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Magnetic properties of $R_2Mn_2O_7$ pyrochlore rare-earth solid solutions

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Three $(R,R')_2Mn_2O_7$ ferromagnetic pyrochlore systems were studied to investigate the role of the $R^{3+}$ ionic size versus $4f$ moment on the magnetic properties of the $Mn_2O_7$ sublattice. The Curie temperature $T_C = 18 \pm 1$ K for $R=\text{Y}$ and Lu remained nearly constant for $(Y_{1-x},\text{Lu}_x)_2Mn_2O_7$ but the magnetization data show characteristics of spin-glass behavior in low magnetic fields, and at 5 T, the magnetization fails to reach the expected $3 \mu_B/\text{Mn}^{4+}$ found by 0.5 T in $\text{Tl}_2\text{Mn}_2O_7$ and $\text{In}_2\text{Mn}_2O_7$. A frustrated, minor antiferromagnetic component apparently competes with the ferromagnetic component of the $\text{Mn}^{4+}-\text{O}-\text{Mn}^{4+}$ interactions to give a minor antiferromagnetic component to the major ferromagnetic spin alignment of the $\text{Mn}^{4+}$ ions. A $T_C = 42 \pm 1$ K for $R=\text{Dy}$ and Yb remains nearly constant in the $(\text{Dy}_{1-x},\text{Yb}_x)_2\text{Mn}_2O_7$ system and $T_C$ increases systematically from 19 to 42 K with Dy concentration in $(\text{Dy}_{1-x},\text{Lu}_x)_2\text{Mn}_2O_7$, which clearly shows that a ferromagnetic interaction between the $R^{3+}$-ion and $\text{Mn}^{4+}$-ion spins favors ferromagnetic alignment of the $\text{Mn}^{4+}$-ion spins to double the magnitude of $T_C$ by relieving the frustration of the $\text{Mn}_2O_7$ sublattice. The $R^{3+}$-ion size has little effect as the $\text{Mn}-\text{O}-\text{Mn}$ bond angle changes by no more than $\sim 1^\circ$ with changing ionic radius of the $R^{3+}$ ion.

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I. INTRODUCTION

Crystals containing geometrically frustrated interacting spins have attracted much attention for their variety of exciting physical properties stemming from the competing interactions that prevent the spin system from an ordering that optimizes every interaction. Pyrochlore oxides with the general formula $A_2B_2O_7$ ($A=$tetravalent cation; $B=$tetravalent cation) form one of the well-known examples of such crystals.1 In the cubic pyrochlore structure, the two cation species, $A$ and $B$, are independently arranged into corner-sharing cation tetrahedra forming three-dimensional mutually interpenetrating sublattices. Oxygen atoms are then situated in such a way that each $A$ cation is surrounded by eight oxygen atoms and each $B$ cation by six oxygen atoms. Interesting magnetic and transport properties such as spin-glass (SG), spin-ice6–8 and spin-liquid10 states, colossal magnetoresistivity,8–9 an anomalous Hall effect,10 a metal-insulator transition,2 and superconductivity11 have been revealed for the pyrochlore oxides.

