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Transport and magnetic properties of a ferromagnetic metal: $\mathrm{Eu}_{1-x}R_x\mathrm{TiO}_3$

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We report the transport and magnetic properties of a series of ferromagnetic metallic compounds, $\mathrm{Eu}_{1-x}R_x\mathrm{TiO}_3$, where the maximum T_C is 8 K at $x=0.1$. Magnetic interaction between Eu $4f$ spins mediated by itinerant Ti $3d$ electrons is essential for the ferromagnetism of this compound, and a clear correlation between transport properties and magnetism exists in this series. Possible roles of the electron-correlation effect in Ti $3d$ electrons are also discussed. [S0163-1829(99)50246-4]

Recent studies of perovskite manganites[1] have revived the interest in ferromagnetic metals. In perovskite manganites, ferromagnetic interaction originates from the Hund's-rule coupling between the localized spins in the t_{2g} state of Mn $3d$ orbitals and the itinerant electrons in the e_g state. Such magnetic coupling between localized spins and itinerant electrons is not unique to perovskite manganites, but is seen in several ferromagnetic compounds. For example, the Curie temperatures of Eu chalcogenides (EuO and EuS) are drastically enhanced with doped carriers in the Eu $5d$ band.[2] In this case, magnetic coupling between $4f$ spins and $5d$ electrons on the Eu site is essential for the enhancement of ferromagnetic interaction. On the other hand, in the case of an ordered perovskite, $\mathrm{Sr_2MoFeO_3}$,[3] magnetic coupling between localized spins on the Fe^{3+} site ($3d^5$) and itinerant electrons on the Mo^{5+} site ($4d^1$) causes the ferrimagnetic ordering of this compound below 410 K. It should be noted that all these compounds show characteristic correlation between magnetism and transport properties, for example, magnetoresistance. In this paper, we report a series of ferromagnetic metals, $\mathrm{Eu}_{1-x}R_x\mathrm{TiO}_3$ (R=rare earth). In this compound, magnetic coupling between $4f$ localized spins on the Eu site and $3d$ itinerant electrons on the Ti site is essential for the ferromagnetism. To the best of our knowledge, ferromagnetic interaction caused by the coupling between $4f$ spins and $3d$ electrons has not been reported so far.

In perovskite titanates ($R\mathrm{TiO}_3$), R (rare earth) is usually trivalent and Ti is also trivalent, which takes the $3d^1$ electron configuration. These compounds have orthorhombic distortion because of the relatively large Ti^{3+} ion and the small R^{3+} ion as a perovskite structure. Many studies have been carried out for these perovskite titanates as a typical series of Mott insulators.[4] In $\mathrm{EuTiO_3}$, however, Eu is divalent because of the stable $4f^7$ (Eu^{2+}) state, and thus Ti is tetravalent ($3d^0$), meaning that $\mathrm{EuTiO_3}$ is a band insulator. In addition, because of the relatively small Ti^{4+} ion and the large Eu^{2+} ion, $\mathrm{EuTiO_3}$ has no lattice distortion but has a simple cubic perovskite structure. Therefore, $\mathrm{EuTiO_3}$ is similar to $\mathrm{SrTiO_3}$, except that $\mathrm{EuTiO_3}$ has large spins on the Eu site ($S=7/2$), which orders antiferromagnetically at 6 K.[5]

As in the case of $\mathrm{SrTiO_3}$, electrons can be introduced into Ti $3d$ states of $\mathrm{EuTiO_3}$ by substituting divalent Eu by trivalent R. We found that such electron-doped $\mathrm{EuTiO_3}$ becomes a ferromagnetic metal with the maximum Curie temperature at 8 K for $x=0.1$. This is a series of ferromagnetic metallic compounds with a simple cubic structure, where the interaction between the localized $4f$ spins mediated by the itinerant $3d$ electrons causes the ferromagnetic ordering.

