Structures and Physical Properties of Metal-Ordered Manganites $R\mathrm{BaMn_2O_6}$ (R: Y and Rare Earth Elements)

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Abstract

New metal-ordered manganites $R\mathrm{BaMn_2O_6}$ with a successive stacking of RO-$\mathrm{MnO_2}$-BaO-$\mathrm{MnO_2}$-RO have been synthesized and investigated in the structures and electromagnetic properties. Comparing to the metal-disordered manganites, two remarkable features are recognized in $R\mathrm{BaMn_2O_6}$; (1) relatively high charge-order transition temperature and (2) the presence of structural transition without any charge and magnetic ordering. These features are closely related to the peculiar structure that the $\mathrm{MnO_2}$ square-lattice is sandwiched by the rock-salt layers of two kinds; RO and BaO with the different lattice-sizes.

Key words: metal-ordered manganites; electromagnetic properties; phase transitions

Recently, magnetic and electrical properties of perovskite-type manganites with a general formula $(R^{3+}_{1-x}A^{2+}_x)\mathrm{MnO_3}$ (R = rare earth elements and A = alkaline earth elements) have been extensively investigated [1]. Almost all the works devoted to a series of perovskite-type manganites so far are on the disordered manganites with the R^{3+} and A^{2+} ions being randomly distributed. Since the physical properties of the perovskite-type manganites are quite sensitive to even a tiny change in lattice distortion, it is important to employ a compound without A-site disorder in order to make clear the effect of A-site randomness.

Very recently we successfully synthesized a metal-ordered manganite $\mathrm{YBaMn_2O_6}$ with a successive stacking of YO-$\mathrm{MnO_2}$-BaO-$\mathrm{MnO_2}$-YO and observed following three phase transitions; a structural transition at $T_\mathrm{S} = 520$ K, a charge order transition at $T_\mathrm{CO} = 480$ K and an antiferromagnetic transition at $T_\mathrm{N} = 195$ K [2]. Across the phase transition at T_S the resistivity shows little change, whereas the magnetic susceptibility drops significantly and the magnetic interaction varies from ferromagnetic above T_S to antiferromagnetic below T_S. Such transition was first observed in the perovskite-type manganites. In this paper, we report the synthesis, structures and physical properties of new metal-ordered manganites $R\mathrm{BaMn_2O_6}$ (R: Y and rare earth elements).

Powder samples were prepared by a solid-state reaction of $R_2\mathrm{O_3}$, $\mathrm{BaCO_3}$ and $\mathrm{MnO_2}$ [2]. The synthesis of compounds with Ce, Yb and Lu was completely failed. The Er- and Tm-compounds included a significant amount of impurity phase.

The crystal structures were determined by powder X-ray diffraction using CuKα radiation. The magnetic properties were studied using a SQUID magnetometer. The electric resistivity of the sintered pellets was measured by a conventional four-probe technique.

$R\mathrm{BaMn_2O_6}$ can be classified into three groups from the obtained electromagnetic properties. The first group includes the compounds with $R = \mathrm{Tb^{3+}}$, $\mathrm{Dy^{3+}}$ and $\mathrm{Ho^{3+}}$ whose ionic radii are close to $\mathrm{Y^{3+}}$. These compounds show successive three phase transitions as observed in $\mathrm{YBaMn_2O_6}$. The magnetic susceptibility

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and resistivity of $DyBaMn_2O_6$ are shown in Fig. 1 as an example. Although the reduction of magnetic susceptibility across T_S is clearly observed, it is difficult to read a ferromagnetic to antiferromagnetic change of magnetic interaction between Mn ions, because of the significant contribution of magnetic rare earth ions to the total magnetic susceptibility. However the distinct transitions at T_S and T_{CO} are commonly observed in this series. The second group $RBaMn_2O_6$ with $R =$ La, Pr and Nd has metallic ferromagnetic transition at T_C followed by the A-type antiferromagnetic transition in $PrBaMn_2O_6$ and $NdBaMn_2O_6$. The third group consists of the intermediate $R =$ Sm, Eu and Gd. The compounds exhibit the structural and charge order transitions simultaneously, followed by the magnetic long range ordering.

