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## Metal-Insulator Transitions in Pyrochlore Oxides $Ln_2Ir_2O_7$

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We report the physical properties of  $Ln_2Ir_2O_7$  ( $Ln = \text{Nd, Sm, Eu, Gd, Tb, Dy, and Ho}$ ), which exhibit metal-insulator transitions (MITs) at different temperatures. The transition temperature  $T_{\text{MI}}$  increases with a reduction in the ionic radius of  $Ln$ . The ionic radius boundary for MITs in  $Ln_2Ir_2O_7$  lies between  $Ln = \text{Pr}$  and  $\text{Nd}$ . MITs in  $Ln_2Ir_2O_7$  have some common features. They are second-order transitions. Under the field cool condition, a weak ferromagnetic component ( $\sim 10^{-3} \mu_{\text{B}}/\text{f.u.}$ ) caused by Ir 5d electrons is observed below  $T_{\text{MI}}$ . The entropy associated with MITs for  $Ln = \text{Nd, Sm, and Eu}$  is estimated to be 0.47, 2.0, and 1.4 J/K mole, respectively. The change in entropy is much smaller than  $2R \ln 2$  [11.5 J /K mole] expected in a magnetic transition due to localized moments of  $S = 1/2$ . The feature of continuous MITs in  $Ln_2Ir_2O_7$  is discussed.

KEYWORDS: metal-insulator transition, pyrochlore oxides,  $\text{Nd}_2\text{Ir}_2\text{O}_7$ ,  $\text{Sm}_2\text{Ir}_2\text{O}_7$ ,  $\text{Eu}_2\text{Ir}_2\text{O}_7$ ,  $\text{Gd}_2\text{Ir}_2\text{O}_7$ ,  $\text{Tb}_2\text{Ir}_2\text{O}_7$ ,  $\text{Dy}_2\text{Ir}_2\text{O}_7$ ,  $\text{Ho}_2\text{Ir}_2\text{O}_7$

### 1. Introduction

In recent years, pyrochlore oxides have been actively researched on account of their structure. These oxides are composed of a network of corner-shared tetrahedra, whose vertices are occupied by spins; these spins may give rise to strong geometrical frustration.<sup>1–6</sup> An important issue that has to be solved is the clarification of how the geometrical frustration influences the ground states of strongly correlated electron systems in three-dimensional triangle-based lattices. In the case of metallic pyrochlore oxides, the frustration originating from the pyrochlore lattice might also lead to novel types of electronic properties. 4d and 5d transition-metal pyrochlore oxides have recently attracted considerable interest because of their novel transport properties such as the anomalous Hall effect in  $\text{Nd}_2\text{Mo}_2\text{O}_7$  and  $\text{Pr}_2\text{Ir}_2\text{O}_7$ , superconductivity in  $\text{Cd}_2\text{Re}_2\text{O}_7$  and  $A\text{Os}_2\text{O}_6$  ( $A = \text{K, Rb, and Cs}$ ), and the metal-insulator transition (MIT) in  $\text{Cd}_2\text{Os}_2\text{O}_7$ .<sup>7–14</sup>

In a recent study, we successfully synthesized purified polycrystalline samples of pyrochlore iridates  $Ln_2Ir_2O_7$ . We observed that  $Ln_2Ir_2O_7$  for  $Ln = \text{Nd, Sm, and Eu}$  exhibits MITs at 36, 117, and 120 K, respectively.<sup>15</sup> In this case, thermal hysteresis and a discontinuous change in the physical properties of pyrochlore iridates were not observed at the MIT temperature

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$T_{\text{MI}}$ ; from this, we concluded that the MITs were second-order transitions. As the ionic radius of  $Ln$  reduces,  $T_{\text{MI}}$  tends to increase. In the case of  $\text{Pr}_2\text{Ir}_2\text{O}_7$ , no MIT was observed, as it exhibited metallic behavior down to 0.3 K.<sup>16</sup> The ionic radius boundary for MITs in  $Ln_2\text{Ir}_2\text{O}_7$  lies between  $Ln = \text{Pr}$  and  $\text{Nd}$ . The electrical conductivity of  $Ln_2\text{Ir}_2\text{O}_7$  depends on the ionic radius of  $Ln$ . Similar behavior of the dependence of electrical conductivity on ionic radius is also observed in  $Ln_2\text{Mo}_2\text{O}_7$ .<sup>17,18</sup> Since the  $Ln$  ion is trivalent, the  $(5d)^5$  electrons from  $\text{Ir}^{4+}$  form an unfilled  $t_{2g}$  band. The  $4f$  electrons are generally well localized, thus, only the  $5d$  electrons contribute to the electrical conductivity. As the ionic radius of  $Ln$  reduces, the Ir-O-Ir bond angle decreases, consequently, the  $t_{2g}$  bandwidth becomes narrower.<sup>19</sup> Finally, for  $Ln = \text{Y}$ , a Mott insulator is realized because of the strong electron correlations.<sup>20</sup> In a recent theoretical study, for this insulating state of  $Ln_2\text{Ir}_2\text{O}_7$ , the possibility of realizing a topological insulator is discussed.<sup>21</sup> However, the origin of MIT in  $Ln_2\text{Ir}_2\text{O}_7$  is still not clear.

In this paper, we report on the physical properties of higher-quality samples of  $Ln_2\text{Ir}_2\text{O}_7$ , where,  $Ln = \text{Nd}, \text{Sm}, \text{and Eu}$ . In addition, we obtained high-quality samples of heavy rare-earth pyrochlore iridates for  $Ln = \text{Gd}, \text{Tb}, \text{Dy}, \text{and Ho}$ . We also report the physical properties of these heavy rare-earth pyrochlore iridates.

## 2. Experimental Procedure

Polycrystalline samples of  $Ln_2\text{Ir}_2\text{O}_7$  ( $Ln = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{and Ho}$ ) were synthesized by a standard solid-state reaction. The mixtures were prepared using rare-earth oxides (99.99%  $Ln_2\text{O}_3$  for  $Ln = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{and Ho}$ ; 99.99% for  $\text{Pr}_6\text{O}_{11}$ ; 99.99% for  $\text{Tb}_4\text{O}_7$ ),  $\text{IrO}_2$  (Tanaka Kikinzoku Kogyo) or Ir metal (Tanaka Kikinzoku Kogyo). The molar ratio of  $Ln$  to Ir was 1 : 1.1. The mixtures were then pressed into pellets, which were then inserted into a Pt tube and heated at 1423 - 1523 K for about 10 days in a vacuum silica tube with several intermediate grindings. After adding 10 mol%  $\text{IrO}_2$ , the process was continued for 4 days with several intermediate grindings. The last process was repeated once. The reaction products were identified by powder X-ray diffraction (XRD) measurements. Their XRD patterns indicated a single phase with a cubic pyrochlore structure. From the result of their XRD patterns, we confirmed that the obtained samples are of high quality; the sample of  $\text{Sm}_2\text{Ir}_2\text{O}_7$  is that denoted by #2 in our previous paper.<sup>15</sup> The obtained lattice parameters are broadly consistent with the previous results.<sup>1,22</sup>

The electrical resistivity of the obtained samples was measured by a DC four-probe method from 4.2 to 300 K. The thermoelectric power was measured by a differential method using a pair of thermocouples (chromel/Au + 7 at% Fe) from 4.2 to 300 K. DC magnetizations were measured using a SQUID magnetometer (MPMS, Quantum Design, Inc.). Specific heat measurements were performed by a thermal relaxation method (PPMS, Quantum Design, Inc.).

