition. It reveals strong spin fluctuation ($\gtrsim 10^8$ s$^{-1}$) below the MI transition, suggesting a predominant role of geometrical spin frustration amongst Os$^{5+}$ ions. Meanwhile, upon further cooling, an incommensurate spin density wave discontinuously develops below $T_{\text{SDW}} \simeq 150$ K. These observations strongly suggest the occurrence of an anomalous magnetic transition and associated change in the local spin dynamics in undistorted pyrochlore antiferromagnet.

KEYWORDS: $\mu$SR, strongly correlated electron, metal-insulator transition, SDW, frustrated magnetism

Pyrochlore lattice is a three dimensional network of corner shared tetrahedra, in which the corners are occupied by metallic ions. It is well known as a stage of the geometrically frustrated magnetism for the magnetic ions interacting antiferromagnetically. A class of pyrochlore compounds, especially having 5$d$ transition metals, is interesting as a testing ground for the implicit relation between charge transfer and spin frustration, since 5$d$ electrons generally occupy one of outer orbits far from the cation, and thus they have itinerant character.

A pyrochlore oxide, Cd$_2$Os$_2$O$_7$, has been known since 1974, as it is reported to exhibit metal-insulator (MI) transition at $T_{\text{MI}} \simeq 225$ K.$^{1,2}$ The resistivity enhances approximately by 10$^4$ times upon cooling below $T_{\text{MI}}$. A sharp step-like reduction of magnetic susceptibility at the MI transition suggests occurrence of antiferromagnetic (AF) order below $T_{\text{MI}}$. Recent discovery of superconductivity in a related pyrochlore oxide, Cd$_5$Re$_2$O$_7$, has triggered renewed attention to this compound.$^{1,3-5}$ From the viewpoint of electronic band structure, Cd$_2$Os$_2$O$_7$ (5$d^2$) differs from Cd$_5$Re$_2$O$_7$ (5$d^5$) by one electron per transition metal. In this regard, it is interesting to note that the recently discovered $\beta$-pyrochlore osmate superconductors, AOs$_2$O$_6$ (A = K, Rb and Cs)$^{6-8}$ are in a mixed valence state (5$d^{2.5}$). While band structure calculations predict a semi-metallic character for both Cd$_2$Os$_2$O$_7$ and Cd$_5$Re$_2$O$_7$, Cd$_2$Os$_2$O$_7$ exhibits successive structural transitions at $\sim 200$ K and $\sim 50$ K with reducing temperature that may give rise to a drastic change on both electronic state and electron-phonon coupling.$^{11}$

Notably in the case of Cd$_2$Os$_2$O$_7$, no evidence is found for the structural change across the MI transition, according to X-ray diffraction study on single crystals.$^{1,2}$ More interestingly, while a slight change of the lattice constant (without changing crystal symmetry) was observed by the recent powder neutron diffraction study, no sign of magnetic Bragg peak was found at the lowest temperature of 12 K.$^{12}$ A very recent attempt to clarify the magnetic ground state by Cd-NMR was unsuccessful, as it turned out that the NMR signal disappeared below $T_{\text{MI}}$. This is in marked contrast to the case of the other compounds having pyrochlore lattice, e.g., Fe$_2$O$_4$, where occurrence of a static magnetic order at lower temperatures is well established,$^{14}$ and thus motivated us to carry out muon spin rotation/relaxation ($\mu$SR) measurements to clarify the magnetic ground state of Cd$_2$Os$_2$O$_7$. In this Letter, we show that the ground state is an incommensurate spin density wave (SDW), which appears at a temperature $T_{\text{SDW}} \simeq 150$ K considerably lower than $T_{\text{MI}} \simeq 225$ K. Moreover, strong evidence for spin fluctuation probably due to the geometrical frustration of local magnetic moments is found over the temperature region between $T_{\text{MI}}$ and $T_{\text{SDW}}$, where no sign of long-range order is observed. The present result demonstrates the role of geometrical frustration competing with the AF order state on the pyrochlore lattice.

