## A First-Order Phase Transition Induced by a Magnetic Field

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An electronic (metal-to-insulator) phase transition of the first order, which can be caused by an external magnetic field, was discovered in  $Nd_{1/2}Sr_{1/2}MnO_3$ . A clear hysteresis was observed during the increase and decrease of an external magnetic field at a fixed temperature. The hysteretic field region was observed to depend critically on temperature and to drastically expand with a decrease of temperature, perhaps as a result of suppression of the effect of thermal fluctuations on the first-order phase transition. Although it has seldom been observed, this is thought to be a generic feature of the first-order phase transition at low temperatures near 0 kelvin.

In general, a first-order phase transition is accompanied by hysteresis; that is, a difference of the transition points as a thermodynamic variable that drives a phase transition is increased and decreased (1). A well-known example is the melting of a solid, which often shows a supercooled (or superheated) state as a metastable state below (or above) the normal melting (or solidification) temperature. Here we describe a first-order phase transition induced by an external magnetic field in one of the manganese oxide compounds with perovskitetype structure,  $Nd_{1/2}^{1}Sr_{1/2}MnO_3$ . On the basis of a peculiar phase diagram in the temperature field plane, a novel reentrant, irreversible behavior of the insulator-tometal transition is demonstrated.

Figure 1 shows the temperature dependence of the magnetization, lattice parameters, and resistivity of the  $Nd_{1/2}Sr_{1/2}MnO_3$ crystal. As a generic feature of hole-doped perovskites of manganese oxide, the crystal undergoes a ferromagnetic transition at the Curie temperature  $(T_c, 255 \text{ K})$  (2, 3). This is attributable to the so-called double-exchange mechanism (4), which is a ferromagnetic coupling between the local 3d electron  $(t_{2g} \text{ state})$  spins through kinetic exchange of the itinerant 3d electron  $(e_g$ state). At temperatures above 160 K, the crystal shows metallic conductivity: The resistivity shows an appreciable decrease below  $T_{\rm c}$ , owing to reduced magnetic scattering of the charge carriers in the spin-ordered ferromagnetic phase. What is unique in the compound  $Nd_{1/2}Sr_{1/2}MnO_3$  is that another distinct phase transition occurs at  $T_{\rm CO}$  = 158 K (Fig. 1). ( $T_{\rm CO}$  represents the critical temperature for the charge-ordering transition.)

When this phase transition occurs at

 $T_{\rm CO}$ , the resistivity jumps by more than two orders of magnitude from a typically metallic value (5  $\times$  10<sup>-4</sup> ohm  $\cdot$  cm), and the ferromagnetic magnetization disappears, which indicates the simultaneous ferromagnetic-to-antiferromagnetic transition. In accord with these changes in electric and magnetic properties, the lattice parameters in the orthorhombically distorted perov-skite lattice  $(a \approx b \approx \sqrt{2}a_p \text{ and } c \approx 2a_p; a_p$ relating to the cubic perovskite) show a distinct change, as shown in Fig. 1. According to recent studies (5, 6) on the analogous crystal Pr<sub>1/2</sub>Sr<sub>1/2</sub>MnO<sub>3</sub>, the transition from ferromagnetic metal to antiferromagnetic insulator can be assigned to the phase transition to the charge-ordered state, in which the nominally Mn<sup>3+</sup> and Mn<sup>4+</sup> species show a real space ordering in the crystal. The charge-ordered pattern is alternating within the *ab* plane or  $(\pi, \pi, 0)$  in the pseudo-cubic setting of the perovskite-type lattice. [The perovskite A site (Nd, Sr) is solid solution or random alloy, but the doped holes show the ordering on the perovskite B site, that is, the Mn site.] It has recently become known that such a chargeordering phase transition is widely seen in the perovskite (or layered perovskite)-type lattice of the transition metal oxides, such as  $La_{2-x}Sr_xNiQ_4$  (7),  $La_{1-x}Sr_{1+x}MnO_4$  (8), and  $La_{1-x}Sr_xFeO_3$  (9), when the doped hole concentration x takes a commensurate value, such as  $x = \frac{1}{3}$ ,  $\frac{1}{2}$ , and  $\frac{2}{3}$ . A unique feature of the perovskite Mn-oxide compounds is that the charge-ordering transition is associated with the ferromagneticto-antiferromagnetic phase transition. The spin structure in the charge-ordered antiferromagnetic state below  $T_{\rm CO}$  is a rather complicated one, with the  $4 \times 4 \times 2$  unit cell in the cubic perovskite setting, called the CE type (10).