As is reported in ref. 15, we were unable to prepare samples free from impurity phases

by a solid-state reaction in air because of the volatility of  $\text{IrO}_2$ . Furthermore, their reflection peaks in XRD patterns were much broader. This result indicates that the samples prepared in air have poorer crystallinity or deviate from their stoichiometry. Note that before our study in ref. 15, all polycrystalline samples were prepared by a solid-state reaction in air.<sup>20,22–26</sup>

### 3. Results and Discussion

#### 3.1 Resistivity

Figure 1 shows the temperature dependence of the electrical resistivities  $\rho(T)$  of  $\text{Ln}_2\text{Ir}_2\text{O}_7$  for  $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy},$  and  $\text{Ho}$ . When  $\text{Ln}$  is changed from Pr to Dy,  $\rho(T)$  at room temperature gradually increases;  $\rho(T)$  for  $\text{Ln} = \text{Ho}$  at room temperature is lower than that for Dy.<sup>27</sup> The gradient of  $\rho(T)$  at room temperature gradually changes from a positive value to a negative value. For  $\text{Ln} = \text{Pr}$  and  $\text{Nd}$ ,  $\text{Ln}_2\text{Ir}_2\text{O}_7$  is metallic. For  $\text{Ln} = \text{Sm}, \text{Eu},$  and  $\text{Gd}$ ,  $\text{Ln}_2\text{Ir}_2\text{O}_7$  is semimetallic. For  $\text{Ln} = \text{Tb}, \text{Dy},$  and  $\text{Ho}$ ,  $\text{Ln}_2\text{Ir}_2\text{O}_7$  is semiconducting. We found that, for  $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy},$  and  $\text{Ho}$ ,  $\text{Ln}_2\text{Ir}_2\text{O}_7$  exhibits MITs at 33, 117, 120, 127, 132, 134, and 141 K, respectively, while  $\text{Pr}_2\text{Ir}_2\text{O}_7$  exhibits no MIT down to 0.3 K; it should be noted that  $T_{\text{MI}}$  for  $\text{Ln} = \text{Nd}$  is revised to 33 K.<sup>28,29</sup> Now, although the conductivity of  $\text{Ln}_2\text{Ir}_2\text{O}_7$  for  $\text{Ln} = \text{Tb}, \text{Dy},$  and  $\text{Ho}$  is semiconducting with a small energy gap at room temperature, we have adopted MIT for convenience because a common feature in their transition is observed.  $T_{\text{MI}}$  increases monotonically as the ionic radius of  $\text{Ln}$  decreases. The ionic radius boundary for MITs in  $\text{Ln}_2\text{Ir}_2\text{O}_7$  lies between  $\text{Ln} = \text{Pr}$  and  $\text{Nd}$ . For  $\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy},$  and  $\text{Ho}$ , a clear upturn due to MIT is shown in Fig. 1(b). Discontinuities and thermal hysteresis were not observed at approximately  $T_{\text{MI}}$ , indicating that these MITs are second-order transitions. It should be noted that  $\rho(T)$  below  $T_{\text{MI}}$  continues to increase without saturation on cooling. This implies that MITs in  $\text{Ln}_2\text{Ir}_2\text{O}_7$  are not of accidental origin but of essential one.

We then attempted the order estimation of the energy gap in the insulating state from the data. For the data just below  $T_{\text{MI}}$ , we tried to estimate the energy gap by assuming the equation  $\rho(T) = \rho_0 \exp(E_g/T)$ , where  $E_g$  is the energy gap. The estimated  $E_g$  is about 300–600 K;  $E_g$  for  $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy},$  and  $\text{Ho}$  is estimated to be 405, 493, 429, 330, 517, 569, and 463 K, respectively. We found that the energy gap for  $\text{Ln} = \text{Tb}, \text{Dy},$  and  $\text{Ho}$  increases by about 100–200 K below  $T_{\text{MI}}$ . These values may roughly correspond to the energy gap, although no systematic change has been confirmed. The band gap in the insulated state is small in comparison with that in  $3d$  electron system.<sup>30</sup> Below  $T_{\text{MI}}$ ,  $\rho(T)$  cannot be described by the thermal activation conduction form  $\rho(T) = \rho_0 \exp(E_g/T)$ . In addition,  $\rho(T)$  below  $T_{\text{MI}}$  cannot be expressed in terms of the variable range hopping except for  $\text{Ln} = \text{Eu}$ .<sup>31</sup> Further investigation on the unconventional temperature dependence of resistivity in the insulating state is required to verify the origin.

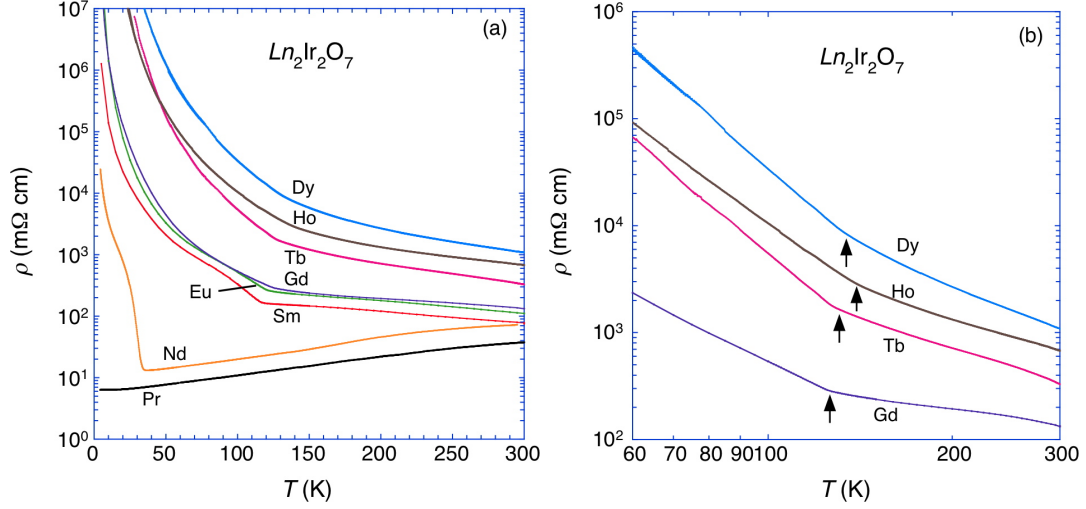


Fig. 1. (a) (Color online) Electrical resistivities of  $\text{Ln}_2\text{Ir}_2\text{O}_7$  for  $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}$ , and  $\text{Ho}$ . (b) (Color online) Enlarged view of electrical resistivities of  $\text{Ln}_2\text{Ir}_2\text{O}_7$  for  $\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$ , and  $\text{Ho}$ .