The Mn-based pyrochlore oxides, $A_2\text{Mn}_2O_7$, can be prepared through high-pressure (HP) synthesis for small rare-earth elements ($R=\text{Sc}, \text{Y}, \text{Dy}-\text{Lu}$) (Refs. 12 and 13) and also for In and Tl (Refs. 8, 9, and 14) as the $A$ constituent. The pyrochlore $\text{Tl}_2\text{Mn}_2O_7$ is metallic, whereas $\text{In}_2\text{Mn}_2O_7$ and $\text{R}_2\text{Mn}_2O_7$ are semiconductive. All the $A_2\text{Mn}_2O_7$ phases are ferromagnetic (FM) at low temperatures, the fact being well explained by a dominant FM Mn-O-Mn superexchange interaction for the peculiar Mn-O-Mn bond angle of about 130°.14 According to the Goodenough-Kanamori rules,15,16 an antiferromagnetic (AFM) 180° Mn-O-Mn superexchange interaction changes to an FM interaction as the Mn-O-Mn bond angle decreases to less than about 135°. However, an AFM Mn-Mn superexchange is also present at smaller bond angles and it dominates the 90° Mn-O-Mn interaction where the Mn$^{4+}$ octahedra share common edges in an oxide. With a 130° Mn-O-Mn bond angle, the larger Mn-Mn separation makes dominant the FM Mn-O-Mn interactions, but it is clear that the strength of a net FM interaction between octahedral-site Mn$^{4+}$ ions depends sensitively on the Mn-O-Mn bond angle. The bond angle changes progressively with $R^{3+}$-ion size in the ROMO$_3$ perovskites but the bond angle is not sensitive to the $R^{3+}$-ion size in the $R_2\text{Mn}_2O_7$ pyrochlore structure.12,14 The FM transition temperature $T_C$ is much higher for $\text{Tl}_2\text{Mn}_2O_7$ and $\text{In}_2\text{Mn}_2O_7$ (over 120 K) than for $\text{Lu}_2\text{Mn}_2O_7$ and $\text{Y}_2\text{Mn}_2O_7$ (below 20 K), which may be attributed to strong hybridization of In(5s) $T$/$\text{TI}(5s)$ orbitals with O(2p) and Mn(3d) orbitals enhancing the FM interaction (and simultaneously the electrical conductivity).12 Within the $R_2\text{Mn}_2O_7$ system, however, the $T_C$ value deviates from any systematic trend expected on the basis of the $R^{3+}$ constituent size, which implies that a magnetic $R^{3+}$ constituent (or $4f$ moment) may give an additional contribution to the magnetic behavior.13,14,17–19 Apparently the $R_2\text{Mn}_2O_7$ system differs in the nature of its magnetic phase transition from other pyrochlore oxide systems such as $R_2\text{Mo}_2O_7$ (Ref. 20) and $R_2\text{Ru}_2O_7$.21–23 So far based on several complimentary experimental techniques, it has been revealed that the magnetism of $R_2\text{Mn}_2O_7$ is of the reentrant-SG (RSG) type at low temperatures.17,18

A so-called magnetic dilution realized, for instance, by gradually substituting nonmagnetic $R^{3+}$ ions for magnetic $R^{3+}$ ions24–25 is a highly useful approach to deepen our understanding of complex magnetic systems, including the present $R_2\text{Mn}_2O_7$ system. However, as different $R$ constituents in general are of different sizes, such a substitution inevitably involves some local structural changes that may affect the nature of the superexchange interactions. For example, the $R_2\text{Mo}_2O_7$ system was extensively studied and shown to exhibit a universal dependence of $T_C$ on the mean ionic radius of the constituent $R^{3+}$ ions, $r(R^{3+})$.26–28 In the present study we investigate three different pyrochlore manganese-oxide solid-solution systems, (i) $(\text{Y}_{1-x}\text{Lu}_x)_2\text{Mn}_2O_7$, (ii) $(\text{Dy}_{1-y}\text{Yb}_y)_2\text{Mn}_2O_7$, and (iii)
(DY1−xLuz)2Mn2O7. In all the three systems (i)–(iii) the lattice shrinks with increasing substitution level, i.e., with increasing x, y, or z, suggesting a systematic increase in the degree of chemical pressure on the Mn2O7 array. The (i) “nonmagnetic-R” system, (Y,Lu)2Mn2O7, contains only nonmagnetic R3+ ions whereas in the other two systems, (ii) and (iii), the host R3+ cation (=Dy3+) is magnetic. In the (ii) “magnetic-moment-diluted” (Dy,Yb)2Mn2O7 system, not only the host but also the substituent is magnetic, but with a smaller magnetic moment compared to that of the host. In the (iii) “magnetic-ion-diluted” (Dy1−xLuz)2Mn2O7 system, the substituent is nonmagnetic. Additionally we synthesize and characterize another type of magnetic-ion-diluted sample, (DY0.5Y0.5)2Mn2O7, in which the two R3+ cation constituents are of nearly equal size.

