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Magnetic properties of iridium pyrochlores $R_2Ir_2O_7$ ($R = Y, Sm, Eu$ and Lu)

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Abstract

Magnetic susceptibility, magnetic hysteresis, Mössbauer effect, and specific heat measurements were performed for $R_2Ir_2O_7$ ($R = Y, Sm, Eu$ and Lu), which show magnetic transitions at 150, 115, 120 and 120 K, respectively. Below the transition temperatures there is a large difference in the temperature dependence of the magnetization measured under zero-field-cooled conditions (ZFC) and under field-cooled conditions (FC), but no magnetic hysteresis loop has been observed. The magnetic properties of the Ir pyrochlores are similar to those of isostructural Ru pyrochlores. No sharp anomaly is observed in specific heat data for any of these compounds down to 1.8 K. These results suggest that $R_2Ir_2O_7$ shows spin-glass-like behaviour below the transition temperatures.

1. Introduction

The cubic pyrochlore structure, space group $Fd\bar{3}m$ (no 227), has eight formula units of the general formula $A_2B_2O_7$ in the unit cell and four crystallographically nonequivalent atoms A , B , O , and O' ; thus, it is sometimes preferred to write the pyrochlore formula as $A_2B_2O_6O'$. The larger A cation, the smaller B cation, the oxygen anions O , and O' occupy the $16d$ sites at $(1/2, 1/2, 1/2)$, $16c$ $(0, 0, 0)$, $48f$ $(x, 1/8, 1/8)$, and $8b$ $(3/8, 3/8, 3/8)$, respectively, when the B cation is chosen as the origin. The parameter x is the only positional parameter for the pyrochlore structure.

The oxidation states for the $A_2B_2O_7$ formulation are generally $A_2^{2+}B_2^{5+}O_7^{2-}$ or $A_2^{3+}B_2^{4+}O_7^{2-}$ [1]. We are interested in the latter formulation, i.e., in those pyrochlores for which the A cation is a trivalent rare earth: $R_2^{3+}B_2^{4+}O_7^{2-}$.

Rare-earth pyrochlores show a wide diversity of properties. Some are electrical insulators, and others are low-activation-energy semiconductors [2–4]. In addition to diamagnetism and paramagnetism, ferromagnetism is also encountered in some rare-earth pyrochlores [5–8].

The iridium pyrochlore oxides $R_2Ir_2O_7$ have been characterized by some investigation. The electrical properties for $R_2Ir_2O_7$ appear to be semiconducting with low ρ and activation

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energy [9]. Heat capacity measurements for $\text{Eu}_2\text{Ir}_2\text{O}_7$ and $\text{Lu}_2\text{Ir}_2\text{O}_7$ have been reported in the temperature range 4.2–20 K. No anomalies were noted and the data could be well fitted by the Debye equation. The large density of state values are probably associated with the $5d^5$ electrons in the Ir^{4+} ions [10]. A Mössbauer effect study on $\text{Eu}_2\text{Ir}_2\text{O}_7$ is available at 4.2 K. This investigation did not indicate any magnetic ordering above 4.2 K [11]. However, detailed magnetic susceptibility studies on $\text{R}_2\text{Ir}_2\text{O}_7$ have not been made.

In this paper, we report the synthesis, crystal structure determination and magnetic properties of iridium pyrochlore oxides $\text{R}_2\text{Ir}_2\text{O}_7$ ($\text{R} = \text{Y}, \text{Sm}, \text{Eu}, \text{and Lu}$). Their magnetic properties are investigated by the measurements of the magnetic susceptibility, Mössbauer effect and specific heat.

2. Experimental details

2.1. Sample preparation

As starting materials, rare-earth sesquioxides R_2O_3 ($\text{R} = \text{Y}, \text{Sm}, \text{Eu}, \text{and Lu}$) and iridium metal powders Ir (purity in all cases was more than 99.9 %) were used. The R_2O_3 and Ir were weighed in the correct ratios, intimately mixed, and heated in air at 1073 K for 12 h. After cooling to room temperature, the samples were crushed into powder, reground, pressed into pellets and then reheated at 1273 K for 600 h, with several intermediate regrindings.