### 3.2 Thermoelectric power

Figure 2 shows the temperature dependences of the thermoelectric powers  $S(T)$  of  $\text{Ln}_2\text{Ir}_2\text{O}_7$  for  $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$ , and  $\text{Gd}$ . When  $\text{Ln}$  is changed from  $\text{Pr}$  to  $\text{Gd}$ , the sign of  $S(T)$  at room temperature changes from negative to positive; this result suggests that the main carrier changes from electron-like for  $\text{Ln} = \text{Pr}$  to hole-like for  $\text{Ln} = \text{Gd}$ .  $S(T)$  for  $\text{Ln} = \text{Pr}$  and  $\text{Nd}$  is negative above 11 K. The sign of  $S(T)$  changes to positive below 11 K. The  $S(T)$  for  $\text{Ln} = \text{Pr}$  and  $\text{Nd}$  have broad minima at around 65 and 80 K, respectively. The temperature dependences of the  $S(T)$  for  $\text{Ln} = \text{Pr}$  and  $\text{Nd}$  are quite different from that of a normal metal. The absolute values of the  $S(T)$  for  $\text{Ln} = \text{Pr}$  and  $\text{Nd}$  are also larger than that of a normal metal.  $S(T)$  for  $\text{Ln} = \text{Nd}$  bends slightly downward at  $T_{\text{MI}}$ . Below  $T_{\text{MI}}$ ,  $S(T)$  for  $\text{Ln} = \text{Nd}$  shows a complex temperature dependence on cooling. On the other hand, the  $S(T)$  for  $\text{Ln} = \text{Sm}, \text{Eu}$ , and  $\text{Gd}$  are positive.  $S(T)$  at room temperature increases when  $\text{Ln}$  is changed from  $\text{Sm}$  to  $\text{Gd}$ . The  $S(T)$  for  $\text{Ln} = \text{Sm}, \text{Eu}$ , and  $\text{Gd}$  gradually increase on cooling. Broad maxima for  $\text{Ln} = \text{Sm}, \text{Eu}$ , and  $\text{Gd}$  appear at 150, 175, and 200 K, respectively. These features are consistent with those of the semimetallic behavior of the  $\rho(T)$  for  $\text{Ln} = \text{Sm}, \text{Eu}$ , and  $\text{Gd}$ . At  $T_{\text{MI}}$ , the  $S(T)$  for  $\text{Ln} = \text{Sm}, \text{Eu}$ , and  $\text{Gd}$  exhibit a clear upturn.

$S(T)$  for  $\text{Ln} = \text{Eu}$  at 300 K ( $36 \mu\text{V}/\text{K}$ ) is larger than that for sample #1 ( $27 \mu\text{V}/\text{K}$ ), as reported in a previous paper.<sup>15</sup> Furthermore, in the first report on the  $S(T)$  of  $\text{Eu}_2\text{Ir}_2\text{O}_7$  synthesized in air,  $S(T)$  ( $10 \mu\text{V}/\text{K}$ ) is much smaller than that of the samples synthesized in a vacuum silica tube.<sup>23</sup> This strong sample dependence on  $S(T)$  suggests an influence of the flat-band structure on the pyrochlore lattice. In particular, because  $\text{Eu}_2\text{Ir}_2\text{O}_7$  is semimetallic, the carrier density is sensitive to deviations from the stoichiometry.

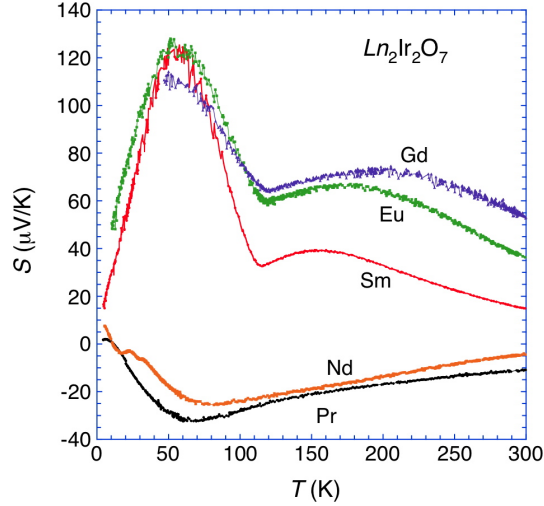


Fig. 2. (Color online) Thermoelectric powers of  $Ln_2Ir_2O_7$  for  $Ln = Pr, Nd, Sm, Eu,$  and  $Gd$ .

### 3.3 Magnetic susceptibility

Figure 3 shows the magnetic susceptibilities  $M/H$  of  $Ln_2Ir_2O_7$  for  $Ln = Nd, Sm, Eu, Gd, Tb, Dy,$  and  $Ho$ ; the applied magnetic fields are 1 kOe for  $Ln = Nd, Sm, Eu,$  and  $Gd$  and 50 G for  $Ln = Tb, Dy,$  and  $Ho$ . It should be noted that a difference in the  $M/H$  measured under the zero-field-cooled (ZFC) and field-cooled (FC) conditions is unexceptionally observed in the MIT of  $Ln_2Ir_2O_7$ .  $M/H$  measured under the ZFC condition show a small peak or a weak kink at  $T_{MI}$ . On the other hand,  $M/H$  measured under the FC condition shows an upturn at  $T_{MI}$  and tends to saturate far below  $T_{MI}$ . Although the anomalies in the  $\rho(T)$  of  $Ln_2Ir_2O_7$  ( $Ln = Tb, Dy,$  and  $Ho$ ) are unclear, there is a clear difference between the  $M/H$  measured under ZFC and FC conditions below  $T_{MI}$ . Therefore, the anomaly in  $M/H$  is a common feature of the MIT of  $Ln_2Ir_2O_7$ . Hereafter, we will discuss the origin of the anomaly in  $M/H$ . The magnetization process at 5 K in  $Sm_2Ir_2O_7$  has been reported by Taira *et al.*<sup>26</sup> The magnetization under the FC condition indicates the emergence of very weak ferromagnetic components ( $\sim 10^{-3} \mu_B/\text{f.u.}$ ) below  $T_{MI}$ . The difference in the  $M/H$  measured under the ZFC and FC conditions is attributed to the very weak ferromagnetic components. The present result indicates that the observed emergence of very weak ferromagnetic components is intrinsic. However, it is very difficult to consider the very weak ferromagnetic ordering as the origin of MIT because the observed ferromagnetic moment is very small as magnetic ordering. Therefore, it is reasonable to consider that the emergence of very weak ferromagnetic components is caused by an additional effect. We should explore another possibility as the origin of MIT. A canted antiferromagnetic ordering is speculated as one of the candidates. Lastly, we have pointed out that a difference in the  $M/H$  measured under the ZFC and FC conditions is also observed in the MIT of  $Cd_2Os_2O_7$  just below  $T_{MI} = 225$  K.<sup>14</sup> Further studies of the magnetic ordered state below  $T_{MI}$  are highly desirable.