$\mu$SR experiment was performed using a pulsed muon beam provided by the Muon Science Laboratory of KEK, Japan. Additional measurements were carried out at TRIUMF, Canada, to obtain data with a time resolution better than the muon pulse width at KEK ($\sim 50$ ns). In both cases, a 100% polarized muon beam with a momentum of 29 MeV/c was implanted into the specimen. Conventional $\mu$SR technique was employed with a He-flow type cryostat to control the temperature of specimen down to $\sim 2$ K. For the measurements under a zero external field (ZF) condition, the residual field was compensated to be smaller than $10^{-5}$ T using a triple-axis

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Fig. 1. (a) Time-dependent $\mu$-e decay asymmetry (x muon polarization) obtained at 239 K and 175 K under zero external field, together with the result at 175 K under a longitudinal field of 0.3 T (KEK data). Each spectrum is shifted (by 0.05) for clarity, where the full polarization corresponds to $\sim 0.15$. (b) Magnetic field dependence of muon spin relaxation rate at 175 K. The solid curve represents the result of fitting analysis by the Redfield model.

Helmholtz coil system. Subsequently, those under a longitudinal field (LF, up to 0.3 T applied along the direction of the initial muon polarization) were performed to examine the influence of spin fluctuation. The time evolution of muon polarization was monitored by measuring the decay positrons which were preferably emitted toward the muon spin direction upon their decay, where the time-dependent asymmetry of positron events between a pair of forward/backward counters was proportional to the instantaneous muon polarization [$G_z(t)$].

Fig. 1(a) shows some examples of ZF-$\mu$SR time spectra observed at temperatures above and below $T_{MI} \simeq 225$ K, together with that observed under a longitudinal field of 0.3 T below $T_{MI}$. As is found for the spectrum at 239 K, the implanted muons retains their initial polarization between $T_{MI}$ and ambient temperature. However, upon lowering temperature below $T_{MI}$, a slow muon spin relaxation is observed. The field dependence of the muon spin relaxation rate ($\Lambda$) measured at 175 K, which is determined by an analysis using a simple exponential function,

$$A_0 G_z(t) = A \exp(-\Lambda t) + \text{const.} \quad (1)$$

is shown in Fig. 1(b), where the last term ($\simeq 0.1$ and independent of time and field) represents a background signal from muons stopped in the sample holder: it was confirmed by the TRIUMF data that the entire fraction of muons stopped in the sample exhibits depolarization by a rate $\Lambda$. [The initial asymmetry ($A_0$) is relatively smaller than the usual magnitude ($\simeq 0.2$) probably due to the formation of muonium state and subsequent loss of polarization at the epithermal stage of muon implantation.] It is established that the Redfield model is a good approximation for evaluating $\Lambda$ under a longitudinal field, where we have

$$\Lambda(B) = \frac{2\delta^2 \nu}{(\gamma_{\mu} B)^2 + \nu^2}. \quad (2)$$

with $\gamma_{\mu} (= 2\pi \times 135.5$ $\mu s^{-1}/T)$ being the gyromagnetic ratio of muon, $\delta$ the dipolar width, $\nu$ the fluctuation rate of the local field, and $B$ the external field, respectively. It is clear in Fig. 1(a) that the muon polarization does not recover even under a field of 0.3 T. This behavior strongly suggests the fluctuation of local fields [namely, $\nu \gg \gamma_{\mu} B$ in eq. (2)]. A fitting of the data in Fig. 1(b) using eq. (2) yields $\delta = 32(5)$ $\mu s^{-1}$ [$\delta/\gamma_{\mu} \approx 38(6)$ mT] and $\nu = 0.52(16) \times 10^9$ s$^{-1}$, where these values should be regarded as lower bounds considering the uncertainty of the fit. This provides a natural explanation for the disappearance of Cd-NMR signal below $T_{MI}$ because the Cd nuclear moments would be subject to strong damping by the spin fluctuation. Thus, the spin correlation just below $T_{MI}$ is characterized by the residual spin fluctuation at a rate of (or greater than) $10^8$–$10^9$ s$^{-1}$, which is in a stark contrast to the simple AF order currently presumed for Cd$_2$Os$_2$O$_7$. It is plausible that the presence of such spin fluctuation is related with the geometrically frustrated spin configuration (see below).