2.2. Analysis

X-ray powder diffraction measurements were performed with $\text{CuK}\alpha$ radiation on a Rigaku MultiFlex diffractometer equipped with a curved graphite monochromator. Intensity data were collected by step scanning in the range 10° – 120° at intervals of 0.02° . The structure and lattice parameters were refined with a Rietveld program RIETAN 2000 [12].

2.3. Magnetic measurements

Magnetic susceptibility measurements were performed with a SQUID magnetometer (Quantum Design MPMS model). The temperature dependence of the magnetic susceptibilities was investigated under zero-field-cooled condition (ZFC) and field-cooled condition (FC). The former was measured on heating the sample to 300 K after zero-field cooling to 5 K. The applied magnetic field was 1000 G. The latter was measured on cooling the sample from 300 to 5 K at 1000 G. The field dependence of the magnetization was measured at 5 K by changing the applied magnetic field between $-50\,000$ G and $50\,000$ G.

2.4. ^{151}Eu Mössbauer spectroscopy

^{151}Eu Mössbauer spectra were measured with a VT-6000 spectrometer (Laboratory Equipment Co, Japan) at 11 K, 130 K and room temperature. In order to measure a good spectrum, the sample was thinned. The absorber material $\text{Eu}_2\text{Ir}_2\text{O}_7$ was mixed with fine graphite powders and ground in an agate mortar. The average thickness of $\text{Eu}_2\text{Ir}_2\text{O}_7$ was 7 mg Eu cm^{-2} . The sample lapped in an aluminium foil was cooled down to each temperature by using a variable temperature cryostat system Cryo Mini (Iwatani Industrial Gases Co). The $^{151}\text{Sm}_2\text{O}_3$ source emitting the 21.6 keV γ -rays was maintained at room temperature. The spectrometer was operated in the velocity range $\pm 10\text{ mm s}^{-1}$. The velocity scale was calibrated with the six-line magnetic hyperfine spectrum of α -Fe using a ^{57}Co source. The zero velocity was taken as the absorption of ^{151}Eu in crystalline EuF_3 .

2.5. Specific heat measurements

The specific heat of the samples was measured in the temperature range 1.8–300 K using a relaxation technique supplied by the commercial heat capacity measurement system (Quantum Design, PPMS model). The sample in the form of a pellet (~ 10 mg) was mounted on an aluminium plate with apiezon for better thermal contact.

3. Results and discussion

The results of the x-ray diffraction measurements show that the desired pyrochlore-type compounds $R_2Ir_2O_7$ ($R = \text{Sm, Eu}$) could be prepared as single-phase materials and that small amounts of impurities remained in the desired compounds $R_2Ir_2O_7$ ($R = \text{Y, Lu}$); these were unreacted starting materials R_2O_3 , and iridium dioxide IrO_2 . Additional heat treatment at 1473 K caused the pyrochlore phase to dissociate into two phases. Since these impurities are diamagnetic or very weakly paramagnetic (Pauli paramagnetic), the effect of such impurities on the magnetic properties of the pyrochlore-type compounds is negligible. The lattice parameters and atomic parameters after refinements are listed in table 1. The lattice parameters of $R_2Ir_2O_7$ ($R = \text{Y, Sm, Eu}$ and Lu) are $a = 1.0179, 1.0311, 1.0288$ and 1.0104 nm, respectively, in excellent agreement with those reported by other workers [13].

Table 1. Structural features for $R_2Ir_2O_7$.

