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Magnetic properties of the layered oxypnictides (LnO)MnAs (Ln = La, Ce, Pr, Nd)

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Abstract. We have investigated the rare earth elements dependence on the magnetism to understand the contribution to physical properties of the 4f electrons of (LnO)MnAs (Pn = La, Ce, Pr, Nd). (CeO)MnAs, (PrO)MnAs and (NdO)MnAs shows the antiferromagnetic behaviors at low temperature. (CeO)MnAs and (NdO)MnAs have the magnetic anomalies around 34 K and 24 K, respectively. So, it is speculated that the anomalies depend on the Mn -Mn distance directly

1 Introduction

Since the iron based superconductors have been found in layered oxypnictide system, two dimensional electronic system consisting of transition metal elements has newly attracted much attention due to the various physical properties such as superconductors in (LaO)FeAs, (LaO)NiAs, (SmO)FeAs[1], ferromagnetic Kondo metal in (LaO)CoAs[2], heavy fermion in (CeO)FeAs[3].

In case of Mn oxypnictides, the system (LaO)MnPn (Pn = P, As, Sb) has been reported to antiferromagnetic semiconductors with Neel temperature above room temperature [4]. Actually, the antiferromagnetic structure has been found through neutron scattering in (NdO)MnAs [5]. So, the Mn 3*d* magnetic moments in (LaO)MnPn are assumed to order antiferromagnetically at room temperature or above. Considering the insulating origin, there are two scenarios to explain; one is a usual band insulator and the other is a Mott insulator standing on the strong coulomb interaction between the Mn atoms since the Mn 3*d*5 state in the tetrahedral coordination is thought to be in either low spin state (s = 1/2) providing a metallic character without magnetic moments or a Mott insulating characters, or high spin state (s = 5/2) for a band insulator based on the localization of the Mn 3*d* magnetic moments. The origin of the insulating character is unclear so far. In case of a Mott insulator, the distance between the Mn atoms which effects on the Coulomb repulsion and the hybridization of the Mn 3*d* orbitals is very important to decide the physical properties.

In this study, we have tried changing the Mn -Mn distance by choosing the rare earth element to control the electron correlation between them. Namely, the La atom has been substituted by the Ln atom (Ln = Ce, Pr and Nd) to obtain the further reduction of the lattice constant of this system. If the possible scenario is a Mott insulator and enough controlling the Mn –Mn distance is provided, the system is expected to show the dramatic character change. Therefore, we have investigated the lanthanoide elements dependences of the physical properties.

2 Experiment

Samples in this study were polycrystals grown through a solid-state reaction. Starting materials were La2O3 (99.9%), CeO2 (99.99%), La (99.9%), Ce (99.9%), P (99.99), As (99.99%), Sb (99.99) powders. These were mixed stoichiometrically and the mixture was pressed into a rectangular shape. The bars were sealed in evacuated quartz tubes and sintered at 950 ˚C for 48 hours. Then, they were mixed and pressed into bars in Ar atmosphere. Pressed bars were sealed in evacuated quartz tubes again, and were heated at 950 ˚C for 48 hours. Structural parameters was determined by powder x-ray diffraction (XRD) with the incident wavelength of 1.546 Å on the Cu *Ka* line. Temperature dependence of electrical resistivity was examined using a high resistance meter. Magnetization was measured down to 4 K under magnetic field up to 1 T using superconducting quantum interference device (SQUID).

3 Result and discussion

Figure 1 shows XRD profiles of rare earth Mn oxypnictides with calculated results based on the space group *P*4/*nmm*. Every profile is in good agreement with the calculation. The peak shifts to the higher angle side are found, which means that the lattice constants decrease with decreasing the ionic radii of the lanthanoid elements. The lattice constants analysed by Rietveld analysis are listed in the Table 1. Substitution of La by other rare

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earth elements gives smaller lattice constants due to the lanthanoid contraction.

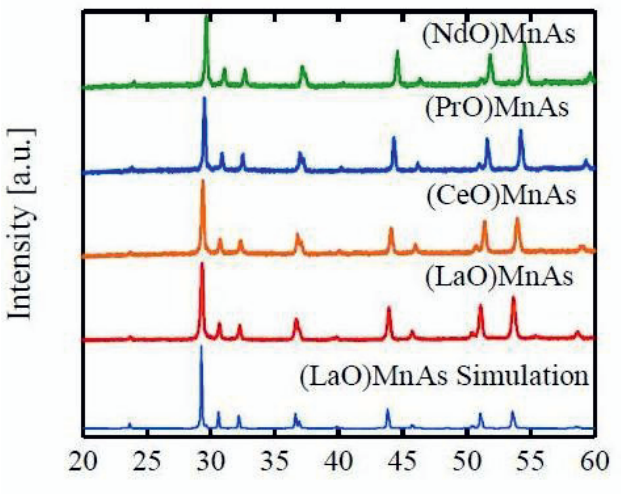

Fig. 1. XRD profiles of (LnO)MnAs : Ln = La, Ce, Pr, Nd

Table I. Lattice constant of (LnO)MnAs

	a	*c*
(LaO)MnAs	4.122	9.048
(CeO)MnAs	4.086	8.957
(PrO)MnAs	4.066	8.921
(NdO)MnAs	4.015	8.819

Figure 2 shows the temperature dependence of the electrical resistivity. All samples show semiconducting behaviors in the entire temperature range and the any metallic behaviors . Expected metallic characters are not found. This results indicates that enough small interatomic distance providing large hybridization to achieve metallic conductivity was not obtained by the rare earth substitution.

