Spin polarized states in bismuth based manganites

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Abstract. Transport properties of crystalline (La,Bi)₁₋ₓSrₓMnO₃ and Bi₁₋ₓ(Ca,Ca)ₓMnO₃ were studied in the spin-polarized states induced by chemical substitution or applied magnetic fields. Substitution of lanthanum for bismuth changes the ground state from antiferromagnetic insulator to ferromagnetic metal. The electronic states in the boundary region remain unclear due to the non-uniform distribution of lanthanum ions. Application of high magnetic fields to Bi₁₋ₓ(Sr,Ca)ₓMnO₃ causes negative magnetoresistance effects in the charge-ordered state. All the samples studied do not show metallic conduction even in the highly spin-polarized state. The nature of the spin-polarized insulating state is discussed in relation to the ferromagnetic insulators in lightly-doped manganites.

1. Introduction

Recent versatile studies on manganites with perovskite-type structures have provided us a load map for materials design to achieve desirable electronic phases [1]. Bismuth-based manganites, however, showcase unique electronic states in this class of manganites. BiMnO₃ is a multiferroic material, i.e. ferroelectric ferromagnet, below about 100 K [2]. Hole doping to this material suppresses the ferromagnetic state contrary to the general trend in the double-exchange system [3]. The hole-doped bismuth manganites realize charge-ordered (CO) states over a wide range of doping from temperatures significantly higher than room temperature [4]. Since phase competition between the CO insulator and ferromagnetic metal plays a crucial role to realize the colossal response to the external perturbations, the stable CO state in bismuth-based manganites can be utilized to derive the colossal effects even at room temperature.

The CO states in bismuth-based manganites are known to be extremely stable against the applied magnetic field. Kirste et al. studied high-field magnetization in powdered Bi₁₋ₓCa₁₋ₓMnO₃ and Bi₁₋ₓSr₁₋ₓMnO₃ at low temperature, and found metamagnetic transitions at µ₀H = 56 T and 50 T, respectively [5]. Judging from prominent deviation of these values from the general trend for the melting field of the CO state, they ascribed the field-induced transitions to magnetic transitions independent of the melting phenomena, and hence, anticipate insulating behavior in the spin-polarized state. Such a spin-polarized insulator reminds us of the multiferroic state in undoped compounds. To clarify the nature of the spin-polarized state in bismuth-based manganites, we carried out magnetic and transport measurements in crystalline (La,Bi)₁₋ₓSrₓMnO₃ and Bi₁₋ₓCa₁₋ₓMnO₃.
2. Experimental

Polycrystals of (La,Bi)$_{2/3}$Sr$_{1/3}$MnO$_3$ were synthesized by using the standard solid-state reaction. Crystals of (La,Bi)$_{1-z}$Sr$_z$MnO$_3$ and Bi$_{1/2}$Ca$_{1/2}$MnO$_3$ were grown by using Bi$_2$O$_3$ as flux in platinum crucibles following the procedure reported by Nevriva et al. [6]. Rectangular parallelepiped crystals were obtained with a typical dimension of about a few mm for each side.

High-field magnetization and magnetoresistance measurements were carried out using pulse magnets at the Institute for Solid State Physics, University of Tokyo. Magnetization was measured by means of an induction method by employing a couple of coaxial pickup coils. Magnetoresistance was measured by the standard four-probe method with a dc current parallel to the magnetic field. Magnetizations at low fields were measured using a commercial superconducting quantum interference device magnetometer (MPMS-XL, Quantum Design).

3. Results and Discussion

Since La$_{2/3}$Sr$_{1/3}$MnO$_3$ is a ferromagnetic metal below about 370 K [7], partial substitution of La for Bi can be effective to induce spontaneous spin-polarization in Bi$_{2/3}$Sr$_{1/3}$MnO$_3$. Figures 1 show the temperature ($T$) dependence of magnetization ($M$) and resistivity ($\rho$) in (a) polycrystalline and (b) crystalline (La$_{1-z}$Bi$_z$)$_{2/3}$Sr$_{1/3}$MnO$_3$. In polycrystals, we observed insulating behavior even below the Curie temperature around 370 K, which is consistent with the early report [8]. In polycrystals, however, we have to be careful for the effect of the grain boundary that sometimes causes spurious enhancements in $\rho$ [9]. The results in crystalline (La,Bi)$_{2/3}$Sr$_{1/3}$MnO$_3$ with comparable ferromagnetic moment shows a clear insulator-metal transition at the Curie temperature. However, since we observed insulating behavior in several crystals having significant ferromagnetic moments (not shown), we cannot conclude which is the intrinsic nature because of the non-uniform distribution of lanthanum and bismuth ions, which is sometimes observed in electron microprobe analyses in our (La,Bi)$_{2/3}$Sr$_{1/3}$MnO$_3$ crystals.