	$Y_2Ir_2O_7$	$Sm_2Ir_2O_7$	$Eu_2Ir_2O_7$	$Lu_2Ir_2O_7$
a (nm)	1.0179(4)	1.0311(2)	1.0288(2)	1.0104(2)
x	0.333(2)	0.329(1)	0.331(1)	0.340(1)
Ir–O (nm)	0.198(1)	0.200(1)	0.200(0)	0.201(1)
$6 \times R\text{--}O$ (nm)	0.248(1)	0.254(1)	0.251(1)	0.240(1)
$2 \times R\text{--}O'$ (nm)	0.220(0)	0.232(0)	0.223(0)	0.219(1)
Ir–O–Ir ($^\circ$)	130(1)	132(1)	131(1)	126(0)

Figure 1 shows the temperature dependence of the susceptibilities for $Y_2Ir_2O_7$. It resembles that for an isostructural ruthenium pyrochlore $Y_2Ru_2O_7$ [14] and shows a magnetic transition at around 150 K. The magnetic susceptibilities measured under the zero-field-cooled condition (ZFC) and under the field-cooled condition (FC) show different temperature dependences. Below the transition temperature, the ZFC susceptibilities are almost constant with decreasing temperature, while the FC susceptibilities increase with decreasing temperature. The temperature dependence of the susceptibilities for $Lu_2Ir_2O_7$ is shown in figure 2. It also resembles that for an isostructural ruthenium pyrochlore $Lu_2Ru_2O_7$ [14] and shows magnetic transition at around 120 K. The magnetic susceptibilities measured under the ZFC and under the FC show different temperature dependences. Their magnetic properties should be attributable to the behaviour of the Ir^{4+} ions in the compounds, because both the Y^{3+} ion and the Lu^{3+} ion are diamagnetic.

Figure 3 shows the temperature dependence of the susceptibilities for $Sm_2Ir_2O_7$. The magnetic transition is observed at around 115 K, below which the large difference between the ZFC and FC magnetic susceptibilities have been found. In this case, not only the iridium ion but also the rare-earth ion is paramagnetic. No further magnetic anomaly has been observed below 115 K, unlike the case for the ruthenium pyrochlore $Sm_2Ru_2O_7$ [15]. The temperature dependence of the susceptibilities for $Eu_2Ir_2O_7$ is shown in figure 4. It shows a magnetic transition at around 120 K, although the previous ^{151}Eu Mössbauer effect measurements did

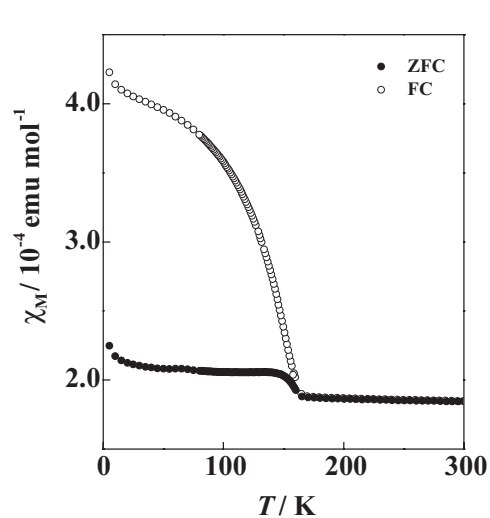


Figure 1. Temperature dependence of the magnetic susceptibilities for $\text{Y}_2\text{Ir}_2\text{O}_7$ per formula unit. Filled symbols: ZFC susceptibilities, open symbols: FC susceptibilities.

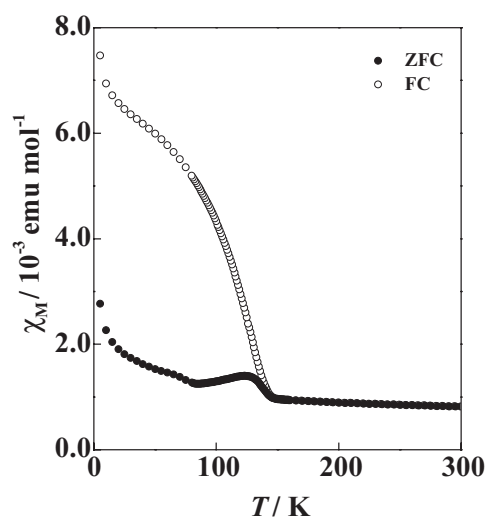


Figure 2. Temperature dependence of the magnetic susceptibilities for $\text{Lu}_2\text{Ir}_2\text{O}_7$ per formula unit. Filled symbols: ZFC susceptibilities, open symbols: FC susceptibilities.