For the analogous compound  $Pr_{1/2}Sr_{1/2}$ -MnO<sub>3</sub>, the present authors recently found (6) that the charge-ordered state collapses under an external magnetic field, accompanying the metamagnetic (that is, the field-induced antiferromagnetic-to-ferromagnetic) transition.

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In other words, the "crystal state" of the doped holes can be melted and changed into a "liquid state" (that is, a metallic state) by application of an external field. A new phenomenon observed for the crystal  $Nd_{1/2}Sr_{1/2}$ -MnO<sub>3</sub> is that an extremely "supercooled liquid state" can exist near 0 K and even below the temperature region of the "crystal state" in a region with a relatively low magnetic field.

The magnetic field dependence of the resistivity at various temperatures below  $T_{\rm CO}$  is shown in Fig. 2. The resistivity shows a steep decrease on a logarithmic scale at a critical field (upper critical field) in a field-increasing scan, indicating the field-induced melting of the charge-ordered state. We observed a metamagnetic-like (that is, an antiferromagnetic-to-ferromagnetic) transition at a corresponding critical



Fig. 1. Temperature dependence of the magnetization (top) (measured at a magnetic field of 0.5 T), lattice parameters (middle), and resistivity (bottom) in a crystal of Nd<sub>1/2</sub>Sr<sub>1/2</sub>MnO<sub>3</sub>, which was grown by the floating-zone method. Units of the magnetization are Bohr magneton  $\mu_{\rm B}$  per Mn site.  $T_{c}$  and  $T_{CO}$  represent the Curie temperature and the critical temperature for the charge-ordering transition, respectively. When the charge-ordering transition occurs, resistivity jumps by several orders of magnitude. Simultaneously, the ferromagnetic magnetization disappears because of the antiferromagnetic spin order in the chargeordered phase, and the lattice parameters in the orthorhombic structure (12) (Pbnm; the so-called GdFeO<sub>2</sub> type) show an abrupt change that is characteristic of the first-order phase transition.

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Fig. 2. Changes of resistivity in field-increasing and field-decreasing runs at various temperatures [(A), 60.0 K; (B), 20.0 K; (C), 8.05 K; and (D), 2.49 K] for

the crystal of  $Nd_{1/2}S\dot{r}_{1/2}MnO_3$ . The resistivity shows a jump on a logarithmic scale at the lower and upper critical fields, as indicated by crosses.

field. Such a field-induced metallic state shows up even at a temperature of 2.5 K, as shown in Fig. 2D. Thus, the charge-ordered state can be totally extinguished over the whole temperature range under an external magnetic field above 12 T. Such a fieldinduced insulator-to-metal transition. which accompanies the melting transition of the charge-ordered state and hence occurs at any temperature below  $T_{CO} = 158$ K, may also be viewed as a new sort of colossal magnetoresistance, with a field-induced change of resistivity of more than three orders of magnitude up to  $T_{\rm CO} = 158$ K. When the field is swept down, the charge-ordered insulating state is recovered at some critical field (lower critical field) as evidenced by a resistivity jump over several orders of magnitude (Fig. 2). At these fields, the lattice parameters as well as the resistivity appear to undergo abrupt changes, which is similar to the case of the thermally induced phase transition (Fig. 1). We confirmed a clear hysteresis of the crystal striction against an external field, which was detected with the use of a strain gauge attached to the crystal.

