

Studies on magnetic susceptibility and specific heat for 6H-perovskite-type oxides $\text{Ba}_3\text{LnIr}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}–\text{Yb}$)

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Abstract

Magnetic properties of the 6H-perovskite-type oxides $\text{Ba}_3\text{LnIr}_2\text{O}_9$ ($\text{Ln} = \text{La}$ and Nd : monoclinic; $\text{Ln} = \text{Sm}–\text{Yb}$: hexagonal symmetry) were investigated. For all the title compounds, a specific heat anomaly was found at 5.3–17.4 K. At the corresponding temperatures, the magnetic susceptibilities show a slight variation in its gradient. These magnetic anomalies suggest the magnetic ordering of the magnetic moments ($S = 1/2$) remaining in the $\text{Ir}_2^{4.5+}\text{O}_9$ face-shared bioctahedra. In addition, the Ln^{3+} ions show the onset of the antiferromagnetic ordering around these temperatures. The $\text{Ba}_3\text{NdIr}_2\text{O}_9$ only shows a ferromagnetic behavior below 17.4 K with a remnant magnetization of $1.25 \mu_B$. This behavior may be due to the ferromagnetic ordering of the Nd^{3+} moments. © 2004 Elsevier Inc. All rights reserved.

Keywords: 6H-perovskite; Lanthanide; Iridium; Magnetic susceptibility; Specific heat

1. Introduction

In recent years, the solid-state chemistry of perovskite-related oxides containing platinum group metals has attracted a great deal of interest. These materials adopt a diverse range of structures and show a wide range of magnetic and electrical properties. Among such perovskite-related oxides, we focus our attention on the 6H-perovskites $\text{Ba}_3\text{LnRu}_2\text{O}_9$ ($\text{Ln} = \text{Y}$, lanthanides). Their crystal structures are represented as the linkage of the LnO_6 octahedra and Ru_2O_9 dimers (Fig. 1). The oxidation states of the B -site ions are $\text{Ba}_3\text{Ln}^{3+}\text{Ru}_2^{4.5+}\text{O}_9$ (for $\text{Ln} = \text{Y}, \text{La}, \text{Nd}, \text{Sm}–\text{Gd}, \text{Dy}–\text{Lu}$) [1–6] or $\text{Ba}_3\text{Ln}^{4+}\text{Ru}_2^{4+}\text{O}_9$ (for $\text{Ln} = \text{Ce}, \text{Pr}, \text{and Tb}$) [3,7]. The Ru compounds $\text{Ba}_3\text{LnRu}_2\text{O}_9$ show a characteristic temperature-dependence of the magnetic susceptibilities: a broad maximum at 135–400 K [5,7] and a magnetic transition at 4–24 K [4–7]. These magnetic properties mainly reflect two kinds of the magnetic interactions: the interaction between Ru ions in the Ru_2O_9 dimer with a

short Ru–Ru distance (2.5–2.6 Å) and that between Ln and Ru ions via the linear $\text{Ln}–\text{O}–\text{Ru}$ pathway.

The Ir compounds $\text{Ba}_3\text{LnIr}_2\text{O}_9$ also adopt the 6H-perovskite-type structures with monoclinic ($\text{Ln} = \text{La}$ and Nd) or hexagonal ($\text{Ln} = \text{Y}$ and other lanthanides) symmetry [8,9] and have the same charge configuration of the B site ions as the Ru series. Recently, we have reported the magnetic susceptibility and specific heat for the Ir compounds $\text{Ba}_3\text{LnIr}_2\text{O}_9$ ($\text{Ln} = \text{Y}, \text{Ce}, \text{Pr}, \text{Tb}, \text{Lu}$) [9]. In these compounds, the magnetic moments of Ir ions form the antiferromagnetic spin-pairing in the Ir_2O_9 dimer even at room temperature. Such a phenomenon has been also found in the Ru_2O_9 dimer in the $\text{Ba}_3\text{LnRu}_2\text{O}_9$ [4–7] and $\text{Ba}_3\text{MRu}_2\text{O}_9$ ($M = \text{Mg}, \text{Ca}, \text{Cd}, \text{Sr}$) [10,11]. The Ce compound $\text{Ba}_3\text{Ce}^{4+}\text{Ir}_2^{4+}\text{O}_9$, which has a nonmagnetic Ce^{4+} ion and magnetically canceled Ir^{4+} ions shows no anomaly down to 1.8 K. On the other hand, the data for the $\text{Ba}_3\text{Pr}^{4+}\text{Ir}_2^{4+}\text{O}_9$ and $\text{Ba}_3\text{Tb}^{4+}\text{Ir}_2^{4+}\text{O}_9$ suggest that the magnetic ordering of the Ln^{4+} ions has occurred at low temperatures (~ 2.0 K). Both $\text{Ba}_3\text{Ln}^{3+}\text{Ir}_2^{4.5+}\text{O}_9$ ($\text{Ln} = \text{Y}$ and Lu) compounds show an antiferromagnetic transition at 4–5 K, which is due to the ordering of the uncanceled magnetic moments remaining in the $\text{Ir}_2^{4.5+}\text{O}_9$ dimers.