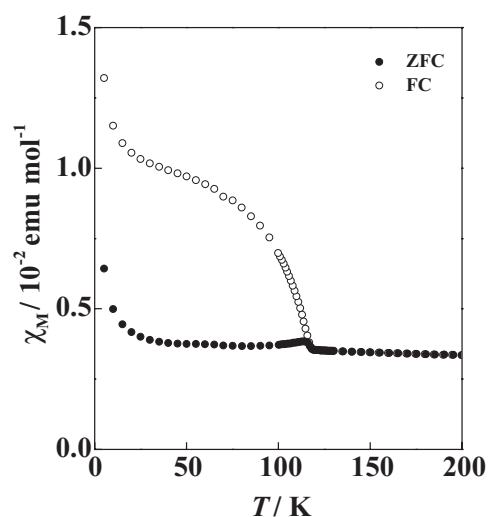


Figure 3. Temperature dependence of the magnetic susceptibilities for $\text{Sm}_2\text{Ir}_2\text{O}_7$ per formula unit. Filled symbols: ZFC susceptibilities, open symbols: FC susceptibilities.

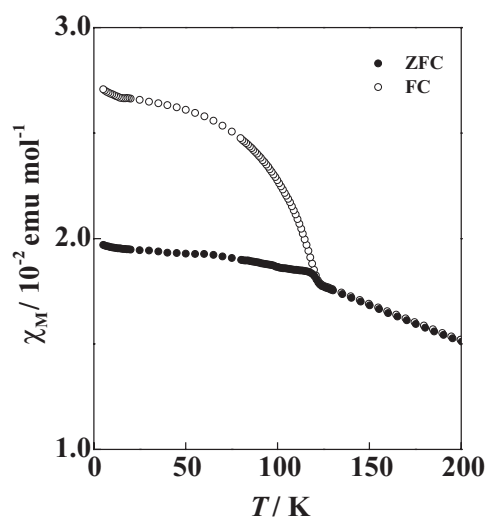


Figure 4. Temperature dependence of the magnetic susceptibilities for $\text{Eu}_2\text{Ir}_2\text{O}_7$ per formula unit. Filled symbols: ZFC susceptibilities, open symbols: FC susceptibilities.

not indicate any magnetic ordering above 4.2 K [11]. Any magnetic anomaly has not been observed below 120 K, which is the same result as that found for $\text{Sm}_2\text{Ir}_2\text{O}_7$.

The ^{151}Eu Mössbauer spectra were measured to observe the magnetic hyperfine interaction for $\text{Eu}_2\text{Ir}_2\text{O}_7$. Their temperature dependence is shown in figure 5. No split of the spectra attributable to the magnetic hyperfine interaction is detected even below the magnetic transition

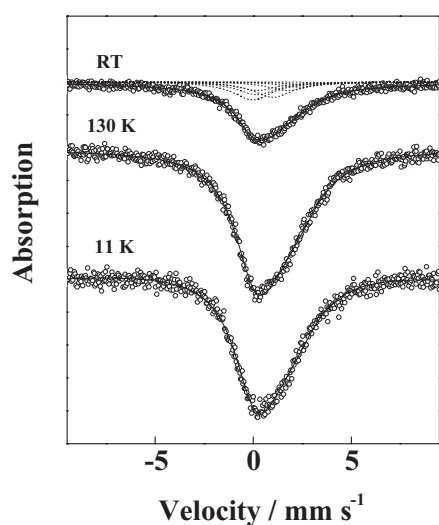


Figure 5. ^{151}Eu Mössbauer spectra of $\text{Eu}_2\text{Ir}_2\text{O}_7$. The solid lines are computer fits with eight Lorentzians.

