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Isotope-driven perturbation of the ground-state properties in (Sm, Gd)-Sr manganites near the half-doped hole concentration

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We report on the effect of isotopic exchange $^{16}O \rightarrow ^{18}O$ on the magnetic and transport properties of the ground state in $(Gd_{0.5}Sm_{0.5})_{0.55}Sr_{0.45}MnO_3$. The ground state of the ^{16}O sample is a ferromagnetic metal. Isotopic exchange drives that state into a antiferromagnetic insulator. Moderate applied magnetic fields have little effect on both ground states. However, higher fields can restore the ferromagnetic metallic properties of the ^{18}O sample. The high-temperature phase at that concentration shows a competition between different ordered phases as evident from the existence of a different scale transition temperature $T^* > T_C$ at which the bulk of the samples transforms into a disordered paramagnetic phase.

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Transition metal oxides with perovskite structure $R_{1-x}A_xMnO_3$, where R and A are trivalent rare earth and divalent alkaline earth ions, respectively, exhibit complex phase diagrams and unusual behavior. Such metal oxides undergo magnetic transitions between different ordered and disordered states accompanied by resistive transitions as well as strong magnetoresistance. The ferromagnetic ordered ground state of these compounds is mediated by the double-exchange mechanism, where itinerant doped holes can align the local spins of the $3d\ t_{2g}$ state ferromagnetically.[1–4] However, many other instabilities such as antiferromagnetic superexchange, Jahn-Teller, orbital ordering, and charge ordering interactions can compete with the double-exchange mechanism. In particular, charge ordering shows up in many of the hole-doped manganese oxides[5–9] as in other layered perovskite-type transition metal oxides,[10,11] accompanied by spin and orbital ordering. Such competition becomes prominent near $x=0.5$ where the charge ordered state is most stabilized. At that level of hole density, small deviations in temperature, pressure, and magnetic field can induce a phase transition to different ordered ground states. In some cases, oxygen isotope substitution might lead to a phase transition when the doping ratio is kept at exactly 0.5,[12] or when the grains are loosely backed in a porus sample.[13]

Close to the half-doped hole concentration, i.e., $x=0.5$, one can control the electron bandwidth, and hence the transition temperature, by varying the tolerance factor via the mean radius of the A site in the perovskite. Tokura *et al.*[14] showed that the system $R_{0.55}Sr_{0.45}MnO_3$ experiences a reduction in T_C upon varying the mean ionic size by using La, Pr, Nd, and Sm for the R element. The ground state of these perovskites is a ferromagnetic metallic ordered state. The samarium compound is of particular interest since it is the closest to the cross-over from the ferromagnetic metallic to the insulating phase. When Gd is substituted for Sm, the ground state is expected to change its basic characteristics and become antiferromagnetic with short-range charge order. The phase transition between the Sm metallic and Gd insulating ground states is first order. The mean ionic radii might be further fine tuned by doping the R site with a different rare-earth element, e.g., $(Gd_ySm_{1-y})_{0.55}Sr_{0.45}MnO_3$, at different y concentration. In this paper, we present evidence that a transition from the ferromagnetic to the antiferromagnetic ordered ground state could be induced by isotopic substitution at a single doping level $y=0.5$ in the compound $(Gd_ySm_{1-y})_{0.55}Sr_{0.45}MnO_3$, which is close to but not exactly at the half-doped concentration ratio $x=0.5$.

Polycrystalline samples of $Sm_{0.55}Sr_{0.45}MnO_3$ and $Gd_{0.55}Sr_{0.45}MnO_3$ were prepared using the standard solid-state reaction method from (samarium/gadolinium) oxide, strontium carbonate, and manganese oxide. The molar proportions were mixed and sintered in air at 1200 °C for a total time of 72 h. The resulting compounds were pulverized and mixed according to their molar weights to produce the powder compound $(Gd_{0.5}Sm_{0.5})_{0.55}Sr_{0.45}MnO_3$ which was sintered in air for an additional 48 h at 1200 °C in the form of two pellets. Isotopic exchange was carried out by further treatment of each pellet in ^{16}O and ^{18}O gas flow under the same conditions. Gas exchange took place at 1050 °C for 60 h. Weight analysis indicated that the ^{18}O sample contained about 90% of the heavier isotope. X-ray diffraction analysis showed that both samples are single-phase compounds. Back exchange in a flow of ^{16}O restored all the properties of the ^{18}O sample to what they were before the initial oxygen isotope treatment. Magnetic measurements were done using a Quantum Design magnetometer. The sample's magnetic moment was measured as a function of temperature in the range $5 < T < 400$ K and applied magnetic field up to 5.0 T. Resistive measurements were done using the standard four-lead technique over the same range of temperature and magnetic field.