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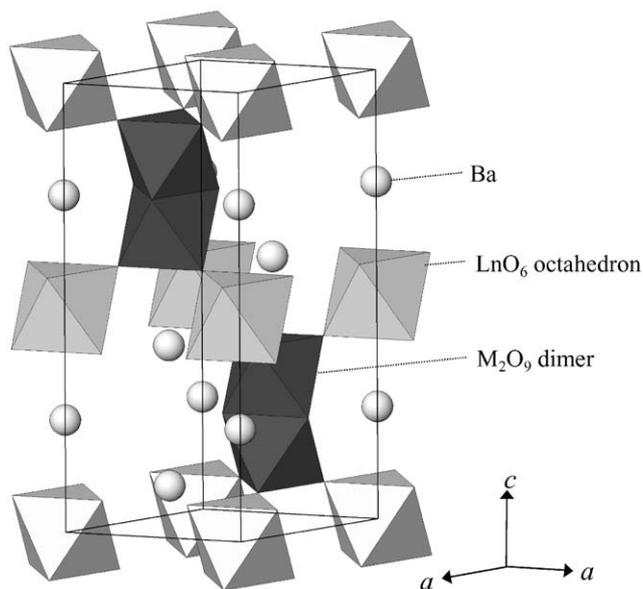


Fig. 1. The crystal structure of the hexagonal $\text{Ba}_3\text{LnM}_2\text{O}_9$ ($M = \text{Ru}, \text{Ir}$).

In this study, we report the magnetic properties of $\text{Ba}_3\text{Ln}^{3+}\text{Ir}_2^{4.5+}\text{O}_9$ (for $\text{Ln} = \text{La}, \text{Nd}, \text{Sm–Gd}, \text{Dy–Yb}$). Except for $\text{Ln} = \text{La}$, these compounds have both magnetic Ln^{3+} ions and $\text{Ir}_2^{4.5+}\text{O}_9$ dimers. Therefore, there exist two kinds of the magnetic interaction (Ir–Ir and Ln–Ir), hence they may bring about interesting magnetic properties. In order to elucidate their detailed magnetic properties, magnetic susceptibility and specific heat measurements were carried out.

2. Experimental

Polycrystalline samples of $\text{Ba}_3\text{LnIr}_2\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm–Yb}$) prepared in the previous study [9] were used. They were synthesized by firing stoichiometric mixtures of barium carbonate, lanthanide oxides, and iridium metal powders in air at 1100–1300°C. The magnetic measurements were carried out using SQUID magnetometer (Quantum Design, MPMS-5S). The temperature dependence of the magnetic susceptibilities was measured under both zero-field-cooled (ZFC) and field-cooled (FC) conditions in an applied field of 0.1 T over the temperature-range 1.8–400 K. For $\text{Ba}_3\text{NdIr}_2\text{O}_9$, the field dependence of the magnetization was measured between 0 and 5 T. Specific heat measurements were performed using a relaxation technique with a commercial physical property measurement system (Quantum Design, PPMS model) in the temperature range 1.8–300 K. The sintered sample in the form of a pellet (~10 mg) was mounted on a thin alumina plate with apiezon grease for better thermal contact.