temperature, while the quadrupole splitting is greater with decreasing temperature. The Eu ions in $\text{Eu}_2\text{Ir}_2\text{O}_7$ occupy a threefold symmetry site ($\bar{3}m$ symmetry), therefore the electric field gradient (EFG) tensors at this site are axially symmetric ($\eta = 0$). The hyperfine quadrupole interaction for the axial EFG can be written as

$$H = [e^2qQ/4I(2I - 1)][3I_z^2 - I(I + 1)] \quad (1)$$

where I is the nuclear spin, Q is the quadrupole moment, $eq = V_{zz}$ is the principal EFG. All the solid curves shown with the spectra in figure 5 are the results of computer fits using equation (1). The fit assumes eight transition lines of equal linewidths. The positions of these lines are specified by a value of an isomer shift δ and a quadrupole coupling constant e^2qQ_0 . The intensity ratios of the eight lines are determined by the Clebsch–Gordan coefficients. The quadrupole moment ratio Q_e/Q_0 is taken to be 1.34 [16]. Table 2 lists the ^{151}Eu Mössbauer parameters determined for $\text{Eu}_2\text{Ir}_2\text{O}_7$. The derived parameters are in excellent agreement with the results reported previously [11].

Table 2. ^{151}Eu Mössbauer parameters of $\text{Eu}_2\text{Ir}_2\text{O}_7$.

	δ (mm s $^{-1}$)	e^2qQ_0 (mm s $^{-1}$)
11 K	0.69(1)	−9.4(2)
130 K	0.75(1)	−9.3(2)
Room temperature	0.68(1)	−8.3(2)

In order to check the origin of the difference between the ZFC and FC magnetic susceptibilities below the transition temperature, magnetic hysteresis measurements (field dependence of the magnetization) were performed on $R_2\text{Ir}_2\text{O}_7$ ($R = \text{Y}, \text{Sm}, \text{Eu}$ and Lu). The results are very similar. Figure 6 shows the magnetic hysteresis curve for $\text{Sm}_2\text{Ir}_2\text{O}_7$. No magnetic hysteresis loop has been observed, but the results of the FC magnetization measurements differ from those of the ZFC magnetization measurements. In the case of field cooling, remanent magnetization exists in zero magnetic field, unlike the case of zero-field cooling, which leads to the spin-frozen state of the magnetic elements [17, 18]. These results show that there is no possibility of a contribution from a ferromagnetic component to the

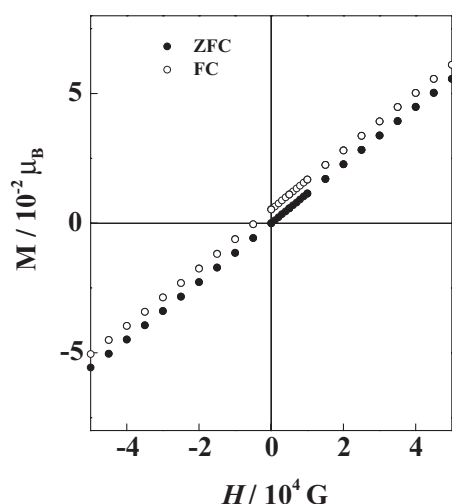


Figure 6. Magnetic hysteresis curves (field-dependence of the magnetization per formula unit) for $\text{Sm}_2\text{Ir}_2\text{O}_7$ at 5 K.

magnetic properties of $\text{R}_2\text{Ir}_2\text{O}_7$, i.e., no ferromagnetic ordering is observed for $\text{R}_2\text{Ir}_2\text{O}_7$ even at 5 K.

