Specific heat measurements of pyrochlore-type $R_2Mo_2O_7$ (R=Nd-Ho)

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Abstract

Specific heat measurements have been performed on pyrochlore-type $R_2Mo_2O_7$ (R=Nd-Ho) single crystals. For the ferromagnetic compounds with R=Nd-Gd (T_C≈50-90 K), Schottky-like specific heat anomalies corresponding to the level splitting for the 4f electrons of R^{3+} are observed at low temperatures, in contrast to the specimens with R=Tb-Ho which show spin-glass-like order below T_g≈20-25 K. Low-temperature specific heat data of $Sm_2Mo_2O_7$ under a magnetic field of 10 T are presented.

Key words: pyrochlore;specific heat;spin-glass;

Pyrochlore oxides with a general formula $A_2B_2O_7$ have a face centered cubic structure and each of R and Mo atoms form a three-dimensional network of corner-sharing tetrahedra. In particular, there has been great deal of interest in pyrochlore molybdates $R_2Mo_2O_7$, because the systems with R=Y and Tb-Er are insulating, geometrically frustrated and undergo a phase transition into a spin-glass-like state despite the absence of apparent structural disorder[1,2], while the systems with R=Nd-Gd exhibit ferromagnetic order with metallic conductivities. Very recently, it has been pointed that the magnetic phase boundary is correlated with the metal-insulator crossover[3] and the structural variation at T_C in $Nd_2Mo_2O_7$ suggests some double-exchange interaction mechanism in metallic $R_2Mo_2O_7$[4].

In the present work, we have performed the precise measurements of specific heat for $R_2Mo_2O_7$ (R=Nd-Ho) using single crystal specimens, to throw further light on the magnetic ordering. To our knowledge, the specific heat measurements have been so far limited on the polycrystalline specimens of $R_2Mo_2O_7$ with R=Sm, Gd, Y[5]. Single crystals of $R_2Mo_2O_7$ were grown in an Ar atmosphere by a floating-zone method and confirmed to be a single crystal by Laue reflection. Specific heat was measured by a thermal relaxation method.

In metallic $R_2Mo_2O_7$, the ferromagnetic ordering of Mo^{4+} ions occurs at T_C, whereas the ordering of R^{3+} ions are interpreted to gradually develop below T_C and become significant below T_F ($\ll T_C$), as evidenced by recent neutron scattering experiments for $Nd_2Mo_2O_7$ (T_C∼93 K, T_F∼20 K)[6]. We show the temperature T dependence of magnetic specific heat C_m for $Sm_2Mo_2O_7$ in Fig.1. In deriving C_m, pyrochlore-type $Y_2Ti_2O_7$ which is insulating and nonmagnetic was used to eliminate the lattice contribution C_{latt}. In Fig. 1, a sharp anomaly corresponding to the ferromagnetic ordering of Mo^{4+} ions is observed at T_C(≈80 K), in contrast to the behavior of the polycrystalline specimen in the previous work[5]. The released magnetic entropy $S=\int C_m/TdT$ between 70 and 90 K we estimate is only ∼10 percent of that expected for the ordering of Mo^{4+} ($4d^2$, S=1), similar to perovskite manganites[7]. The anomaly at T_C was also observed for the specimen with R=Nd but not for R=Gd, which is in the vicinity of spin-glass-like state.

In Fig. 1, a Schottky-like anomaly, which is associ-

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ated with the ordering of Sm^{3+} ions, is observed at low-T and was also observed for the specimens with R=Nd and Gd. The estimated magnetic entropies for these anomalies nearly correspond to that of a two-level system for R=Nd and Sm and an eight-level system for R=Gd, although the peaks of the anomalies are small and broad, compared with standard multilevel Schottky anomalies[5]. In the inset of Fig.1, low-T $C_m(T)$ data for H=0 and 10 T parallel to the (111) direction are displayed. In the inset, the peak temperature of the anomaly T_p becomes slightly lower by applying a magnetic field of 10 T, indicating that the splitting of the doublet for 10 T (Δ_{10T}) is smaller than that for H=0 (Δ_0), though the behaviors with $\Delta_{H\neq 0}>\Delta_0$ have been found in various materials. To derive $\Delta_{10}<\Delta_0$, we need to assume that the ordering of the Sm^{3+} moments μ_{Sm} is arising from antiferromagnetic Sm-Mo interactions inferred by the spin arrangement in $Nd_2Mo_2O_7$, where the net magnetization of the Nd and Mo sublattices are opposite in direction to each other[6]. In this case, the effective molecular field at the Sm sites H_m would be antiparallel in average to the applied magnetic field H. Accordingly, we may give the splitting of the doublet as, $\Delta_0=2\mu_{Sm}H_m(0)$ for H=0, and $\Delta_{10T}=2\mu_{Sm}[H_m(10)-10]$ for H=10 T. These equations satisfy $\Delta_{10}<\Delta_0$ for $H_m(0)\leq H_m(10)$ and yield $\mu_{Sm}=0.065\mu_B$ when $H_m(0)=H_m(10)$. This value of μ_{Sm} is fairly smaller than the free-ion value of $0.7\mu_B$, similar to that of Nd^{3+} in $Nd_{0.67}Sr_{0.33}MnO_3$[7].