II. EXPERIMENTAL

Essentially single-phase samples of (Y1−xLuz)2Mn2O7 (x = 0.0, 0.2, 0.5, 0.8, and 1.0), (DY1−xYby)2Mn2O7 (y = 0.0, 0.2, 0.5, 0.8, and 1.0), (DY1−xLuz)2Mn2O7 (z = 0.0, 0.2, 0.5, 0.7, 0.9, and 1.0), and (DY0.5Y0.5)2Mn2O7 were synthesized by means of an HP technique from stoichiometric ratios (in terms of cation stoichiometry) of R2O3 and Mn2O3/MnCO3. Prior to HP syntheses, raw-material powder mixtures were calcined in air at 1300 °C for 24 h. The excess oxygen required for stabilizing the Mn-based pyrochlore phases was provided from KClO3 which was mixed with the precursor powder before loading the calcined powder in a gold capsule. High-pressure syntheses were then carried out with a cubic-anvil-type HP apparatus at 5 GPa and 1000 °C for 30 min. From the HP product, residual KCl was washed out with distilled water. All the samples were then characterized for phase purity by x-ray powder diffraction (XRD; Rigaku: RINT2550VK/U equipped with a rotating Cu anode; Cu Kα radiation). The diffraction patterns were readily indexed with cubic space group Fd3m expected for the Mn-based pyrochlore oxides.12,19 The lattice parameter a was determined from the XRD data with the software JANA2000 (Ref. 29) in the profile-fitting mode. The dc magnetization (M) was measured for the samples in a temperature range of 5–400 K in both zero-field-cooled (ZFC) and field-cooled (FC) modes with a superconducting quantum interference device magnetometer (Quantum Design: MPMS-XL5).

III. RESULTS AND DISCUSSION

Judging from the XRD patterns (not presented here), all the samples were essentially single phase. The lattice parameters a calculated from the XRD data are plotted in Figs. 1(a)–1(c) for the three sample series, (i) (Y1−xLuz)2Mn2O7, (ii) (DY1−xYby)2Mn2O7, and (iii) (DY1−xLuz)2Mn2O7, against the tabulated average ionic radius, r(R3+), for eightfold coordination.30 For the end members, i.e., R3Mn2O7 with single R constituents, the a values are in good agreement with those previously reported.12–14 For solid-solution compositions, the a value depends linearly on the average ionic radius r(R3+). Therefore we may conclude that the mean Mn-O bond length systematically decreases with decreasing r(R3+); however, the Mn-O-Mn bond angle changes by no more than ∼1°.12,14

The magnetic susceptibility (χ) versus temperature (T) curves for the (i) nonmagnetic R (Y1−xLuz)2Mn2O7 system are presented in Fig. 2(a). All the samples show an FM transition around Tc = 17 ± 1 K; accordingly it is clear that Tc does not depend significantly on r(R3+). Magnetization data for the (ii) magnetic-moment-diluted (DY1−xYby)2Mn2O7 and (iii) magnetic-ion-diluted (DY1−xLuz)2Mn2O7 systems are shown in Figs. 2(b) and 2(c), respectively. All the (DY1−xYby)2Mn2O7 samples show an FM transition at Tc = 42 ± 1 K, whereas for the (DY1−xLuz)2Mn2O7 samples Tc decreases from 42 K (for z = 0.0) to 19 K (for z = 1.0). Here we should mention that for the ad hoc (DY0.5Y0.5)2Mn2O7 sample, the Tc value was determined at 35 K (not shown in Fig. 2), which is close to the value (39 K) observed for (DY0.5Lu0.5)2Mn2O7. To visualize the above findings, we plot Tc against r(R3+) in Fig. 3 for all the samples (i)–(iii) and also include, for comparison, the Tc values of nondoped R3Mn2O7 phases with single R constituents as given in Ref. 31. From Fig. 3 it is clearly revealed that the Tc value does not depend simply on r(R3+) but increases with increasing additional concentration of magnetic R3+ ions. It moreover seems that the primary factor is not the average magnetic moment [cf. the essentially constant Tc for the magnetic-moment-diluted (DY1−xYby)2Mn2O7 system] but the concentration of magnetic ions in the rare-earth sublattice [cf. the decreasing Tc in the magnetic-ion-diluted (DY1−xLuz)2Mn2O7 system with z].