3. Results and discussion

3.1. Magnetic susceptibilities of $\text{Ba}_3\text{LnIr}_2\text{O}_9$ ($\text{Ln} = \text{Sm–Gd}, \text{Dy–Yb}$)

Fig. 2 shows the variation of the reciprocal magnetic susceptibilities for $\text{Ba}_3\text{LnIr}_2\text{O}_9$ ($\text{Ln} = \text{Gd}, \text{Dy–Yb}$) as a function of temperature. The susceptibility data in the high-temperature region ($T > 100$ K) are fitted using the Curie–Weiss law. The effective magnetic moments and Weiss constants are listed in Table 1. The effective magnetic moments for $\text{Ln} = \text{Gd}, \text{Dy–Yb}$ compounds are close to those for the free Ln^{3+} ions rather than those calculated from all magnetic ions $\mu_{\text{cal}} = \sqrt{\mu_{\text{Ln}^{3+}}^2 + \mu_{\text{Ir}^{4+}}^2 + \mu_{\text{Ir}^{5+}}^2}$. This result indicates that the Ir ions hardly contribute to the effective magnetic moment in these compounds. Such small Ir moments have been found in the $\text{Ba}_3\text{LnIr}_2\text{O}_9$ ($\text{Ln} = \text{nonmagnetic } \text{Y}^{3+} \text{ and } \text{Lu}^{3+}$); they are about 0.15 and 1.1 μ_{B} (per Ir ion) at 1.8 and 300 K, respectively [9]. We consider that these small magnetic moments are due to the strong antiferromagnetic interaction between Ir ions in the Ir_2O_9 dimer or the spin–orbit coupling of the Ir^{5+} ions. In the former case, the magnetic moments of two Ir ions (Ir^{4+} and Ir^{5+}) in the dimer are partially cancelled, i.e., an uncanceled magnetic moment ($S = 1/2$) remains. In the latter case, the Ir^{5+} ions are in a singlet ground state [13]. On the other hand, there exist the magnetic moments of Ir^{4+} ions with $S = 1/2$ (the low-spin state). At least, a small magnetic moment still remains in the $\text{Ir}_2^{4.5+}\text{O}_9$ dimer even at low temperatures.

Fig. 3 illustrates the magnetic susceptibilities for Sm and Eu compounds. Their magnetic susceptibilities do not obey the Curie–Weiss law. This result is due to the influence from the low-lying excited state of Sm^{3+}

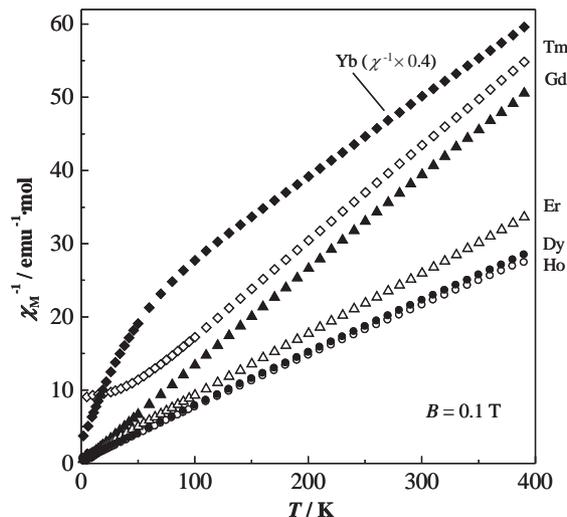


Fig. 2. Temperature dependence of the reciprocal magnetic susceptibilities for $\text{Ba}_3\text{LnIr}_2\text{O}_9$ ($\text{Ln} = \text{Gd}, \text{Tb–Yb}$).

Table 1

The effective magnetic moments (μ_{eff}), magnetic moments for free Ln^{3+} ($\mu_{Ln^{3+}}$) and calculated magnetic moments from all magnetic ions (μ_{cal}), Weiss constants (θ), magnetic transition temperature (T_m), and estimated magnetic entropy changes (ΔS_M) for $Ba_3LnIr_2O_9$

Ln	μ_{eff}/μ_B	$\mu_{Ln^{3+}}/\mu_B$	μ_{cal}/μ_B	θ/K	T_m/K	$\Delta S_M/J \text{ mol}^{-1} \text{ K}^{-1}$
Y ^a	1.61(1) ^b	—	3.32	—	4.0	3.7
La	1.82(1) ^b	—	3.32	—	14.6	0.3
Ce ^a	0.31(1)	—	2.45 ^c	-0.55(2)	—	—
Pr ^a	0.75(1)	2.54 ^c	3.53 ^c	-5.3(7)	<1.8	>0.5
Nd	3.40(1)	3.62	4.91	-0.9(7)	17.4	8.9
Sm	2.27(1) ^b	1.55 ^d	3.66	—	14.4	7.3
Eu	3.66(1) ^b	3.40 ^d	4.75	—	8.2	3.0
Gd	7.89(1)	7.94	8.60	-6.8(5)	10.2, 6.4	18.4
Tb ^a	8.10(1)	7.94 ^b	8.31 ^b	-0.7(2)	2.0	12.6
Dy	10.28(1)	10.63	11.14	-5.2(2)	8.9	8.2
Ho	10.27(1)	10.58	11.09	-3.4(2)	5.6	14.0
Er	9.72(5)	9.59	10.15	-10(1)	6.0	8.1
Tm	7.59(1)	7.55	8.25	-25(1)	5.5	3.0
Yb	4.93(3)	4.54	5.62	-123(2)	5.3	7.1
Lu ^a	1.58(1) ^b	—	3.32	—	5.1	3.6