Figure 7 shows the temperature dependence of the specific heat for $\text{R}_2\text{Ir}_2\text{O}_7$ ($\text{R} = \text{Y}, \text{Sm}, \text{Eu}$ and Lu). No sharp anomaly is observed for any of these compounds down to 1.8 K. At low temperatures, the specific heat C can be well described by the relation $C = \gamma T + \beta T^3$. The values of γ , β , and the Debye temperature, θ_D for $\text{R} = \text{Y}, \text{Eu}$ and Lu are determined by least-squares fitting in the temperature range below 6 K. Since the specific heat data for $\text{Sm}_2\text{Ir}_2\text{O}_7$ were not well described by the expression $C = \gamma T + \beta T^3$, the value of γ was not determined. The value of θ_D was calculated by using the expression

$$\beta = N(12/5)\pi^4 R(1/\theta_D)^3 \quad (2)$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and $N = 11$. The values of γ , β , and θ_D are listed in table 3. They are in good agreement with the results reported previously for $\text{R} = \text{Eu}, \text{Lu}$ [10]. The absence of sharp anomalies in the specific heat versus temperature curves indicates that these transitions are not due to long-range magnetic ordering. These experimental results are similar to the case for molybdenum pyrochlores rather than ruthenium pyrochlores, where sharp λ -type peak is seen at its magnetic transition temperature in the specific heat data [19]. The behaviour of magnetic specific heat and magnetic entropy for $\text{R}_2\text{Mo}_2\text{O}_7$ indicates that magnetic transitions in these compounds are due to the spin-glass-like ordering of Mo^{4+} ions [20]. For $\text{R}_2\text{Ir}_2\text{O}_7$, it is quite likely that the magnetic transitions are caused by the spin-glass-like ordering of Ir^{4+} ions.

Table 3. Values of γ , β , and θ_D for $\text{R}_2\text{Ir}_2\text{O}_7$.

	$\text{Y}_2\text{Ir}_2\text{O}_7$	$\text{Eu}_2\text{Ir}_2\text{O}_7$	$\text{Lu}_2\text{Ir}_2\text{O}_7$
γ ($\text{mJ mol}^{-1} \text{ K}^{-2}$)	8.1(6)	14.4(5)	10.1(1)
β ($\text{mJ mol}^{-1} \text{ K}^{-4}$)	0.32(2)	0.53(2)	0.50(2)
θ_D (K)	406(8)	343(4)	350(5)

In conclusion, the magnetic properties of the Ir pyrochlores are similar to those of isostructural Ru pyrochlores, except that for $\text{R}_2\text{Ru}_2\text{O}_7$ ($\text{R} = \text{Sm}, \text{Eu}$) another magnetic anomaly

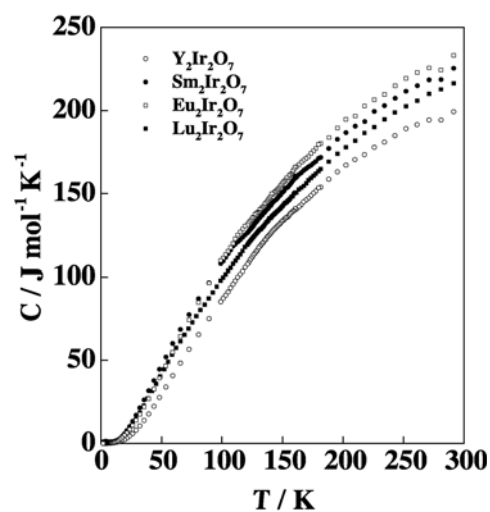


Figure 7. Temperature dependence of the specific heat for $R_2Ir_2O_7$.

has been observed at further lower temperatures. The most striking feature is the difference of the ZFC and FC magnetic susceptibilities below the transition temperatures for $R_2Ir_2O_7$. The magnetic hysteresis and specific heat measurements suggest that the magnetic behaviour of these below the transition temperatures is spin-glass-like. It is supposed that this spin-glass behaviour is caused by a geometrical peculiarity of the pyrochlore structure. In pyrochlore compounds, Ir atoms form a three-dimensional network of corner-sharing tetrahedra. Such an arrangement leads to a very high degree of magnetic frustration if the nearest-neighbour interactions are antiferromagnetic. It is considered that the spin-glass behaviour found for $R_2Ir_2O_7$ may originate from this magnetic frustration.

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