Single crystals of $\mathrm{Eu}_{1-x}\mathrm{La}_x\mathrm{TiO}_3$ for $x=0$, 0.1, and 0.2 were grown by the floating-zone method. Starting materials are $\mathrm{Eu_2O_3}$, $\mathrm{La_2O_3}$, Ti, and $\mathrm{TiO_2}$. Stoichiometric amounts of these compounds were mixed and pressed into rods with ~5 mm diameter. We have skipped a sintering process, but directly melted the pressed bar under Ar atmosphere by using a floating-zone furnace equipped with two halogen lamps and ellipsoidal mirrors. Typical feed speed was 10 mm/h. Many pieces of single crystals with shiny surfaces were obtained in the molten rod. X-ray-diffraction measurements indicate that the crystal structure is a simple cubic, and the lattice constant is 3.905, 3.909, and 3.911 Å , for $x=0$, 0.1, and 0.2, respectively. Note that although we start only from Eu^{3+} ($\mathrm{Eu_2O_3}$), Eu^{2+} can be obtained owing to the charge transfer between Eu and Ti during synthesis. Melt-grown polycrystals of $\mathrm{Eu}_{1-x}\mathrm{Gd}_x\mathrm{TiO}_3$ for $x=0.5$ and 0.7 were also made by a similar method with a much higher feed speed (60 mm/h). Resistivity was measured by a conventional four-probe technique. Indium solder was used as the electrodes. A 7-T superconducting magnet was used for the measurement under the magnetic field. Magnetization measurements were done by using a superconducting quantum interference device (SQUID) magnetometer.

The inset of Fig. 1 shows the temperature dependence of resistivity for $\mathrm{EuTiO_3}$ and $\mathrm{Eu_{0.9}La_{0.1}TiO_3}$ in a logarithmic scale. It is clear from this figure that $\mathrm{EuTiO_3}$ is a (band) insulator, but becomes metallic with La substitution for the Eu site. The main panel of Fig. 1 shows the temperature dependence of resistivity for $\mathrm{Eu_{0.9}La_{0.1}TiO_3}$, and $\mathrm{Sr_{0.9}La_{0.1}TiO_3}$ having no localized spins. Various studies on $\mathrm{Sr}_{1-x}\mathrm{La}_x\mathrm{TiO}_3$ have clarified that itinerant electrons are introduced into Ti $3d$ states with the La substitution for the Sr site, and the number of electrons per Ti site equals the La concentration, x.[4,6] Thus, 0.1 electron per Ti site exists in $\mathrm{Sr_{0.9}La_{0.1}TiO_3}$. Similar behaviors in the resistivity of $\mathrm{Eu_{0.9}La_{0.1}TiO_3}$ and that of $\mathrm{Sr_{0.9}La_{0.1}TiO_3}$ indicate that the electronic structure of the Eu compound is almost the same as the Sr compound, i.e., 0.1 electron per Ti site. However, a clear kink at low temperature (shown by an arrow in Fig. 1) is observed only for $\mathrm{Eu_{0.9}La_{0.1}TiO_3}$, suggesting the ordering of Eu spins.

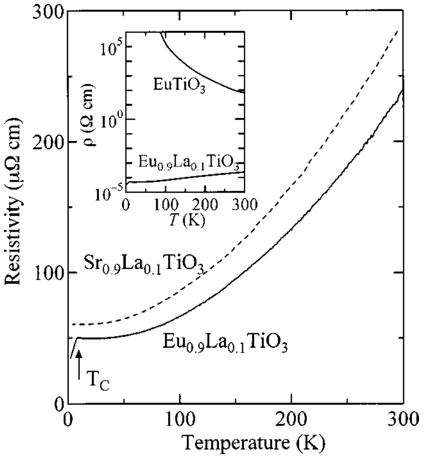

FIG. 1. Temperature dependence of resistivity for $Eu_{0.9}La_{0.1}TiO_3$ (a solid line) and $Sr_{0.9}La_{0.1}TiO_3$ (a dashed line). The arrow shows the temperature of the ferromagnetic ordering of Eu spins. The inset shows the temperature dependence of resistivity for $EuTiO_3$ and $Eu_{0.9}La_{0.1}TiO_3$ in a logarithmic scale.