^a Ref. [9].

^b Data at 300 K.

^c Magnetic moments calculated from the Ln^{4+} and/or Ir^{4+} ion.

^d Values calculated by the Van Vleck formula when the screening constant σ is 33 [12].

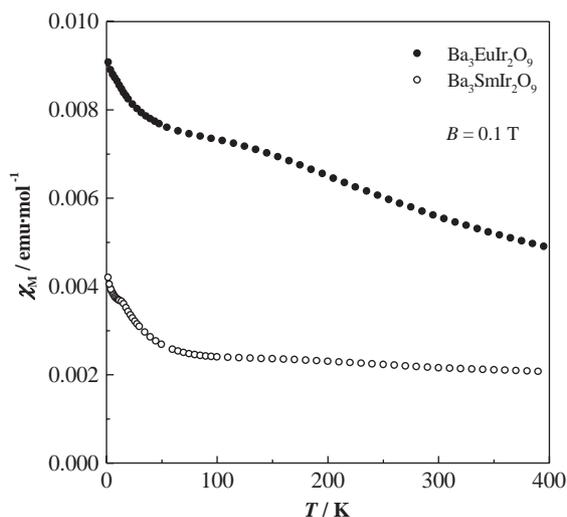


Fig. 3. Temperature dependence of the magnetic susceptibilities for $Ba_3LnIr_2O_9$ ($Ln=Sm$ and Eu).

(6H_J , $J=7/2, 9/2, \dots$) and Eu^{3+} (7F_J , $J=1, 2, \dots$) ions. The effective magnetic moments at room temperature are 2.27(1) and 3.66(1) μ_B , respectively. These values are comparable to the effective magnetic moments calculated by the Van Vleck formula [12].

3.2. Calculation of the magnetic entropy for $Ba_3LnIr_2O_9$ ($Ln=Sm-Gd, Dy-Yb$)

The temperature dependences of the magnetic susceptibility and specific heat for $Ba_3LnIr_2O_9$ ($Ln=Sm-Gd, Dy-Yb$) in the low temperature region are plotted in Fig. 4. The specific heat anomaly is found for all the

compounds below 15 K. The magnetic susceptibility also shows a slight variation in its gradient at the corresponding temperatures. In order to clarify the origin of this anomaly, the magnetic contribution to the specific heat was calculated. The other contributions (the lattice, electronic, and nuclear specific heat) to the observed specific heat were estimated by using a polynomial function of the temperature, $f(T) = aT^3 + bT^5 + cT^7$ [14], in which the constants were determined by fitting this function to the observed specific heat data between 20 and 40 K. Each calculated curve is shown as a dotted curve in Fig. 4. The specific heat data below 1.8 K were extrapolated by $C_p \propto T^3$ curve [15] except for the Ho and Er compounds in which this extrapolation was unsuccessful. The magnetic specific heat (C_m) for $Ba_3LnIr_2O_9$ is obtained by $C_m(T) = C_p(T) - f(T)$. The temperature dependence of the magnetic entropy calculated by $S_m = \int C_m/T dT$ is shown in Fig. 5.