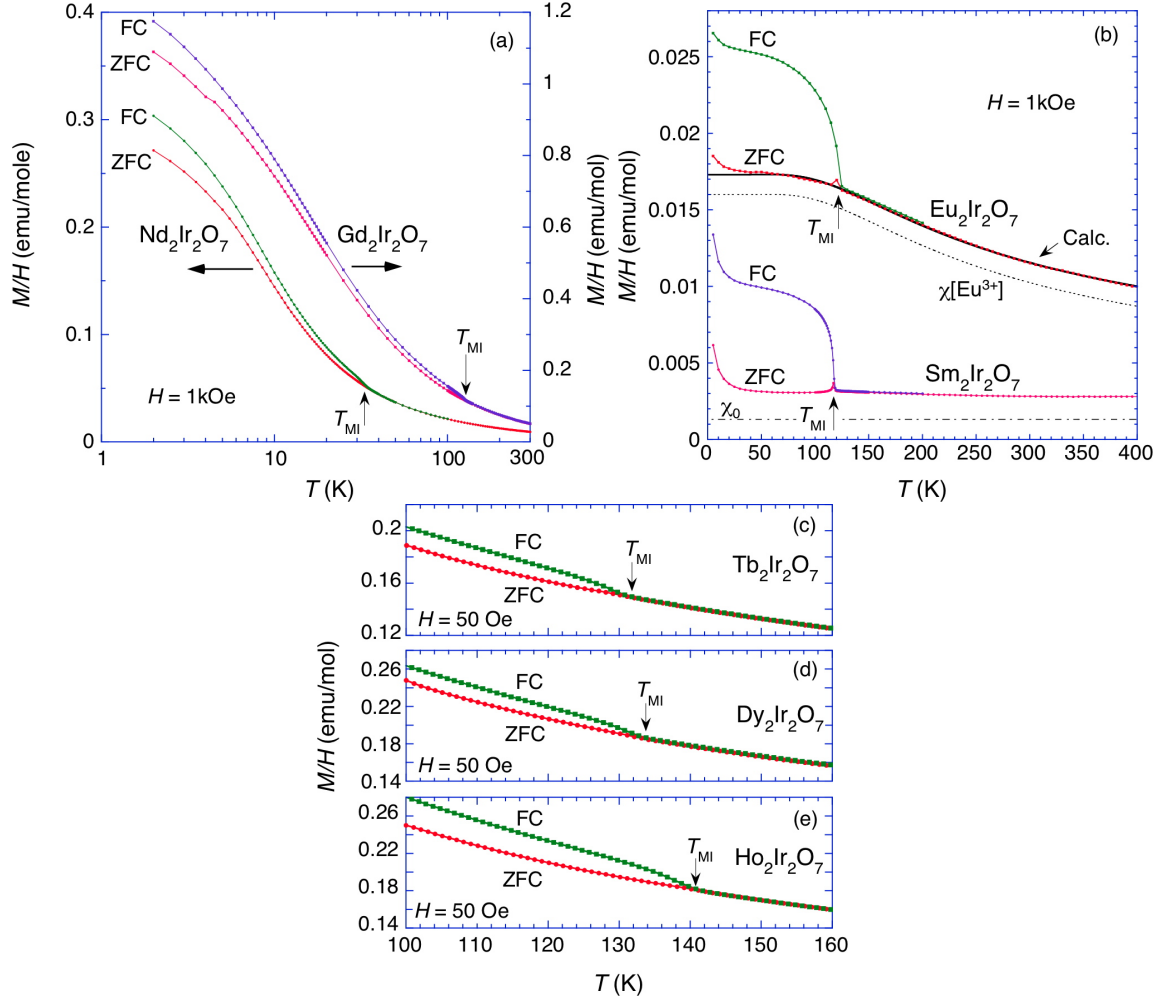


Fig. 3. (a) (Color online) Magnetic susceptibilities  $M/H$  of  $\text{Nd}_2\text{Ir}_2\text{O}_7$  and  $\text{Gd}_2\text{Ir}_2\text{O}_7$  in a magnetic field of 1 kOe. (b) (Color online)  $M/H$  of  $\text{Sm}_2\text{Ir}_2\text{O}_7$  and  $\text{Eu}_2\text{Ir}_2\text{O}_7$  in a magnetic field of 1 kOe. The data of  $\text{Sm}_2\text{Ir}_2\text{O}_7$  is the same as that reported in ref. 15. Fitting curve (solid line) for magnetic susceptibility of  $\text{Eu}_2\text{Ir}_2\text{O}_7$  above  $T_{\text{MI}}$ . The dotted line indicates the contribution of the Van Vleck susceptibility due to  $\text{Eu}^{3+}$  with a spin-orbit coupling constant  $\lambda = 375 \text{ K}$ . The dash-dotted line shows a constant contribution  $\chi_0 = 1.3 \times 10^{-3} \text{ emu/mole}$ .  $M/H$  in a magnetic field of 50 Oe around  $T_{\text{MI}}$  for (c) (Color online)  $Ln = \text{Tb}$ , (d) (Color online)  $Ln = \text{Dy}$ , and (e) (Color online)  $Ln = \text{Ho}$ .