As shown in Fig. 2, $\Lambda$ exhibits a remarkable peak at $\sim 150$ K with a noticeable lambda-shaped tail typically seen for the critical slowing down of spin fluctuation. With further decreasing temperature below $\sim 150$ K, a spontaneous muon spin precession signal is observed (see Fig. 3). These observations apparently suggest a drastic change of the magnetic correlation time at $\sim 150$ K. It is interesting to compare the temperature dependence of $\Lambda$ with that of dc susceptibility shown in the inset of Fig. 2 obtained on the same specimen used for the $\mu$SR measurement. The susceptibility exhibits a pronounced peak at $T_{MI}$ as previously reported,$^{1,2}$ whereas no clear anomaly is observed at $\sim 150$ K where a magnetic transition is inferred from the present $\mu$SR study. A similar situation is suggested for the specific heat, where the anomaly is observed only at $T_{MI}$.$^2$ Thus, while it bears some features common to conventional magnetic order, microscopic detail of the transitions observed by $\mu$SR seems to be quite unconventional.
Now we focus on the nature of magnetically ordered state below 150 K. It is clear in Fig. 3 that a spontaneous precession of muon polarization under zero external field is observed at 1.9 K. This unambiguously demonstrates the development of a static internal field associated with long-range magnetic order. In the case of uniform magnetic ordering in a powder specimen, 1/3 of the implanted muons shows no relaxing behavior, since the direction of the internal field coincides with its polarization. However, the ZF-μSR spectra in Fig. 3 has a character that the center of the precession signal exhibits an exponential damping with an initial value greater than 1/3 of the total asymmetry. [They were obtained at TRIUMF, where the use of muon veto counter as a sample holder allowed us to obtain background-free spectra (i.e., const. in eq.(1) is zero).] This suggests that the local field have a strong spatial modulation, where the internal field is much reduced from the maximal value over a certain fraction of the total volume due to incommensurate distribution of local moment size. The absence of depolarization in the μSR time spectrum under a longitudinal field of 0.1 T (see Fig. 3) eliminates the possibility that the exponential damping is that of the longitudinal component due to residual spin fluctuation. Another possibility of macroscopic phase separation into AF and non-magnetic phases is also ruled out by the fact that the previous powder neutron diffraction study was unsuccessful to identify the magnetic order down to 12 K. Thus, we are led to conclude that the magnetic ground state of Cd$_2$Os$_2$O$_7$ is a quasi-static and incommensurate spin density wave (SDW) below $T_{SDW}$ $\simeq$ 150 K.

For the quantitative discussion, the ZF-μSR time spectra below $T_{SDW}$ (obtained at TRIUMF) are analyzed by using the following formula for powder specimen,

$$A_0 G_z(t) = A_1 \left[ \frac{1}{3} + \frac{2}{3} \exp(-\lambda_1 t) \cos(2\pi ft + \phi) \right] + A_2 \left[ \frac{1}{3} + \frac{2}{3} \exp(-\lambda_2 t) \right] + A_0,$$

where the total asymmetry $A_0$ is split into two signals with $A_1$ being thier partial asymmetry ($i = 1, 2$) and a time-independent background $A_0$, $\lambda_i$ is the relaxation rate, and $f = \gamma_\mu B/2\pi$ is the precession frequency with $B$ being the spontaneous local field. Eq. (3) corresponds to the model in which the density distribution of the internal field [$n(B) \propto \int G_z(t) \exp(-i\gamma_\mu B t) dt$] is approximated by a square wave pattern with the duty ratio being $A_1/(A_1 + A_2)$. The temperature dependence of $A_1$, $A_0$, and $f$ is shown in Fig. 4. Unlike the case of conventional magnetic phase transition, the development of the internal field is quite steep, as $f$ exhibits a discontinuous change at $T_{SDW}$ with least dependence on temperature immediately below $T_{SDW}$. It is thus suggested that the transition may not be driven solely by magnetic interaction but some other degrees of freedom. The relative yield of two components is mostly independent of temperature, where $A_1/(A_1 + A_2) \simeq 3/4$. Based on the two component approximation, we obtain that the volume-averaged internal field $(2\pi f A_1/\gamma_\mu \sum A_i)$ is $\sim$46 mT at 1.9 K, which is fairly close to the dipolar width ($\delta/\gamma_\mu$) deduced at 175 K.