3.3. Magnetic properties of $Ba_3LnIr_2O_9$ ($Ln=Sm-Gd, Dy-Yb$)

$Ba_3GdIr_2O_9$ (Fig. 4(a)) shows three specific heat anomalies at 3.0, 6.4 and 10.2 K. Among them, the anomaly at 6.4 K greatly contributes to the magnetic entropy change (ΔS_m), and at this temperature, the magnetic susceptibility also shows a magnetic transition with the divergence of the ZFC and FC susceptibilities. The magnetic entropy change associated with these anomalies is 18.4 J/mol K (Fig. 5). This value is close to $R \ln W = R \ln 8 = 17.3$ J/mol K (R : a molar gas constant, W : number of states for Ln^{3+} ion) which is expected from the ${}^8S_{7/2}$ ground state of the Gd^{3+} ion; thus this

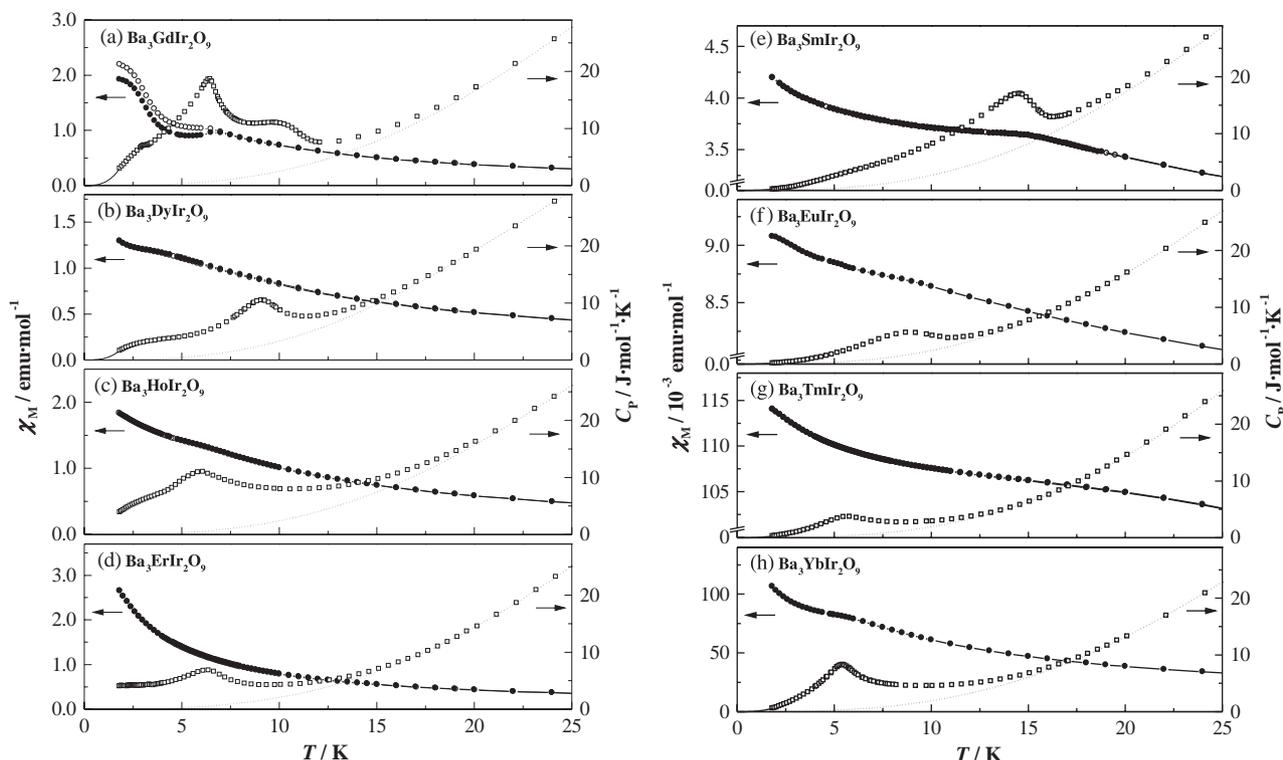


Fig. 4. (a–h) Temperature dependence of the magnetic susceptibility, specific heat for $Ba_3LnIr_2O_9$ ($Ln = Sm-Gd, Dy-Yb$).