The main panel of Fig. 2 shows the magnetization vs temperature under 100 G for $EuTiO_3$ and $Eu_{0.9}La_{0.1}TiO_3$. The undoped $EuTiO_3$ shows a cusp at 6 K in the magnetization curve, which corresponds to the antiferromagnetic ordering of Eu spins, as previously reported.[5] By electron doping into the Ti 3d states, however, magnetization shows a sharp increase at 8 K, and resistivity shows a sharp drop at the same temperature. The inset of Fig. 2 shows the field dependence of magnetization for $Eu_{0.9}La_{0.1}TiO_3$ at 5 K. Magnetization is saturated above ~ 0.5 T, and the saturation moment is $7\mu_B$ per Eu, which well coincides with the spin moment of Eu ($S=7/2$). These results indicate that $Eu_{0.9}La_{0.1}TiO_3$ is a ferromagnetic metal below 8 K, where the Eu spins are fully polarized.

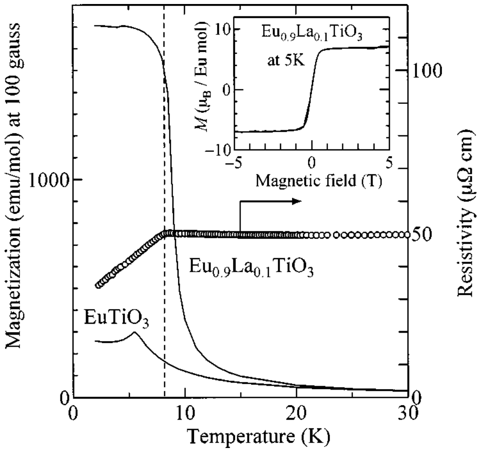

FIG. 2. Temperature dependence of magnetization under 100 G for $EuTiO_3$ and $Eu_{0.9}La_{0.1}TiO_3$ (solid lines, left axis) as well as resistivity for $Eu_{0.9}La_{0.1}TiO_3$ (open circles, right axis). The inset shows the field dependence of magnetization at 5 K for $Eu_{0.9}La_{0.1}TiO_3$ normalized to the number of Eu.

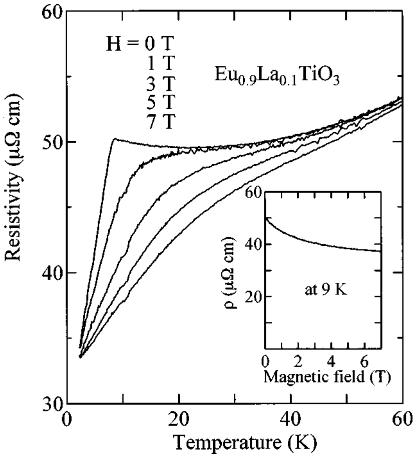

FIG. 3. Resistivity vs temperature under magnetic field for $Eu_{0.9}La_{0.1}TiO_3$. The inset shows the field dependence of resistivity at 9 K for the same sample.

Here, let us consider the mechanism of magnetic interaction in these compounds. In the undoped $EuTiO_3$, there are Eu 4f spins ($S=7/2$) but no itinerant electrons, and interaction between Eu 4f spins is dominated by (i) the superexchange (antiferromagnetic) interaction through the oxygen 2p state, and also by (ii) the indirect exchange through the Eu 5d state. In the case of Eu chalcogenides (EuO and EuS), the latter interaction, which is ferromagnetic, is dominant between the nearest-neighbor spins.[2] On the other hand, for $Eu_{0.9}La_{0.1}TiO_3$, itinerant electrons are introduced into the triply degenerated t_{2g} orbitals of Ti 3d states. These orbitals elongate toward the center between neighboring Eu atoms, and so there is a small but finite overlap of the oribtals with the Eu spins. As a result, another channel of magnetic interaction between the Eu spins mediated by the itinerant Ti 3d electrons appears, which is analogous to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between localized spins of magnetic impurities in metals. This type of magnetic interaction can cause the ferromagnetic ordering of the Eu spins in $Eu_{0.9}La_{0.1}TiO_3$. Such a situation looks similar to doped Eu chalcogenides. We note, however, that Eu chalcogenides originally have ferromagnetic interaction without itinerant carriers (due to the indirect exchange interaction through Eu 5d). Therefore, the present system is different from the Eu chalcogenides in the sense that the interaction changes from antiferromagnetic to ferromagnetic with carrier doping. Such a sign change of magnetic interaction with carrier doping is rather analogous to perovskite manganites.