The results of the magnetic and transport measurements for both isotopic samples are presented in Fig. 1, in which we show the susceptibility and the resistance as a function of temperature in an applied field of 25 G. The magnetization (and hence the susceptibility) of the ^{16}O sample increased

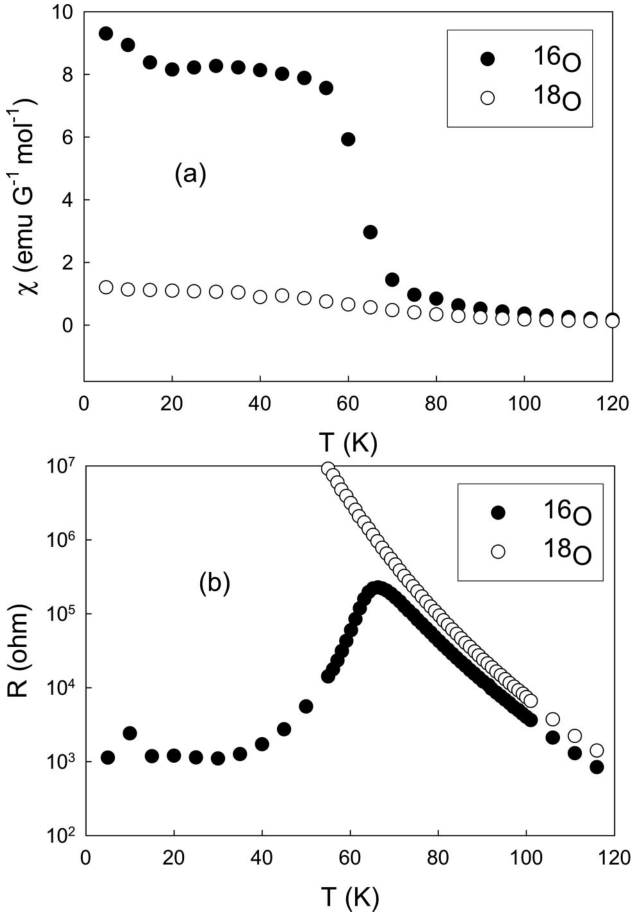

FIG. 1. Temperature dependence of the magnetic susceptibility and electrical resistance for two isotopic samples.

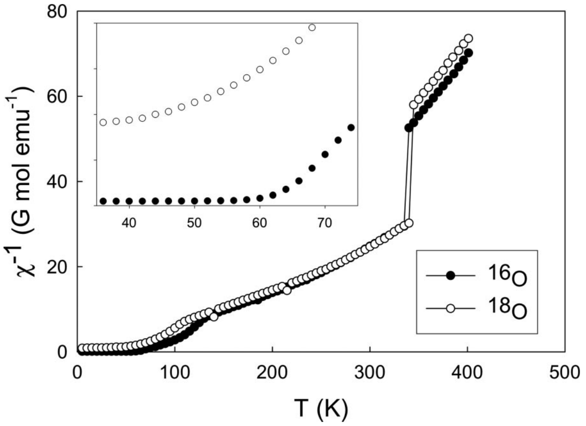

FIG. 2. Temperature dependence of the inverse susceptibility for two isotopic samples measured in a low magnetic field $H=25$ G. Linear Curie-Weiss-like behavior is observed at temperatures much higher than T_C where the dominant phase is paramagnetic. The charge ordered phase at intermediate temperatures is insensitive to the isotopic mass.