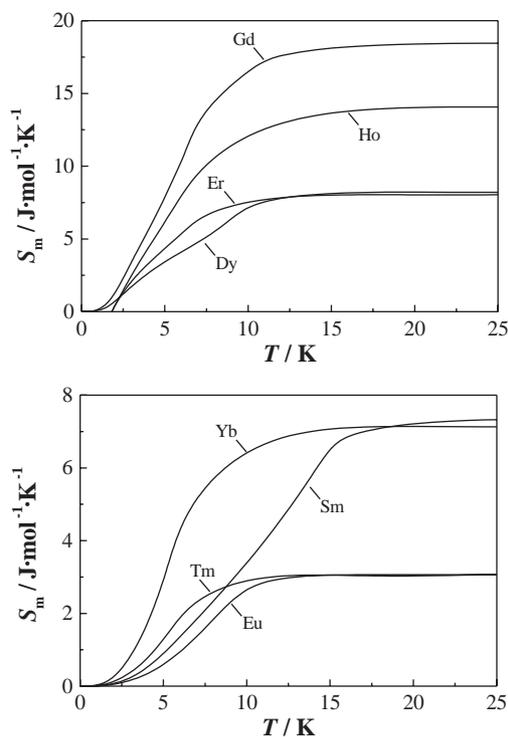


Fig. 5. Temperature dependence of the magnetic entropy for $Ba_3LnIr_2O_9$ ($Ln = Sm-Gd, Dy-Yb$).

result indicates that the magnetic anomaly at 6.4 K is due to the antiferromagnetic ordering of Gd^{3+} ions. A broad anomaly in the heat capacity is observed at

10.2 K; however, the magnetic susceptibility shows no variation at the temperature. We consider that this anomaly is due to a magnetic ordering of the remaining magnetic moments ($S=1/2$) in the $Ir_2^{4.5+}O_9$ dimers, because similar magnetic ordering has been found for the isostructural $Ba_3Y^{3+}Ir_2^{4.5+}O_9$ and $Ba_3Lu^{3+}Ir_2^{4.5+}O_9$ [9]. On the other hand, the cause of a specific heat anomaly at 3.0 K is unclear. Through this temperature, the temperature-dependence of its magnetic susceptibility changes. This behavior may indicate the occurrence of a spin reorientation of the Gd^{3+} moments.

The specific heats for the $Ba_3DyIr_2O_9$, $Ba_3HoIr_2O_9$ and $Ba_3ErIr_2O_9$ (Fig. 4(b)–(d)) show anomalies at 8.9, 5.6 and 6.0 K, respectively. Around each temperature, the variation of the magnetic susceptibility with temperature is very slight. These anomalies may be due to a magnetic ordering of the $Ir_2^{4.5+}O_9$ dimers. The magnetic entropy changes calculated from the data below 25 K are 8.2 (for $Ln = Dy$), 14.0 (Ho), and 8.1 J/mol K (Er), respectively (Fig. 5). These values are much larger than those derived from the magnetic ordering of the remaining magnetic moment in the $Ir_2^{4.5+}O_9$ dimer of $Ba_3Y^{3+}Ir_2^{4.5+}O_9$ (3.6 J/mol K) and $Ba_3Lu^{3+}Ir_2^{4.5+}O_9$ (3.7 J/mol K) [9]. Thus, the Ln^{3+} ions should greatly contribute to the magnetic entropy changes. However, the magnetic specific heats are broad in shape and extending for a wide range of temperature. This result is in contrast with the antiferromagnetic transition found in the $Ba_3LnRu_2O_9$ ($Ln = Ho$ and Er) [6]. They show a

sharp λ -type anomaly in the specific heat and a distinct maximum in the magnetic susceptibility at 10.2 K (for $Ln=Ho$) and 6.0 K (Er), which are due to the antiferromagnetic ordering of the Ln^{3+} ions. We consider that in the case of Ir compounds $Ba_3LnIr_2O_9$ ($Ln=Dy, Ho,$ and Er), the magnetic ordering of Ln^{3+} ions may be a short range ordering and gradually growing toward a long range ordering with decreasing temperature.

The temperature dependences of the specific heat and magnetic susceptibility for $Ba_3LnIr_2O_9$ ($Ln=Sm, Eu, Tm,$ and Yb) are plotted in Fig. 4(e)–(h). They also show a specific heat anomaly at 14.4, 8.2, 5.5, and 5.3 K, respectively, and their magnetic susceptibility-temperature curves only indicate a slight variation of their gradient at the corresponding temperatures. It is thought that the magnetic ordering of the remaining magnetic moment in the $Ir_2^{4.5+}O_9$ dimer also occurs in these compounds. The magnetic entropy vs. temperature curves are illustrated in Fig. 5. The magnetic entropy changes are 7.3 (for $Ln=Sm$), 3.0 (Eu), 3.0 (Tm), and 7.1 J/mol K (Yb). The values for the Eu and Tm compounds are near to those for the Y and Lu ones (3.6–3.7 J/mol K) [9]. This result is due to the non-magnetic ground states for Ln^{3+} ions: a 7F_0 state for Eu^{3+} and a singlet ground state (Γ_1 or Γ_2) in the octahedral crystal field for Tm^{3+} [16]. On the other hand, the magnetic entropy change for the Sm and Yb compounds are much larger than those for the Y and Lu compounds and it should have a contribution from the magnetic moments of Ln^{3+} ions. The excess entropy, S_m (Sm or Yb)– S_m (Y, Lu) = 3–4 J/mol K, indicates the existence of the doublet ground state ($R\ln 2 = 5.76$ J/mol K) of Ln^{3+} ions, i.e., the Γ_7 doublet state of $^6H_{5/2}$ for Sm^{3+} ion and the Γ_6 doublet state of $^2F_{7/2}$ for Yb^{3+} ion [16].