Next, we show the T-dependence of specific heat C_p for the specimens with R=Tb-Ho in the temperature range $2\leq T\leq 20$ K in Figs. 2(a)-2(c). As seen in Figs. 2(a) and 2(b), the specimens with R=Tb and Dy do not show any Schottky-like anomaly at low-T, in contrast to those with R=Nd-Gd, although $C_p(T)$ for R=Dy appears to show a very slight hump below 10 K. On the other hand, a low-T anomaly, which was a clear peak but not Schottky-like in shape in the C_m ($=C_p-C_{latt}$) versus T plot, is observed at ~5 K for R=Ho in Fig. 2(c). No anomaly was observed at $\sim T_g$ for R=Tb-Ho. The behaviors of $C_p(T)$ for R=Tb and Dy are also forming a contrast with those for $Tb_2Ti_2O_7$ and $Dy_2Ti_2O_7$, where $C_p(T)$ exhibits a peak at low-T[8,9]. It should be noted that the specific heat anomaly associated with R^{3+} ions remarkably depends on the magnetic order at the Mo site, indicating that the ordering of the R^{3+} moments are much affected by the Mo^{4+} moments through interactions. The absence of anomaly at low-T for R=Tb and Dy is attributable to the R^{3+} moments involved in the spin freezing of the Mo^{4+} moments at T_g, so that the magnetic entropies are released in the wide T-range above and below T_g. In $Ho_2Mo_2O_7$, it has been found that the magnetic susceptibility obeys a Currie-Weiss law and is fairly slightly history dependent below T_g, contrasting the behaviors in $Tb_2Mo_2O_7$, suggesting that the Ho^{3+} moments are remain almost paramagnetic even below T_g[10]. The appearance of the low-T anomaly for R=Ho is thought of due to relatively weak R-Mo couplings.

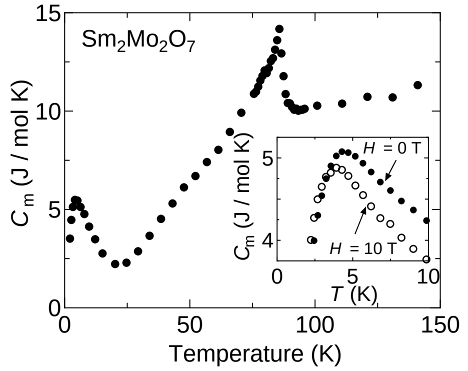

Fig. 1. Temperature dependence of magnetic specific heat C_m for $Sm_2Mo_2O_7$. Low-T $C_m(T)$ data for H=0 and 10 T are shown in the inset.

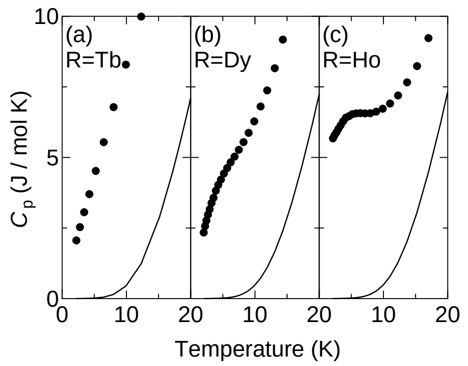

Fig. 2. Temperature dependence of specific heat for $R_2Mo_2O_7$ with R=Tb (a), Dy (b), Ho (c). The solid lines indicate the lattice contributions.

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