It would be worth mentioned at this stage that a slight but distinctive change in the temperature dependence of various parameters has been indeed observed at $T_{SDW}$ in the earlier neutron diffractometry. Furthermore, the temperature dependence of electric resistivity shows a hump (or a narrow plateau) at $T_{SDW}$ regardless of crystal quality. The activation energy estimated from the temperature dependence of resistivity starts to drop to zero with decreasing temperature below $T_{SDW}$. These anomalies coherently point to the presence of a transition that is revealed by μSR experiment.
Here, we discuss the local configuration of Os moments relative to muons, and possible models to interpret the results of $\mu$SR and other measurements including magnetic susceptibility in a coherent manner. Provided that muon occupies the center of an Os tetrahedron to form an inner $\mu^+ \text{Os}^6^-$ octahedron suitable for accommodating a positively charged muon, which being also consistent with small muon depolarization rate at ambient temperature (see Fig. 1a) as it is estimated to be $2.5 \times 10^{-3}$ MHz from random local fields of Cd nuclear magnetic moments, the hyperfine coupling constant is calculated to be $\delta/\gamma_{\mu} \approx 0.21 \text{T}/\mu_B$ (with $\mu_B$ being the Bohr magneton). The comparison of $\delta$ with that deduced at 175 K leads to the estimated average moment size of 0.18$\mu_B$ per Os ion which is much smaller than that expected for completely localized 5$d$ electrons. This is again in line with the presence of strong magnetic frustration of electrons that often leads to the shrinkage of effective local moment. In such a situation, it is commonly observed in many spinel and pyrochlore oxides that structural transition to a lower crystal symmetry occurs to lift the geometrical degeneracy. Interestingly, however, no indication of structural transition is reported for the case of Cd$_2$Os$_2$O$_7$.

This may have a relevance to the fact that the $t_{2g}$ manifold in the electronic state is fully occupied by 5$d$ electrons ($5d^5$) so that the Jahn-Teller like distortion may not be favored. In any case, the geometrical frustration and associated fluctuation of local spins naturally explains the absence of truly static magnetic order for $T_{\text{SDW}} \leq T \leq T_{\text{MI}}$, as it is suggested by $\mu$SR.

On the other hand, the susceptibility clearly indicates the development of quasi-static magnetization below $T_{\text{MI}}$. Provided that the Os ions have an Ising-like single ion anisotropy, this seemingly contradictory behavior is understood by considering a complex magnetic order parameter consisting of static and dynamically fluctuating components. While the absence of orbital degeneracy disfavors such an anisotropy, it might be caused by a higher order exchange interaction. Then, one possibility is that the internal fields due to the quasi-static component (e.g., along [111] axis) may cancel with each other at the muon site due to the symmetric spin configuration, while the fluctuating (transverse) component leads to complete muon depolarization.

Another intriguing possibility would be a situation similar to the partially disordered (PD) phase observed in the Ising antiferromagnets on the two-dimensional triangular lattice (2D-TL), where one of the sublattices remains disordered due to the second nearest exchange interaction and dynamically replaces with each other.\textsuperscript{15–19} Very recently, an interesting observation similar to the present case has been reported on NaCrO$_2$ (a candidate for 2D-TL consisting of the edge-sharing CrO$_6$ octahedra), where a quasi-static internal field detected by $\mu$SR and Na-NMR measurements develops only over a lower temperature range that is far below the temperature at which the susceptibility and specific heat exhibit an anomalous peak.\textsuperscript{20} The wipe-out of NMR signal at the intermediate temperature strongly suggests the presence of fast spin fluctuation, whereas its recovery at further lower temperatures is explained by the freezing of the fluctuating spins. Despite the difference in the lattice dimensionality between those systems, the observed tendency suggests a possible common background between 2D-TL and the pyrochlore. It might be also interesting to note that they share a feature of completely filled $t_{2g}$ orbitals (3$d^1$ for Cr$^{3+}$) that may keep the system away from the Jahn-Teller like distortion. Unfortunately, this in turn give rise to the absence of anisotropy in the exchange interaction: such anisotropy is presumed to be a key prerequisite for the PD phase in 2D-TL.

In the case of NaCrO$_2$, they discuss possible role of so-called “$Z_2$ vortices” predicted for the 2D Heisenberg antiferromagnets,\textsuperscript{21} where the dynamical character of the $Z_2$ vortices leads to spin fluctuation over an intermediate temperature range, while a short-range order due to the pairing of $Z_2$ vortices is anticipated at lower temperatures. The present result on Cd$_2$Os$_2$O$_7$ seems to share a remarkable similarity with the behavior predicted for the 2D-TL case. However, it is clear that the three-dimensional version of the theoretical model is needed to understand the microscopic property of the Heisenberg antiferromagnets on the pyrochlore lattice.

In summary, it is inferred from $\mu$SR measurements in Cd$_2$Os$_2$O$_7$ that strong spin fluctuation persists below the MI transition, which is followed by the transition to a quasi-static SDW ground state with decreasing temperature below $T_{\text{SDW}} \simeq 150$ K. These observations suggest the predominant role of geometrical frustration and occurrence of anomalous magnetic ground state on the undistorted pyrochlore lattice. Further study including the development of appropriate theoretical model for the pyrochlore magnets is required for the quantitative understanding of the ground state.

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