Next we will discuss the contribution of the  $Ln$  site in the magnetic susceptibility of  $Ln_2\text{Ir}_2\text{O}_7$ . In Fig. 3(a), below  $T_{\text{MI}}$ , the  $M/H$  of  $\text{Nd}_2\text{Ir}_2\text{O}_7$  under both the FC and ZFC conditions increase up to 2 K. This increase is caused by the magnetic moment of the  $\text{Nd}^{3+}$  ion as the crystalline electric field (CEF) with the  $D_{3d}$  symmetry splits the ground state  $J = 9/2$  multiplet in  $\text{Nd}^{3+}$  into five Kramers doublets. Figure 4(a) shows the reciprocal magnetic susceptibility  $(M/H)^{-1}$  of  $\text{Nd}_2\text{Ir}_2\text{O}_7$  measured in a magnetic field of 1 kOe. The ZFC data in the temperature range of 10 to 30 K ( $< T_{\text{MI}}$ ) is fitted by using the Curie-Weiss (CW) law. It

is known that the magnetic moment of  $\text{Nd}^{3+}$  in the pyrochlore oxide  $\text{Nd}_2\text{Mo}_2\text{O}_7$  has a  $\langle 111 \rangle$  local Ising anisotropy axis.<sup>7</sup> Assuming  $\langle 111 \rangle$  local Ising anisotropy, we obtained an effective moment  $\mu_{\text{eff}} = 2.73 \mu_{\text{B}}$  and a CW temperature  $\Theta_{\text{CW}} = -3.0$  K by CW fitting. The estimated  $\mu_{\text{eff}}$  is close to that of the pyrochlore oxide  $\text{Nd}_2\text{Sn}_2\text{O}_7$  ( $\mu_{\text{eff}} = 2.63 \mu_{\text{B}}$ ), where the  $\text{Sn}^{4+}$  ion is non-magnetic and shows an AFM ordering at 0.91 K.<sup>32</sup> The deviation from the CW law becomes clear below 8 K. The increase in  $M/H$  is suppressed to below 8 K.

Next, the  $M/H$  of  $\text{Sm}_2\text{Ir}_2\text{O}_7$  exhibits a very weak temperature dependence above  $T_{\text{MI}}$  [Fig. 3(b)]. Both the ZFC and FC results indicate that  $M/H$  increases below 40 K. This increase in the  $M/H$  of  $\text{Sm}_2\text{Ir}_2\text{O}_7$  is caused by the magnetic moment of the  $\text{Sm}^{3+}$  ion; this is because the CEF with the  $D_{3d}$  symmetry splits the ground state  $J = 5/2$  multiplet in  $\text{Sm}^{3+}$  into three Kramers doublets. Further study of the CEF states is needed in order to characterize the magnetic properties of  $\text{Sm}_2\text{Ir}_2\text{O}_7$ .

Next, the  $M/H$  of  $\text{Eu}_2\text{Ir}_2\text{O}_7$  exhibits Van Vleck paramagnetism at low temperatures as  $\text{Eu}^{3+}$  has the ground state  $J = 0$  multiplet [Fig. 3(b)]. In the case of  $\text{Eu}^{3+}$  ( $4f^5$ ), the energy splitting between the ground state ( $J = 0$ ) and the 1st excited states ( $J = 1$ ) is known to be  $\sim 300$  K. This energy splitting corresponds to the spin-orbit coupling constant  $\lambda$ . The equation for the  $\chi(T)$  of  $\text{Eu}^{3+}$  ions was obtained by Van Vleck; in the equation, the CEF effect is not considered.<sup>33</sup> Therefore, the slight upturn in the  $M/H$  of  $\text{Eu}_2\text{Ir}_2\text{O}_7$  below 10 K is caused by a small amount of magnetic impurity [Fig. 3(b)]. By using the Van Vleck equation, we tried to reproduce the  $M/H$  of  $\text{Eu}_2\text{Ir}_2\text{O}_7$  above  $T_{\text{MI}}$  using  $\lambda$  and a constant ( $\chi_0$ ) as fitting parameters. Then, we obtained a good fit for the parameters of  $\lambda = 375$  K and  $\chi_0 = 1.3 \times 10^{-3}$  emu/mol [see Fig. 3(b)]. This result suggests that the  $5d$  electrons from Ir are not localized above  $T_{\text{MI}}$ . A low carrier from the  $t_{2g}$  band, indicating semimetallic behavior, shows Pauli paramagnetism above  $T_{\text{MI}}$ . Note that this value of Pauli paramagnetism is close to that estimated in  $\text{Pr}_2\text{Ir}_2\text{O}_7$ .<sup>16</sup> Since  $\text{Pr}_2\text{Ir}_2\text{O}_7$  is metallic, the carrier density is much higher than that of  $\text{Eu}_2\text{Ir}_2\text{O}_7$ . Therefore, it is speculated that the Pauli paramagnetism from  $5d$  electrons in  $\text{Eu}_2\text{Ir}_2\text{O}_7$  is enhanced by an electron correlation effect.

Next, in Fig. 3(a), the  $M/H$  of  $\text{Gd}_2\text{Ir}_2\text{O}_7$  under both the FC and ZFC conditions increase up to 2 K. This increase is caused by the magnetic moment of the  $\text{Gd}^{3+}$  ion ( $^8S_{7/2}$  ground state), which exhibits magnetic isotropy. Figure 4(b) shows the reciprocal magnetic susceptibility  $(M/H)^{-1}$  of  $\text{Gd}_2\text{Ir}_2\text{O}_7$  measured in a magnetic field of 1 kOe. Above  $T_{\text{MI}}$ , the  $(M/H)^{-1}$  of  $\text{Gd}_2\text{Ir}_2\text{O}_7$  is well followed by the CW law. Assuming the CW law in the temperature range of 150-300 K, we obtained  $\Theta_{\text{CW}} = -7.9$  K and  $\mu_{\text{eff}} = 7.91 \mu_{\text{B}}$ . The estimated  $\mu_{\text{eff}}$  is very close to  $7.94 \mu_{\text{B}}$  for the  $^8S_{7/2}$  ground state of the  $\text{Gd}^{3+}$  ion. In fact,  $\mu_{\text{eff}} = 7.96 \mu_{\text{B}}$  in the highly frustrated pyrochlore magnet  $\text{Gd}_2\text{Sn}_2\text{O}_7$  (where the  $\text{Sn}^{4+}$  ion is nonmagnetic and shows AFM ordering at 1.0 K) is consistent with the above-mentioned value.<sup>32,34</sup> If  $5d$  electrons from  $\text{Ir}^{4+}$  show a localized magnetism of  $S = 1/2$ ,  $\mu_{\text{eff}}$  is expected to be  $8.124 \mu_{\text{B}}$ . Because the observed



value is much smaller than the expected value, we should consider the itinerant magnetism of  $5d$  electrons above  $T_{\text{MI}}$ . The negative  $\Theta_{\text{CW}}$  suggests an AFM correlation between Gd moments. However, the  $M/H$  under both FC and ZFC conditions show CW behavior below  $T_{\text{MI}}$ . Therefore, Gd moments have no long-range ordering at least down to 2 K.