3.4. Magnetic properties of $Ba_3LnIr_2O_9$ ($Ln=La$ and Nd)

The temperature dependence of the magnetic susceptibility for monoclinic $Ba_3LaIr_2O_9$ is shown in Fig. 6(a). The temperature dependence of its specific heat and magnetic entropy are plotted in Figs. 7(b) and (c), respectively. The magnetic susceptibility does not obey the Curie–Weiss law. The small effective magnetic moment is obtained from $\mu_{\text{eff}} = \sqrt{3k_B\chi_M T/N_A}$ (k_B : Boltzmann constant, N_A : Avogadro constant): $0.15 \mu_B$ at 1.8 K and $1.29 \mu_B$ at 300 K (per Ir ion). An antiferromagnetic maximum is observed at 14.6 K, and at the same temperature, the specific heat anomaly is also found. Its magnetic entropy change is extremely small ($\Delta S_m \sim 0.3$ J/mol K) compared with those for the Y and Lu compounds. Such a small magnetic entropy change has been also found in the Ru analogue

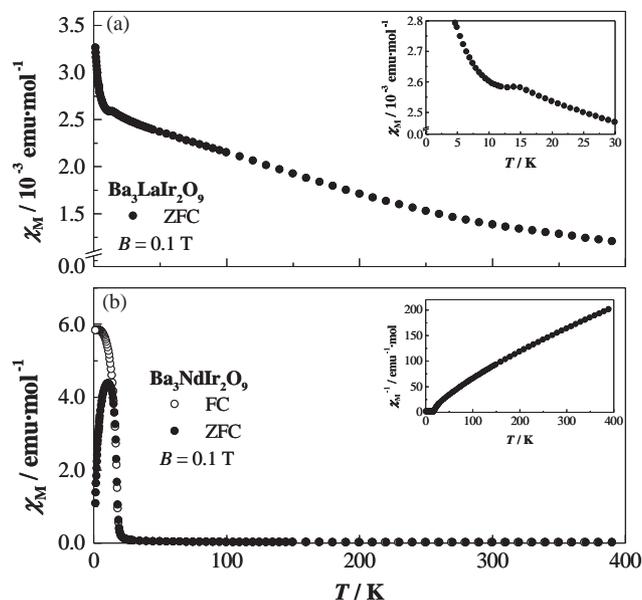


Fig. 6. Temperature dependence of the magnetic susceptibility for $Ba_3LnIr_2O_9$ ($Ln=La$ and Nd). The insets in (a) and (b) are an enlarged graph at low temperatures and a plot of the reciprocal magnetic susceptibility vs. temperature, respectively.

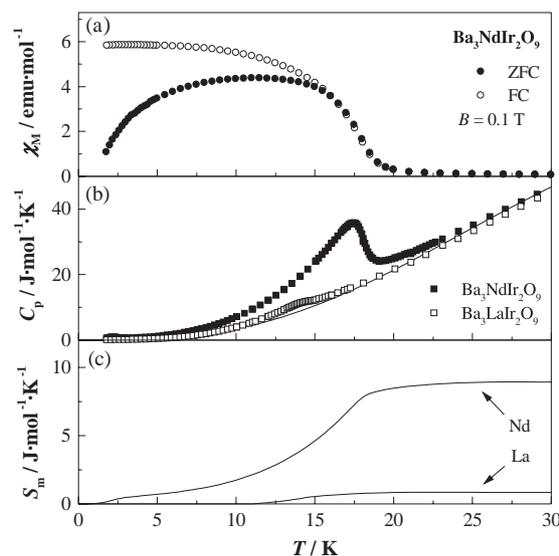


Fig. 7. Temperature dependence of (a) the magnetic susceptibility for $Ba_3NdIr_2O_9$, (b) the specific heat for $Ba_3LnIr_2O_9$ ($Ln=La$ and Nd), and (c) the magnetic entropy for $Ba_3LnIr_2O_9$ ($Ln=La$ and Nd).