A trace of the resistivity as a function of the magnetic field draws a typical hysteresis loop, indicating the first-order nature of this field-induced phase transition. An important feature is that the hysteretic field region is drastically expanded by the lowering of temperature. It is also notable that the hysteresis loop is not completely closed at low temperatures (below  $\sim 20$  K), even when the field is decreased to zero. This implies that a remnant or "fragment" of the charge-ordered state may remain at low temperatures. Nevertheless, the change in resistivity is large and steep enough on a logarithmic scale to determine the lower and upper critical fields of the phase transition (as indicated by crosses in Fig. 2).

To more clearly illustrate the temperature dependence of the critical fields, we show the electronic phase diagram in the plane of temperature and external magnetic field in Fig. 3. A hatched area in Fig. 3 shows a hysteretic region (between the lower and upper critical fields) that is characteristic of the first-order phase transition, that is, a bistable region where the charge-ordered state and the metallic state can coexist. The hysteretic region becomes anomalously broader when temperature is lowered to below  $\sim 20$  K. In particular, the lower critical field for the metal-to-insulator transition is conspicuously decreased with decrease of temperature, as shown on a magnified scale in the inset in Fig. 3.

Such a conspicuous change of the critical field value with change of temperature can be interpreted as follows: In terms of the free energy as a function of the thermodynamic variable [that is, the magnetization (M) in the present case], the charge "liquid" and "crystal" states correspond to the two local minima with large and small M values, respectively, which are separated by a potential barrier (U). In this case, an external magnetic field (H) tends to stabilize the high-M state by means of the energy term -MH, and hence the potential is subject to change with the field. (It is easily shown that the barrier height U, which is measured from the potential local minimum corresponding to the metastable state, is proportional to |H| $- H_c^{(0)}|^{3/2}$ ,  $H_c^{(0)}$  being the critical value where U becomes zero.) According to classical thermodynamics, the first-order phase transition of the metastable state takes place when the formation energy of the critical nucleus of the stable state in the metastable phase is comparable with temperature (T). In the present case, the shape of the free energy function is supposed not to change significantly at low temperatures well below  $T_{\rm CO}$ . Therefore, the decrease of temperature suppresses the thermal fluctuation and hence the transition of the metastable state even near  $H_{c}^{(0)}$ . This is a qualitative explanation

of why the hysteretic field region is expanded in such a temperature-dependent manner (as seen in Fig. 3).

Although it has seldom been observed, this behavior must be a generic feature of the first-order phase transition at very low temperatures, which can be caused by a thermodynamic variable other than temperature, such as an external magnetic field and pressure. In order to quantitatively investigate the first-order phase transition at temperatures near zero, we must consider a



**Fig. 3.** The electronic phase diagram of the Nd<sub>1/2</sub>-Sr<sub>1/2</sub>MnO<sub>3</sub> crystal, which was determined by use of the critical fields (as indicated by crosses in Fig. 2) for the insulator-to-metal and metal-to-insulator transitions induced by scanning of an external field at a fixed temperature. "Nonmetal" and "metal" represent the antiferromagnetic state with the charge ordering (as schematically depicted in the figure) and the ferromagnetic metallic state realized by the double-exchange interaction, respectively. The inset shows a magnification of the temperature dependence of the lower critical field for the metal-to-insulator transition;  $\mu_0$  is the magnetic permeability in vacuum.

temperature-dependent critical nucleation of the stable state in the metastable phase, as well as the effect of the quantum nucleation or tunneling that will give rise to temperature-independent transition probability at temperatures near zero (11). As seen in the inset in Fig. 3, however, the lower critical magnetic field  $(H_{cl})$  for the metal-to-insulator transition appears to show no sign of saturation down to 1.5 K, indicating that a negligible contribution is made by the quantum tunneling process in the temperature range investigated here. The experimental data for  $H_{cl}$  can be approximately scaled with an empirical func-tion  $(H_{cl} - H_{cl}^{(0)}) \propto T^{\alpha}$ , where the critical exponent  $\alpha$  was estimated to be in the range of 1/4 to 1/3, depending on the choice of  $H_{cl}^{(0)}$ . A solid line in the inset represents the case in which  $\alpha = \frac{4}{15}$ .