rapidly as the temperature decreased indicating the onset of ferromagnetic ordering. The ferromagnetic transition temperature was estimated to be 65 K as inferred from the maximum dM/dT. A cusp at about 20 K is visible in the magnetization curve and is thought to be caused by the magnetic ordering on the samarium sublattice. This cusp is seen in both isotopic samples and at different fields [see, for instance, Figs. 3(a) and 3(b) below]. The magnetization of the ^{18}O sample, on the other hand, experienced a much slower growth as a function of decreasing temperature, its value did not level off by comparison to the ^{16}O sample, and the maximum attainable magnetization/mol at 5 K is an order of magnitude less than that of the ^{16}O sample. Such features indicate that the transition is smeared out and is probably absent in this sample. Figure 1(b) shows that the resistance for both isotopic samples increased as the temperature was reduced from 120 K. In general, the resistance of the heavier isotope sample is larger even at room temperature. As the temperature is reduced, the ^{16}O sample's resistance approached a maximum at 65 K, indicating that the sample is in the metallic phase. The resistance of the ^{18}O sample grew continuously and reached very large values, beyond the range of our instruments, below $T=45$ K. This sample is essentially insulating even at 5 K. The above results confirm that the ^{16}O sample undergoes a phase transition into a ferromagnetic metallic state at $T=65$ K, while the ^{18}O sample remains in the same phase upon reducing the temperature. Thus, the substitution $^{16}\mathrm{O} \rightarrow {}^{18}\mathrm{O}$ leads to the narrowing of the electron bandwidth and the weakening of the ferromagnetic interaction. The effect of substitution is attributed to the zero-point oscillations and the polaronic effects associated with the different masses of the two oxygen isotopes at low temperatures.[15,16] In our case, the effect is so strong that it inhibits the formation of the ordered ferromagnetic, metallic state in the heavier isotope sample at any finite temperature. The temperature dependence of inverse susceptibility for both isotopic samples is shown in Fig. 2. The ferromagnetic transition is observed for the ^{16}O sample as a sudden change in the χ^{-1} slope around $T=65$ K, while the ^{18}O sample shows a gradual decrease and higher value for the low-temperature χ^{-1}. This supports the prediction that the ferromagnetic transition is absent for the ^{18}O sample. Above the transition temperature of the ^{16}O sample, the behavior of the χ^{-1} curves is rather complicated. At very high temperatures (above 350 K) the inverse susceptibility is linear in temperature for both samples, which indicates that the paramagnetic phase dominates over this temperature range and the susceptibility shows a Curie-Weiss-like behavior. There is sharp discontinuity at $T=335$ K (^{16}O) and $T=345$ K (^{16}O). This is related to the arising of antiferromagnetic correlations accompanied by short-range charge ordering at the corresponding temperatures and leads to a picture of competing and interacting ferromagnetic and antiferromagnetic correlations.[17] The short-range charge ordered state is insensitive to the isotope composition and the inverse susceptibility of the two isotopic samples is essentially the same over the temperature range $65 < T < 350$ K. This is quite natural if the mechanism of charge ordering is predominantly electron-lattice interaction[18] since the dimensionless electron-phonon coupling constant λ does not depend on the mass of the ion. On the contrary, T_C in the double-exchange model scales with the bandwidth, and the decrease in T_C with the growth of oxygen mass is consistent with this interpretation. An applied magnetic field should have a profound effect on both ferro-

TABLE I. Transition temperatures and isotope exponents for the two isotopic samples ^{16}O and ^{18}O in different applied magnetic fields.

H (T)	T_C^{16} (K)	T_C^{18} (K)	ΔT_C (K)	α_O
25×10^{-4}	65			
1	65			
2	83	58	25	3.04
3	93	69	24	2.53
4	100	77	23	2.22
5	104	83	21	1.92

magnetic and charge ordered states in manganites. Table I shows such effect on the transition temperatures and the isotope exponent, defined as $\alpha_O = -\Delta \ln(T_C)/\Delta \ln(M)$, for both isotopic samples.