We also observe from Figs. 2(a)–2(c) that, in contrast to the (Y,Lu)2Mn2O7 system, a clear branching of the magnetization curve between ZFC and FC modes is observed for both the (DY,Yb)2Mn2O7 and the (DY,Lu)2Mn2O7 systems, which is consistent with the presence of an RSG-like magnetic state.17–19 This is in accordance with the fact that be-
besides the magnetic Mn$^{4+}$ ions, there are magnetic R$^{3+}$ ions in the latter two systems such that additional R$^{3+}$-R$^{3+}$ and/or R$^{3+}$-Mn$^{4+}$ magnetic interactions may exist.

Magnetization ($M$) data measured at 5 K with respect to applied magnetic field ($H$) are shown in Figs. 4(a)–4(c). Nearly complete saturation is seen for all the samples; the slight but continuous rise of magnetization with increasing magnetic field infers the presence of an SG-like state since the orbital angular momentum on the Mn$^{4+}$ ions is quenched. For the (Y$_{1-x}$Lu$_x$)$_2$Mn$_2$O$_7$ samples, the estimated magnetic moment per Mn$^{4+}$ ion approaches but does not reach the theoretical value of 3 $\mu_B$, see Fig. 4(a), consistent with a frustrated AFM spin component of the Mn sublattice. As reported previously for R$_2$Mn$_2$O$_7$ (Ref. 18) and also revealed in our earlier study on (Dy$_{1-x}$Lu$_x$)$_2$Mn$_2$O$_7$, saturation of the Mn sublattice, which couples ferromagnetically with the R sublattice, does not depend significantly on the R composition. Hence we subtracted the magnetization curve of Lu$_2$Mn$_2$O$_7$ from those for (Dy$_{1-x}$Yb$_x$)$_2$Mn$_2$O$_7$ and (Dy$_{1-x}$Lu$_x$)$_2$Mn$_2$O$_7$ in Figs. 4(b) and 4(c), respectively, in order to reveal the magnetization contribution purely from the magnetic rare-earth sublattice. Let us discuss the $M$-$H$ curves for the (Dy$_{1-x}$Yb$_x$)$_2$Mn$_2$O$_7$ system given in Fig. 4(b).

We synthesized and characterized three types of R$_2$Mn$_2$O$_7$ pyrochlore rare-earth solid-solution systems, i.e., (i) nonmagnetic $R$ (Y,Lu)$_2$Mn$_2$O$_7$, (ii) magnetic-moment-diluted (Dy,Y)$_2$Mn$_2$O$_7$, and (iii) magnetic-ion-diluted (Dy,Lu)$_2$Mn$_2$O$_7$. The saturation magnetization of the (Y,Lu)$_2$Mn$_2$O$_7$ system approaches, but does not reach by 5
In $\text{In}_2\text{Mn}_2\text{O}_7$, which indicates the presence of a minor, frustrated AFM component competing with the FM Mn$^{3+}$-O-Mn$^{4+}$ interactions in the (Y$_1$Lu$_{2-x}$)Mn$_2$O$_7$ system. In low applied magnetic fields at low temperatures, the AFM component of the interactions gives a magnetic susceptibility characteristic of an RSG like. The systems containing a spin on the R$^{3+}$ ion exhibit a $T_C$ that increases significantly with the concentration of the R$^{3+}$ ions having a spin. This observation shows that FM R$^{3+}$-Mn$^{4+}$ interactions favor FM alignment of the Mn$^{4+}$-ions, thus reducing the net AFM fraction of the interactions to relieve the frustration and raise $T_C$ remarkably. The R$^{3+}$-ion size has little effect on the magnetic interactions; in the pyrochlore structure, the Mn-O-Mn bond angle varies little with R$^{3+}$-ion size.

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**FIG. 4.** (Color online) Magnetic field ($H$) dependence of magnetization ($M$) for (a) (Y$_1$Lu$_{2-x}$)Mn$_2$O$_7$, (b) (Dy$_{1-x}$Yb$_x$)$_2$Mn$_3$O$_7$, and (c) (Dy$_{1-x}$Lu$_x$)$_2$Mn$_3$O$_7$. The magnetization curves per R/Dy cation [(b) and (c)] were estimated by subtracting that of Lu$_2$Mn$_2$O$_7$ (see the text in detail).