Figure 3 shows temperature dependences of the magnetization. The antiferromagnetic sample of (LaO)MnAs has almost temperature independent properties with small positive value due to the antiferromagnetic order. On the other hand, Ce, Pr and Nd systems clearly show temperature dependences. The absolute value of magnetization increases in order of Ce, Pr and Nd. Those samples seem to obey the Curie-Weiss behavior in the temperature range between about 50 K and 300 K. (CeO)MnAs and (NdO)MnAs have magnetic anomalies at 34 K and 23 K, respectively. Regarding to the magnetic anomalies of (NdO)MnAs, it has been reported that the ordered Mn 3*d* magnetic moments along the *c*-axis are reoriented into the *ab* plain and the Nd 4*f* moments also order antiferromagnetically at the same time. (CeO)MnAs is thought to be the similar case of the Nd system. In the meanwhile, the magnetization of (PrO)MnAs obeys the Curie -Weiss law in the wide temperature range and has no anomaly until the antiferromagnetic order temperature of 32 K. Effective magnetic moments calculating from the Curie tail are 1.99 μB in (CeO)MnAs, 3.85 μB in (PrO)MnAs and 4.29 μB in (NdO)MnAs. Considering antiferromagnetic ordered Mn magnetic moments below room temperature, the magnetic moments with paramagnetic behaviors come from the rare earth 4*f* electrons. We should note that the magnetic moment of (CeO)MnAs is relatively small comparing with other materials. It might indicate that all of cerium 4f electrons don't contribute to magnetic moments. Actually, the density of state tends to locate at the top of valence band so that small valence fluctuation effects on the magnetic properties.

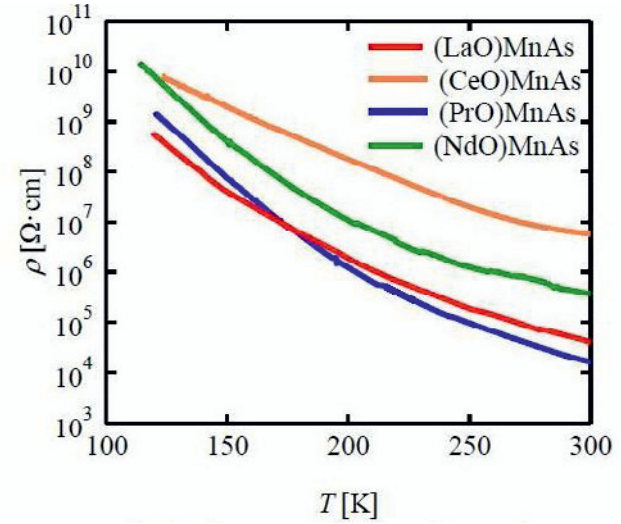

Fig. 2. Temperature dependence of electrical resistivity of (LnO)MnAs

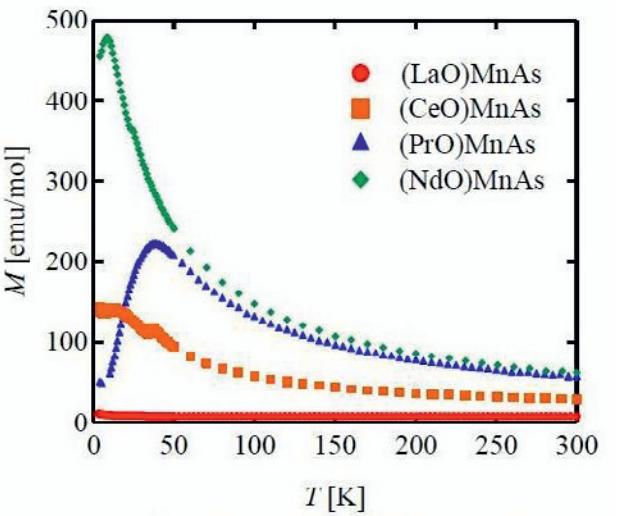

Fig. 3. Temperature dependences of the magnetization of (LnO)MnAs

4 Conclusion

We have investigated the lattice constant dependences of the physical properties by substitution of rare earth elements against La to reveal the insulating origin of the layered Mn oxypnictides. In these substitutions between La and Nd, the expected dramatic changes of the resistivity were not found in this study. Enough short interatomic distances of Mn could not be obtained by the rare earth substitution. Namely, the Mn magnetic moments are still in the antiferromagnetic order. In

addition, the rare earth 4f magnetic moments were introduced into the systems. As reported in (NdO)MnAs, the Nd 4f spins also show antiferromagnetic order at low temperature, which are induced by the the Mn spin reorientation. In (CeO)MnAs, the same anomaly was observed. These results reveal that the Mn magnetic interaction is much stronger than that of Ce and Nd. So, weak coupled interaction is affected easily by the neighbor strong interaction.

Lattice constant controlling by choosing pnictogen elements is needed to obtain enough short interatomic distances for further understanding the insulating origin.

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