The results are summarized in Fig. 2 as a phase diagram. It is very interesting to compare the obtained phase diagram to the generalized phase diagram of the metal-disordered $(R^{3+}_{0.5}A^{2+}_{0.5})MnO_3$ [1]. The generalized phase diagram is expressed as a function of the tolerance factor (f), where the ferromagnetic metallic (FM) state appears near $f \sim 1$, the charge order (CO) state is most stabilized for $f < 0.975$ and the middle region ($f \sim 0.975$) is responsible for various phenomena including CMR.

In the metal-ordered $RBaMn_2O_6$, however, the tolerance factor cannot be defined because the MnO_2 square-lattice is sandwiched by the rock-salt layers of two kinds; RO and BaO with the different lattice-sizes. Hence we express the phase diagram as a function of the ratio of ionic radius; $r_{R^{3+}}/r_{Ba^{2+}}$.

The phase diagram of $RBaMn_2O_6$ is similar to the generalized phase diagram as a whole. There exist the characteristic phases such as FM phase due to double exchange interaction and CE-type CO phase. The FM state appears around $R =$ La and the CO state is more stable for Nd and later rare earth. The T_{CO} increases with decreasing the ratio of $r_{R^{3+}}/r_{Ba^{2+}}$ and reaches the champion record $T_{CO} = 480$ K in $YBaMn_2O_6$. However there are two striking features in the phase diagram of $RBaMn_2O_6$; (1) the high T_{CO} and (2) the presence of structural transition at T_S above T_{CO}. The relatively high T_{CO} in the metal-ordered manganites is easily understood because the absence of A-site randomness is favorable for the charge ordering of Mn^{3+}/Mn^{4+}. The phase transition at T_S is not accompanied by any charge ordering and magnetic ordering but by the reduction of magnetic susceptibility and the change of magnetic interaction from ferromagnetic to antiferromagnetic. This transition is characteristic of the compounds with small ionic radii of R^{3+} in which the MnO_2 square-lattice is sandwiched by two rock-salt layers with the extremely different lattice-sizes. This situation introduces a strong frustration to the MnO_2 sub-lattice and as a result MnO_6 octahedron

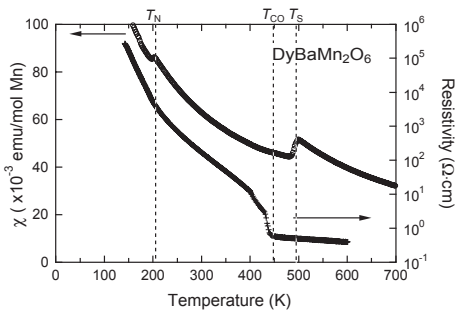

Fig. 1. Magnetic susceptibility and electrical resistivity as a function of temperature for $DyBaMn_2O_6$

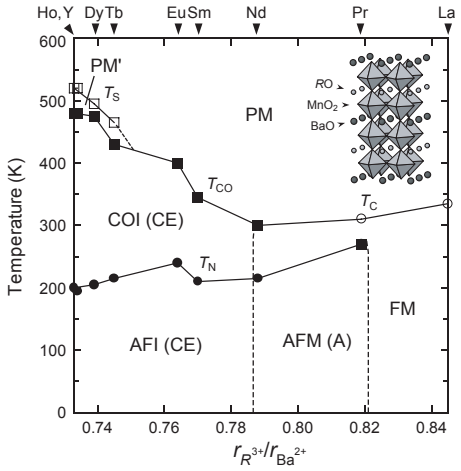

Fig. 2. Phase diagram for metal-ordered manganites $RBaMn_2O_6$ (R=Y and rare earth elements). PM: paramagnetic metal, FM: ferromagnetic metal, AFM(A): A-type antiferromagnetic metal, COI(CE): CE-type charge and orbital ordered insulator, AFI(CE): CE-type antiferromagnetic insulator.

itself is distorted leading to a complex structural deformation (triclinic or monoclinic). Such deformation must give a new perturbation to the competition of multi-degrees of freedom, that is, spin, charge, orbital and lattice. We propose a possible orbital ordering, presumably $d_{x^2-y^2}$-type orbital ordering, at T_S. The freezing of the orbital, charge and spin degrees of freedom at the independent temperatures might be closely related to the peculiar structure of the metal ordered perovskite-type manganites.

References

[1] See for reviews: C. N. R. Rao and B. Raveau, *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides*; World Scientific, Singapore (1998).

[2] T. Nakajima, H. Kageyama and Y. Ueda, J. Phys. Chem. Solids **63** (2002) 913.