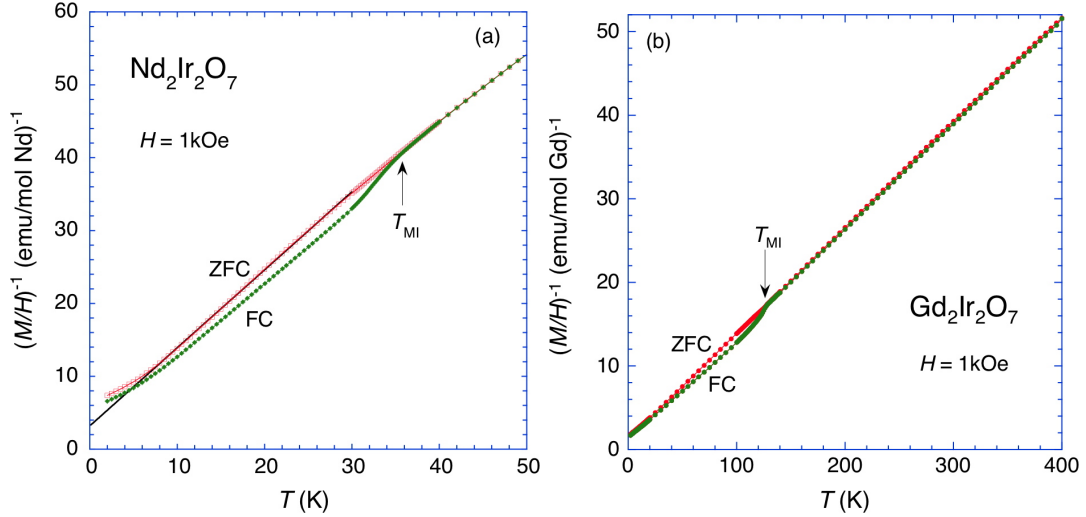


Fig. 4. (a) (Color online) Reciprocal magnetic susceptibility  $(M/H)^{-1}$  of  $\text{Nd}_2\text{Ir}_2\text{O}_7$  below 50 K. The solid line shows a fitting for ZFC data in the temperature range of 10 to 30 K. (b) (Color online) Reciprocal magnetic susceptibility  $(M/H)^{-1}$  of  $\text{Gd}_2\text{Ir}_2\text{O}_7$ .

### 3.4 Specific heat

Figure 5(a) shows the  $C/T$  of  $\text{Nd}_2\text{Ir}_2\text{O}_7$  below 40 K. An anomaly due to MIT is observed at  $T_{\text{MI}}$ , which is consistent with the anomalies in the resistivity, thermoelectric power, and magnetization. The entropy associated with the MIT will be discussed later. Next, Fig. 5(b) shows the  $C/T$  of  $\text{Nd}_2\text{Ir}_2\text{O}_7$  below 25 K.  $C/T$  shows a broad peak at 4 K and a shoulder at 1 K. From the entropy variation, this broad peak is caused by the CEF ground state doublet in  $\text{Nd}^{3+}$ . Then, we can fit the data using the Schottky specific heat of two levels with energy splitting  $\Delta = 13$  K; the lattice contribution estimated from the data of  $\text{Eu}_2\text{Ir}_2\text{O}_7$  is also considered in this fitting. A good fitting is obtained above 5 K. Because  $\text{Nd}^{3+}$  is a Kramers ion, the splitting is caused by the internal field due to a  $d-f$  interaction. This suggests the appearance of an internal field due to MIT below  $T_{\text{MI}}$ . A slight deviation below 5 K may be caused by the influence of a weak interaction between Nd moments.

Figure 6 shows the  $C/T$  of  $\text{Eu}_2\text{Ir}_2\text{O}_7$  and  $\text{Sm}_2\text{Ir}_2\text{O}_7$ . A sharp anomaly in both compounds is observed at  $T_{\text{MI}}$ , which confirms a bulk transition. An upturn in the  $C/T$  of  $\text{Ln} = \text{Sm}$  observed below 7 K is attributed to the tail of a Schottky anomaly due to the CEF ground state doublet in  $\text{Sm}^{3+}$ , as previously reported.<sup>15</sup> Indeed, there is no upturn in the  $C/T$  of

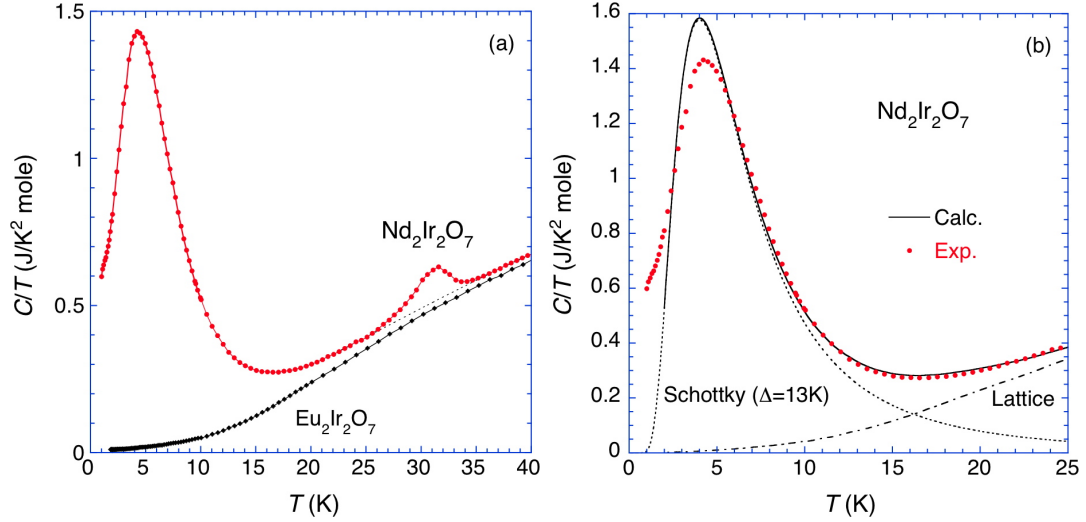


Fig. 5. (a)(Color online) Specific heat divided by temperature  $C/T$  of  $\text{Nd}_2\text{Ir}_2\text{O}_7$ . The broken line shows a smooth polynomial fitted to the data outside the region of the anomaly. (b)(Color online) Analysis of specific heat divided by temperature  $C/T$  of  $\text{Nd}_2\text{Ir}_2\text{O}_7$  below 25 K. The broken line shows the Schottky specific heat with energy splitting  $\Delta = 13$  K. The dash-dotted line shows the lattice contribution estimated from the data of  $\text{Eu}_2\text{Ir}_2\text{O}_7$ . The solid line shows the sum of these contributions.