$Ba_3LaRu_2O_9$ ($T_m = 22$ K, $\Delta S_m \sim 0.3$ J/mol K) [5]. The origin of this anomaly is unclear at present.

Fig. 6(b) shows the magnetic susceptibility of monoclinic $Ba_3NdIr_2O_9$. A rapid increase below 17.4 K and the large divergence between the ZFC and FC susceptibilities are observed. These features indicate that a ferromagnetic or ferrimagnetic transition has occurred. The field dependence of the magnetization at 1.8, 10, 20, and 30 K is shown in Fig. 8. A hysteresis loop was

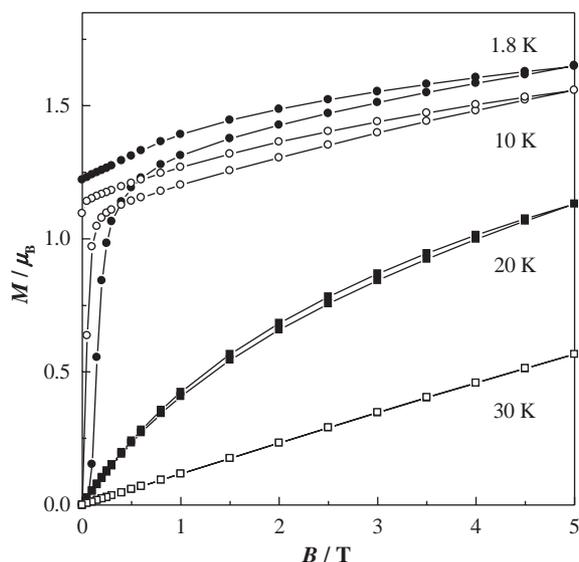


Fig. 8. Field dependence of the magnetization for $\text{Ba}_3\text{NdIr}_2\text{O}_9$.

observed below the transition temperature, which means that there exists a ferromagnetic moment. The remnant magnetization is $1.25 \mu_B$ from the 1.8 K data. The specific heat anomaly is also found at the same temperature with the magnetic entropy change of 8.9 J/molK (Fig. 7(b) and (c)). For the Ru-series of compounds $\text{Ba}_3\text{LnRu}_2\text{O}_9$, only the Nd compound shows a ferromagnetic behavior ($T_c = 24.0 \text{ K}$ and remnant magnetization is $1.05 \mu_B$) [4]. By its neutron diffraction measurements below T_c , the ferromagnetic moment found in the $\text{Ba}_3\text{NdRu}_2\text{O}_9$ has been found to be due to the ferromagnetic ordering of Nd^{3+} ions. We consider that the ferromagnetic moment observed in the $\text{Ba}_3\text{NdIr}_2\text{O}_9$ should also be due to the same Nd^{3+} ordering.

4. Summary

The magnetic susceptibility and specific heat measurements for 6H-perovskite-type oxides $\text{Ba}_3\text{Ln}^{3+}\text{Ir}_2^{4.5+}\text{O}_9$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm} - \text{Yb}$) were carried out. These compounds have both magnetic Ln^{3+} ions and $\text{Ir}_2^{4.5+}\text{O}_9$ dimers; in the latter. A specific heat anomaly found at $5.3 - 17.4 \text{ K}$ indicates the magnetic ordering of the uncanceled magnetic moments ($S = 1/2$) in the $\text{Ir}_2^{4.5+}\text{O}_9$ dimer. The magnetic ordering of the Ln^{3+} ions also occurs around this temperature; however, for almost all

compounds, a slight variation of the magnetic susceptibility and the magnetic specific heat extending for a wide range of temperature indicate that the magnetic ordering is not completed down to very low temperatures (1.8 K). These features are in contrast with those of the Ln^{3+} ordering for the Ru analogues $\text{Ba}_3\text{Ln}^{3+}\text{Ru}_2^{4.5+}\text{O}_9$: a distinct maximum in the magnetic susceptibility and a sharp λ -type anomaly in the specific heat. The $\text{Ba}_3\text{NdIr}_2\text{O}_9$ only shows a ferromagnetic behavior below 17.4 K with a remnant magnetization of $1.25 \mu_B$. This behavior may be due to the ferromagnetic ordering of the Nd^{3+} ions.

Acknowledgments

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