For perovskite manganites and Eu chalcogenides, the conduction of itinerant electrons, which is strongly coupled with localized spins, can be controlled by aligning the localized spins with magnetic field, and such a process gives rise to large negative magnetoresistance. That phenomenon is also expected for the present compounds. Figure 3 shows the temperature dependence of resistivity under various magnetic fields. With decreasing temperature, resistivity without magnetic field shows a slight increase from 30 K down to $T_C=8$ K, then shows a sharp kink at T_C, and decreases below T_C. Under the magnetic field, however, such a kink at T_C in resistivity is rounded and negative magnetoresistance appears. The inset shows the field dependence of resistivity at 9 K (immediately above T_C). These are universal features for the ferromagnetic compounds that have strong coupling between itinerant electrons and localized spins.

In $Sr_{1-x}La_xTiO_3$, the number of carriers per Ti can be varied from 0 to 1 by substituting divalent Sr by trivalent

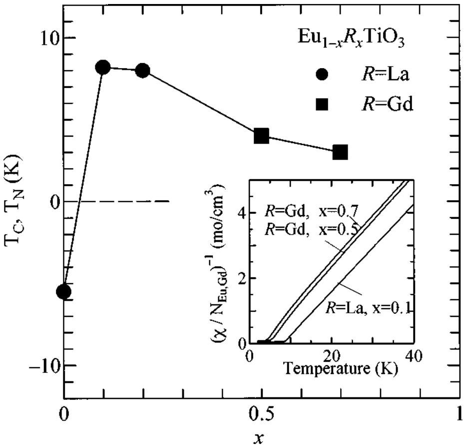

FIG. 4. x dependence of T_C for $Eu_{1-x}R_xTiO_3$ for $R=La$ (circles) and $R=Gd$ (squares). The inset shows the inverse susceptibility normalized to the number of Eu and Gd.

La.[6] In $EuTiO_3$, however, too much La substitution breaks the Eu network itself. To further increase the number of itinerant electrons, therefore, we choose Gd as a trivalent ion, which has the same electron configuration with Eu^{2+} $(4f^7)$ and can maintain the network of $4f^7$ spins. Figure 4 plots T_C as a function of the number of electrons per Ti site $(=x)$. The inverse susceptibility for $x=0.1$, 0.5, and 0.7 is plotted in the inset. As can be seen, T_C is maximized at $x=0.1$, and then it again decreases with further increasing x. One possible origin for that behavior of T_C vs x is a RKKY oscillation.[2] In the case of a RKKY interaction, the sign of interaction changes oscillatorily according to the relation between the Fermi wave number and the distance between neighboring sites. Thus, with increasing the number of electrons, T_C can change oscillatorily. Another possible origin is the electron-correlation effect in the Ti $3d$ state. Various studies on $Sr_{1-x}R_xTiO_3$ indicate that the electron-correlation effect in the Ti $3d$ state is pronounced as x approaches 1.[6] In other words, because of the on-site Coulomb interaction on the Ti site, the effective mass of the itinerant $3d$ electrons is enhanced as x approaches 1, where the system becomes a Mott insulator. This mass enhancement of the Ti $3d$ electrons effectively reduces the interaction between the localized $4f$ spins, and hence reduces T_C. Such an issue, i.e., how the correlation effect of itinerant electrons modifies the magnetic interaction mediated by them, has not been well studied so far, and the present compounds would be an ideal system for future studies on that issue.

It also should be noted that the compound on the other end of this series, $GdTiO_3$, is a Mott insulator with a distorted perovskite structure, and becomes ferromagnetic below 34 K.[7] The ferromagnetic interaction in this compound is believed to be dominant between neighboring Ti and to be associated with the ordering of Ti t_{2g} orbitals.[8] In other words, the origin of the ferromagnetic interaction in $GdTiO_3$ is different from that in the doped $EuTiO_3$. The present experimental result indicates that two different types of ferromagnets, the metallic and the insulating ones, do not continuously change from one to the other with x, but T_C takes the minimum in between.

In summary, we found a series of ferromagnetic compounds, $Eu_{1-x}R_xTiO_3$. In this series, the magnetic interaction changes from antiferromagnetic to ferromagnetic with carrier doping, and the ferromagnetic interaction originates from the interaction between Eu $4f$ spins mediated by itinerant Ti $3d$ electrons. The electron-correlation effect of itinerant electrons also plays a key role for the magnetism in a large x regime.

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