$L_n = \text{Eu}$  at low temperatures because  $\text{Eu}^{3+}$  has the ground state multiplet of  $J = 0$ . The  $C(T)$  of  $\text{Eu}_2\text{Ir}_2\text{O}_7$  between 1.8 and 9 K can be well fitted by  $C/T = \alpha + \beta T^2$  (the Debye  $T^3$  law); the Debye temperature  $\Theta_D = (12\pi^4 R_g n / 5\beta)^{1/3}$ , where  $R_g$  is the gas constant and  $n = 11$ . In this manner, we obtained  $\alpha = 8.6$  mJ/K<sup>2</sup> mole and  $\Theta_D = 374$  K.  $\Theta_D$  is slightly larger than the previous value ( $\Theta_D = 304$  K).<sup>24</sup> Here, note that  $\alpha$  does not correspond to an electronic specific heat coefficient because the electrical conductivity for  $L_n = \text{Eu}$  below 10 K extends beyond  $10^6$  m $\Omega$  cm. The result means that  $C(T)$  has a small  $T$ -linear contribution in the insulator. Firstly, the contribution of magnon associated with the AFM order induced by MIT can be considered at low temperatures. However, the  $T$ -linear contribution in  $C(T)$  is known to be attributed to spin wave excitations for one-dimensional antiferromagnets; it is difficult for the pyrochlore lattice to induce a  $T$ -linear contribution. As another possible origin for  $T$ -linear contribution in  $C(T)$  in the insulating state, Anderson localization may be considered.<sup>35</sup> Further investigation is required to reveal the origin of the  $T$ -linear contribution.

Now we will discuss the  $L_n$  dependence of the entropy associated with the MIT ( $\Delta S$ ). To estimate  $\Delta S$ , a smooth polynomial was fitted to the data outside the region of the anomaly; these fitting lines (broken line) for  $L_n = \text{Nd}$ ,  $\text{Sm}$ , and  $\text{Eu}$  are shown in Figs. 5(a), 6(a), and 6(b), respectively. The background contribution was subtracted from the raw data; the electronic portions of the  $C/T$  ( $\Delta C/T$ ) for  $L_n = \text{Sm}$  and  $\text{Eu}$  are shown in the inset. By integrating  $\Delta C/T$ , we obtained  $\Delta S = 0.47$ , 2.0, and 1.4 J/K mole for  $L_n = \text{Nd}$ ,  $\text{Sm}$ , and  $\text{Eu}$ , respectively.

$\Delta S$  is much smaller than  $2R \ln 2$ . If we assume that a localized  $5d$  electron from  $\text{Ir}^{4+}$  ions with  $S = 1/2$  causes a conventional magnetic transition, we can expect a change in entropy of  $2R \ln 2 = 11.5 \text{ J/K mole}$ . The reduction in the amount of change in entropy is considered to be caused by a short-range ordering due to frustration or a reduction in magnetic moment due to the itinerancy of  $5d$  electrons. Next, recently, the Raman scattering spectra of  $\text{Ln}_2\text{Ir}_2\text{O}_7$  for  $\text{Ln} = \text{Nd}, \text{Sm}, \text{and Eu}$  have been measured.<sup>36</sup> Below  $T_{\text{MI}}$ , new peaks appear for  $\text{Ln} = \text{Sm}$  and  $\text{Eu}$ , but no remarkable change is seen for  $\text{Ln} = \text{Nd}$ . The result indicates that  $\text{Sm}_2\text{Ir}_2\text{O}_7$  and  $\text{Eu}_2\text{Ir}_2\text{O}_7$  accompany a structural change with MIT, but this does not occur with  $\text{Nd}_2\text{Ir}_2\text{O}_7$ . Therefore, the  $\Delta S$  for  $\text{Ln} = \text{Sm}$  and  $\text{Eu}$  involve the lattice contribution. Indeed,  $\Delta S$  for  $\text{Ln} = \text{Nd}$  is smaller than those for  $\text{Ln} = \text{Sm}$  and  $\text{Eu}$ . If we consider this  $\Delta S$  in  $\text{Ln} = \text{Nd}$  to be caused by only the electronic contribution without the lattice contribution, we can estimate the electronic specific heat coefficient above  $T_{\text{MI}}$   $\gamma = 14 \text{ mJ/K}^2 \text{ mole}$  by the relation  $\gamma = \Delta S/T_{\text{MI}}$ . As  $\text{Sm}_2\text{Ir}_2\text{O}_7$  and  $\text{Eu}_2\text{Ir}_2\text{O}_7$  are both semimetallic from the behaviors of their  $\rho(T)$  and  $S(T)$ , it is speculated that the  $\gamma$  for  $\text{Ln} = \text{Sm}$  and  $\text{Eu}$  are smaller than that for  $\text{Ln} = \text{Nd}$ .

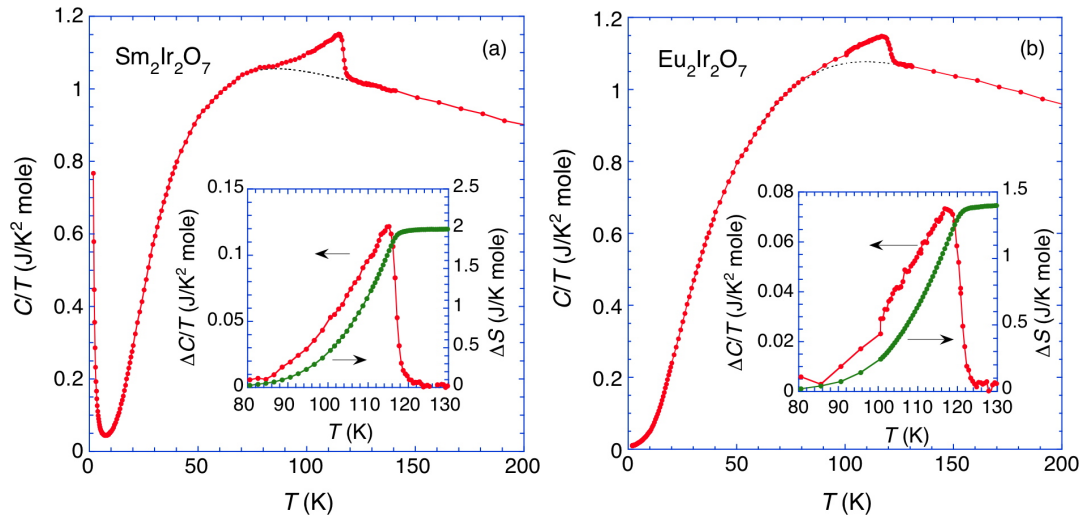


Fig. 6. (Color online) Specific heat divided by temperature,  $C/T$ , of (a)  $\text{Sm}_2\text{Ir}_2\text{O}_7$  and (b)  $\text{Eu}_2\text{Ir}_2\text{O}_7$ . The broken line shows a smooth polynomial fitted to the data outside the region of the anomaly. The inset shows the electronic portion of  $C/T$  ( $\Delta C/T$ ) obtained, as described in the text. The inset also shows the entropy  $\Delta S$  estimated from  $\Delta C/T$ .