For the ferromagnetic state, magnetic fields suppress the resistance at low temperatures, lower the resistance peak at the insulator-metal transition, and shift the transition temperatures to higher values. The magnetization curve becomes flatter and the transition broadens as higher fields are applied. On the other hand, if a charge ordered state is present, it should melt under magnetic fields and undergo a first order metamagnetic transition, accompanied by a drastic decrease in resistivity and a pronounced temperature hysteresis.[19,20] Supporting evidence of such behavior is presented in Fig. 3 where we plotted the magnetization and the resistance of both isotopic samples as a function of temperature for various magnetic fields up to 5 T. As the magnetic field increased, the magnetic moment of the ^{16}O sample increased. The ^{18}O sample started to show ferromagnetism at low temperatures for applied fields of 2 T and higher. Moderate magnetic fields up to 1.0 T had little effect on the resistance of either isotopic sample at all temperatures. However, magnetic fields in excess of 1 T induced magnetic and resistive transitions in the ^{18}O sample and restored its ground state to the ferromagnetic metallic behavior. The fact that magnetic fields less than 1 T are not strong enough to cause ferromagnetic alignment and induce percolation appears to be universal for all types of manganites where oxygen substitution modifies the ground-state properties. Babushkina *et al.* observed similar behavior in $La_{0.175}Pr_{0.525}Ca_{0.3}MnO_3$ in which the transition temperature is higher (95 K).[15] It appears that the resistance at 5 K for the ^{16}O sample is still large at fields up to 1 T and we expect that percolation is not complete until strong ferromagnetism is established in the sample at applied fields larger than 1 T.

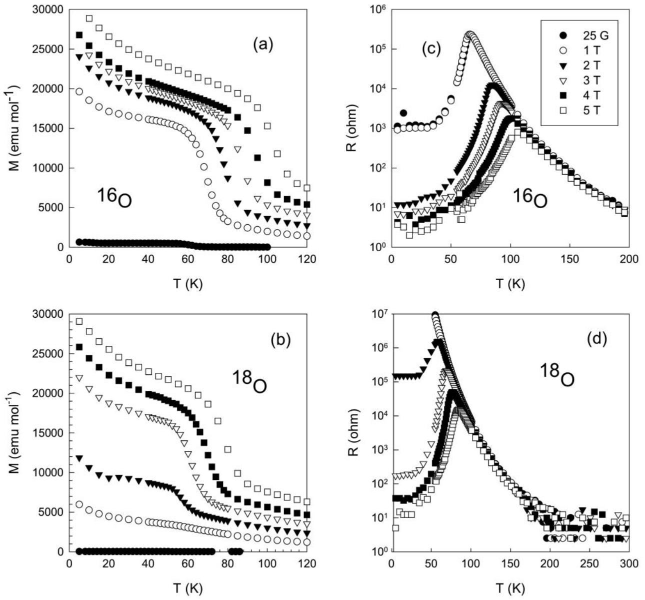

FIG. 3. The effect of an applied magnetic field on the magnetization and resistance of both isotopic samples. The legend in (c) applies to all four panels.

Both the isotopic shifts in the transition temperature and the isotope exponent are remarkably high compared to other manganites, and the isotope exponent is sensitive to the magnetic field. It has been shown that such features might arise from oxygen excess in the samples and different oxygen contents.[21] This possibility is ruled out since annealing temperatures were high enough to prevent any inconsistency in oxygen stoichiometry. Moreover, the properties of the entire family of the compound (Sm/Gd)-Sr appear to be insensitive to the preparation conditions. We conclude that the effect is merely due to polaronic effects much stronger than those observed in the La-Ca manganites.

In summary, we studied the system $(Gd_{0.5}Sm_{0.5})_{0.55}Sr_{0.45}MnO_3$ where a crossover from a ferromagnetic metallic to an antiferromagnetic insulating ground state is induced by isotopic substitution. We also showed that antiferromagnetism is accompanied by charge ordering that competes with the ferromagnetic phase and persists up to temperatures much higher than the transition temperatures. High magnetic fields can melt the charge ordered state in the heavier isotope sample and restore ferromagnetism at low temperatures.

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