Next let us move to the results on the spin-polarized states induced by application of magnetic fields. Fig. 2 shows magnetization curves in a Bi$_{1/2}$Sr$_{1/2}$MnO$_3$ crystal at several temperatures. We do not observe clear metamagnetic transitions in the studied temperature and field range. Small hystereses at around 40 T might indicate the onset of the magnetic transitions. We need further studies up to higher fields to clarify whether it is intrinsic or not. If the metamagnetic
The transition is purely magnetic in origin as is mentioned by Kirste et al., the transition may disappear in the paramagnetic state, while the rare-earth-based manganites show steep changes in $M$ even in the paramagnetic CO phase. The Néel temperature ($T_N$) of the Bi$_{1/2}$Sr$_{1/2}$MnO$_3$ is determined to be 140 K from the cusp in the $M$-$T$ curve at $\mu_0H = 0.5$ T [the closed arrow in Fig. 3(a)]. Although we cannot discuss the presence or absence of the metamagnetic transition in the present results, we can say that there is no significant change in the $M$-$H$ curves below and above $T_N$.

Magnetoresistance in a Bi$_{1/2}$Sr$_{1/2}$MnO$_3$ crystal is shown in Fig. 3(b). The resistance monotonically decreases with increasing the field at all temperatures. The ln $\rho$ decreases roughly in proportion to the $M^2$ as is often observed in the other rare-earth manganites. We plot the resistance at 30 T by open circles in Fig. 3(a) together with the $\rho$-$T$ curve at zero-field. It clearly indicates indicate that Bi$_{1/2}$Sr$_{1/2}$MnO$_3$ remains insulating in the spin-polarized state of at least 30 % of the full moment.

We also studied magnetoresistance in a Bi$_{1/2}$Ca$_{1/2}$MnO$_3$ crystal up to 40 T (not shown). In this sample, the melting temperature of the CO state is about 325 K, which is about 200 K lower than that in Bi$_{1/2}$Sr$_{1/2}$MnO$_3$. Magnetoresistance up to 40 T does not show steep change even at 30 K below the melting temperature. Further studies in higher magnetic fields are highly desirable to clarify whether field-induced melting of charge ordering takes place or not in bismuth-based manganites.

Finally, let us discuss the results on Bi$_{3/4}$Sr$_{1/4}$MnO$_3$. This system locates closer to the multiferroic BiMnO$_3$ than the Bi$_{1/2}$Sr$_{1/2}$MnO$_3$, and hence, shows traces of ferromagnetic fluctuations at low temperatures [Fig. 4(a)]. Figure 4(b) shows magnetoresistance at various

**Figure 3.** (a) Temperature dependence of the $M$ and $\rho$ in crystals of Bi$_{1/2}$Sr$_{1/2}$MnO$_3$. Open circles represent the resistivity at 30 T. (b) Magnetoresistance in Bi$_{1/2}$Sr$_{1/2}$MnO$_3$ at various temperatures.

**Figure 4.** (a) Temperature dependence of the $M$ (at $\mu_0H = 0.5$ T) and $\rho$ in crystals of Bi$_{3/4}$Sr$_{1/4}$MnO$_3$. Open circles represent the resistivity at 30 T. (b) Magnetoresistance in Bi$_{3/4}$Sr$_{1/4}$MnO$_3$ at various temperatures.
temperatures. Although the sample shows negative magnetoresistance, resistivity at 30 T again shows insulating temperature dependence [Fig. 4(a)]. Although we do not have experimental data of $M$-$H$ curves in high-fields for this crystal, extrapolation of the low-field data indicate that manganese spins are almost fully polarized in high fields below about 150 K, which suggests that Bi$_{3/4}$Sr$_{1/4}$MnO$_3$ is insulating even in the fully spin-polarized state.

Ferromagnetic insulator states have been widely observed and discussed in lightly-doped manganites [10, 11, 12]. The ferromagnetic interactions in these systems are regarded to originate from the superexchange interaction instead of the double-exchange mechanism in the metallic state. Such ferromagnetic superexchange interactions are caused by special types of charge or orbital ordering. Hotta and Dagotto theoretically showed that Pr$_{1-x}$Ca$_x$MnO$_3$ can be a ferromagnetic insulator at $x = 0.25$ when a certain type of charge ordering sets in having the unit cell of $\sqrt{2}a_p \times \sqrt{2}a_p \times 4a_p$, where $a_p$ is the lattice parameter in the pseudocubic cell [13].

We studied the superlattice reflections in the Bi$_{3/4}$Sr$_{1/4}$MnO$_3$ crystal using an X-ray four-circle diffractometer. Although we could not determine the exact deformation of each ion, the observed superspots indicate the presence of a superstructure with a unit cell of $2\sqrt{2}a_p \times \sqrt{2}a_p \times 4a_p$, which is similar to that observed in Bi$_{2/3}$Sr$_{1/3}$MnO$_3$ by transmission electron microscope [14].

In bismuth-based manganites, highly polarizable Bi $6s$ electrons may be active in the insulating state. In relation to the multiferroic states in undoped BiMnO$_3$, detailed structural analyses using single crystals are highly desirable.

4. Conclusion

We studied transport properties of crystalline (La,Bi)$_{1-x}$Sr$_x$MnO$_3$ and Bi$_{1/2}$(Sr,Ca)$_{1/2}$MnO$_3$ in the spin-polarized state induced by chemical substitution or applied magnetic fields. Forced spin polarization does not cause insulator-metal transitions in lightly-doped bismuth-manganites.

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