### 3.5 Phase diagram

Figure 7 shows the phase diagram of  $\text{Ln}_2\text{Ir}_2\text{O}_7$ , which is based on the  $\text{Ln}^{3+}$  ionic radius dependence of  $T_{\text{MI}}$ ; the ionic radius of  $\text{Ln}^{3+}$  is for an 8-coordination-number site.  $T_{\text{MI}}$  monotonically increases as the ionic radius of  $\text{Ln}^{3+}$  decreases. Obviously,  $T_{\text{MI}}$  does not depend on the de Gennes factor  $(g_J - 1)^2 J(J + 1)$  or the magnetism of  $\text{Ln}^{3+}$ . This MIT is not associated

with the magnetic ordering of  $Ln^{3+}$ . For  $T > T_{MI}$ ,  $Ln = Pr$  and  $Nd$  are metallic. Then,  $Ln = Sm, Eu$  and  $Gd$  are semimetallic and  $Ln = Tb, Dy,$  and  $Ho$  are semiconducting.  $Ln = Pr$  is a unique metal located near the critical point of MIT. In this figure, the extrapolation between  $Ln = Nd$  and  $Pr$  is based on a recent result for resistivity in the solid solution  $(Pr_{1-x}Nd_x)_2Ir_2O_7$ .<sup>37</sup> From the result, the substitution of  $Pr$  by 20%  $Nd$  leads to MIT at around 3 K; below  $T_{MI}$ , the increasing resistivity in this sample is suppressed, and resistivity reaches a finite value at lower temperatures.

Next, we discuss the phase diagram of  $Ln_2Ir_2O_7$  in comparison with that of other rare-earth pyrochlore oxides. The phase diagrams of  $Ln_2Mo_2O_7$  ( $Mo^{4+}: (4d)^2$ ) have already been reported.<sup>38-40</sup> Now, we point out the difference in the phase diagram between  $Ir$  and  $Mo$  pyrochlore oxides. As is described in the introduction, as the ionic radius of  $Ln^{3+}$  decreases, the electrical conductivity in  $Ln_2Mo_2O_7$  becomes semiconducting. Interestingly, the magnetic transition of  $Ln_2Mo_2O_7$  goes from the spin glass insulating state ( $Ln = Gd, Tb, Dy,$  and  $Ho$ ) to the ferromagnetic metallic state ( $Ln = Eu, Sm,$  and  $Nd$ ) as the ionic radius of  $Ln^{3+}$  increases; the ferromagnetic transition comes from  $4d$  electrons. Although the spin glass transition temperature  $T_g$  is independent of  $Ln$  ( $T_g \sim 20$  K), the ferromagnetic transition temperature increases as the ionic radius of  $Ln^{3+}$  increases. In addition, semiconducting  $Ln_2Ru_2O_7$  ( $Ru^{4+}: (4d)^4$ ) shows the frustrated AFM transition originating from  $4d$  electrons.<sup>41</sup> The Néel temperature  $T_N$  monotonically increases from  $T_N = 84$  K for  $Ln = Yb$  to  $T_N = 160$  K for  $Ln = Pr$  as the ionic radius of  $Ln^{3+}$  increases. The present result shows that the magnetic transition (or MIT) in  $Ln_2Ir_2O_7$  decreases as the ionic radius of  $Ln^{3+}$  increases. Then, the opposite dependence of the ionic radius of  $Ln^{3+}$  on the magnetic transition temperature is realized in  $Ln_2Ir_2O_7$ . It is speculated that the difference in their phase diagrams is due to the feature of the  $5d$  electron system, which has a strong spin-orbit interaction and a reduced on-site Coulomb repulsion in comparison with the  $4d$  electron system.<sup>21</sup> Further theoretical study is needed to understand this phase diagram in  $Ln_2Ir_2O_7$ .

#### 4. Conclusions

We report the physical properties (resistivity, thermoelectric power, magnetization, and specific heat) of  $Ln_2Ir_2O_7$  for  $Ln = Nd, Sm, Eu, Gd, Tb, Dy,$  and  $Ho$ .  $Ln_2Ir_2O_7$  for  $Ln = Nd, Sm,$  and  $Eu$  show MITs at 33, 117, and 120 K, respectively. In this study, we revealed that  $Ln_2Ir_2O_7$  for  $Ln = Gd, Tb, Dy,$  and  $Ho$  exhibit MITs at 127, 132, 134, and 141 K, respectively. These MITs in  $Ln_2Ir_2O_7$  has some common features: They are second-order transitions since no thermal hysteresis or no discontinuous change in their physical properties is observed at  $T_{MI}$ . Under the FC condition, a weak ferromagnetic component ( $\sim 10^{-3} \mu_B/f.u.$ ) caused by  $5d$  electrons from  $Ir$  is observed below  $T_{MI}$ . The entropy associated with MIT supports the notion that this system above  $T_{MI}$  is a  $5d$  itinerant electron system. The analysis of the specific heat of  $Nd_2Ir_2O_7$  reveals that an internal field due to the  $d-f$  interaction affects the splitting

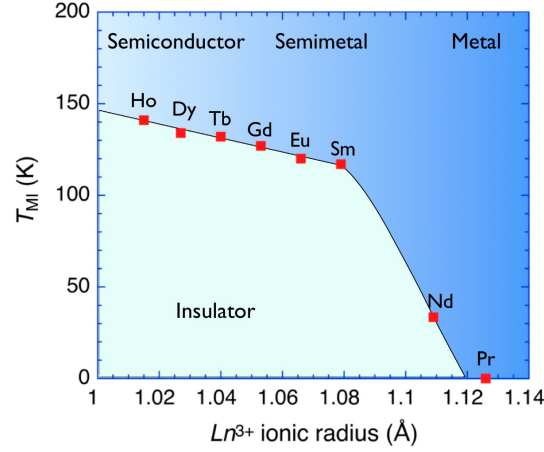


Fig. 7. (Color online) Phase diagram of  $Ln_2Ir_2O_7$  based on  $Ln^{3+}$  ionic radius dependence of  $T_{MI}$ .

of the Kramers ground state doublet below  $T_{MI}$ . Furthermore, we have obtained the phase diagram of  $Ln_2Ir_2O_7$ . The present result shows that  $T_{MI}$  in  $Ln_2Ir_2O_7$  decreases as the ionic radius of  $Ln^{3+}$  increases. Further experimental and theoretical studies are necessary to clarify the origin of MITs in  $Ln_2Ir_2O_7$ .

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present sample; the specific heat data is shown in Fig. 5(a). Therefore, we concluded that  $T_{\text{MI}}$  for  $Ln = \text{Nd}$  is 33 K. The resistivity of  $\text{Nd}_2\text{Ir}_2\text{O}_7$  shows a slight upturn just above  $T_{\text{MI}} = 33$  K, which is affected by the fluctuation in MIT.

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