Finally, we demonstrate the occurrence of reentrant metal-to-insulator transitions as a consequence of the peculiar electronic phase diagram of Fig. 3. Figure 4 exemplifies the resistivity change in a course of scans within the temperature field plane as shown in the inset: First, the crystal of Nd<sub>1/2</sub>Sr<sub>1/2</sub>MnO<sub>3</sub> was cooled from 300 K down to 4.2 K under a field of 7.5 T (route I), and then the magnetic field was decreased down to 4 T while the temperature was kept at 4.2 K. Then the crystal was warmed up to 300 K (route II) and cooled again down to 4.2 K (route III), while the field was maintained at 4 T. Corresponding to such a trajectory in the electronic phase diagram (inset, Fig. 4), the resistiv-



**Fig. 4.** Irreversible reentrant behaviors of resistivity in the crystal of Nd<sub>1/2</sub>Sr<sub>1/2</sub>MnO<sub>3</sub> under magnetic fields. The inset shows the trajectory of the scans of the temperature and magnetic field on the electronic phase diagram. The difference in the resistivity for routes I and II, III around  $T_c = 255$  K is due to the conventional magnetoresistance (3) arising from the difference of the field strength (4 T and 7.5 T).

ity shows an irreversible behavior. In route I, the resistivity is metallic over the whole temperature range, due to the complete melting of the charge-ordered state down to 0 K, as expected from the phase diagram. The resistivity in route II shows a characteristic reentrant behavior, that is, a sequential metal-insulator-metal transition, corresponding to the traverse of the charge-ordered insulating state as temperature increased from the supercooled state at 4.2 K along route II. In this field (4 T) however, the supercooled metallic state is metastable and hence cannot be realized in such a field-cooling scan as that of route III, where only the metal-to-insulator transition is observed around 115 K. Thus the electronic (and perhaps magnetic as well as lattice-structural) properties of this compound are remarkably route dependent because of the hysteretic nature of this first-order phase transition.

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- We thank H. Fukuyama and N. Nagaosa for enlightening discussions. Supported by the New Energy and Industrial Technology Development Organization of Japan.

19 June 1995; accepted 30 August 1995

## Chemical Generation of Acoustic Waves: A Giant Photoacoustic Effect

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An anomalous photoacoustic effect is produced when a suspension of carbon particles in water is irradiated by a high-power, pulsed laser. The photoacoustic effect has an amplitude on the order of 2000 times that produced by a dye solution with an equivalent absorption coefficient and gives a distinctly audible sound above an uncovered cell. Transient grating experiments with carbon suspensions show a doubling of the acoustic frequency corresponding to the optical fringe spacing of the grating. The effect is thought to originate in high-temperature chemical reactions between the surface carbon and the surrounding water.

The photoacoustic effect (1-8) takes place when radiation is absorbed by a body: the thermal expansion of the body that occurs when optical radiation is converted to heat causes mechanical motion of the body, which, in turn, launches a sound wave into the surrounding medium. In this report, we describe an anomalously large photoacoustic effect in aqueous suspensions of fine carbon particles. We used a conventional photoacoustic apparatus together with a pulsed laser to compare the amplitude of the effect in carbon suspensions with that produced by an absorbing dye solution. Suspensions of carbon (30 nm in diameter) were made by the addition of dry carbon

black (9) to distilled water in a standard spectrophotometer cuvette at a concentration of 55 mg liter<sup>-1</sup>. The suspensions were sonicated in an ultrasonic cleaning bath for 30 s until the carbon was uniformly dispersed in the water.

In preliminary experiments, the photoacoustic effect displayed an induction period where the magnitude of the acoustic signal gradually increased as the suspension was irradiated by the laser. The cuvette was therefore first irradiated with the 15-ns, 532-nm output of a Q-switched Nd:yttriumaluminum-garnet laser for 3000 shots, with the laser operating at 160 mJ per shot. Then a small sample of the irradiated suspension was withdrawn from the cuvette, diluted with distilled water, and placed in a photoacoustic cell equipped with a polyvinyl-

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