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Phase separation and isotope effect in the ferromagnetic insulating state of the $Pr_{1-x}Ca_xMnO_3$ system $(0.2<x<0.33)$

L. M. Fisher, A. V. Kalinov, and I. F. Voloshin
All-Russian Electrical Engineering Institute, Krasnokazarmennaya Str. 12, Moscow 111250, Russia

N. A. Babushkina
Institute of Molecular Physics, Russian Research Center "Kurchatov Institute," Kurchatov Sqr. 1, Moscow 123182, Russia

K. I. Kugel
Institute for Theoretical and Applied Electrodynamics, Russian Academy of Sciences, Izhorskaya Str. 13/19, Moscow 125412, Russia

D. I. Khomskii
Solid State Physics Laboratory, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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The magnetic and transport properties of the $Pr_{1-x}Ca_xMnO_3$ system were studied at the characteristic points of the phase diagram corresponding to the ferromagnetic insulating and charge-ordered antiferromagnetic states. The magnetization M and resistivity ρ of the ceramic samples with $x=0.2$, 0.25, 0.27, 0.29, 0.30, and 0.33 were measured at temperatures $T=4-300$ K and applied magnetic fields H up to 7 T. It was shown that the Curie temperature T_C exhibits a nonmonotonic change with x. The maximum value of T_C was achieved at $x=0.25$. The isotope substitution $^{16}O\rightarrow{}^{18}O$ was performed for the samples with $x=0.2, 0.25$, and 0.30. A pronounced isotope effect in T_C was found. A noticeable drop in the activation energy E_a below the Curie temperature and a decrease of resistivity in the magnetic field both in the ferromagnetic insulator phase and in the phase-separated region at $x>0.3$ were observed. Special attention is paid to the possible manifestations of the phase separation in the ferromagnetic insulating state.

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I. INTRODUCTION

The colossal magnetoresistance (CMR) phenomenon is usually observed in manganites with a metal-like behavior. There are only several types of compositions having both CMR and the insulating ground state. One type of such manganites, $Pr_{1-x}Ca_xMnO_3$ (PCMO), is an insulator for any Ca doping in zero magnetic field. For $x=0.3$–0.5, this system is a charge-ordered (CO) antiferromagnetic (AF) insulator with a ferromagnetic component at low temperatures.[1] The energy barrier between insulating and metallic states is rather small. At x close to 0.3, the system can be easily transformed to a metal by applying magnetic fields of a few tesla[1,2] as well as under effect of light,[3] x-ray irradiation,[4,5] pressure,[6] and electric field.[7,8] This transformation is usually accompanied by a phase separation, which is an intrinsic feature of most manganites.[9] In contrast to many other manganites in which the ferromagnetic state is characterized by a metal-like behavior, $Pr_{1-x}Ca_xMnO_3$ is a ferromagnetic insulator (FI) at $x<0.3$ even at high magnetic fields. Such a situation is quite rare. Another well-known example is $La_{1-x}Sr_xMnO_3$, which is a ferromagnetic insulator in a narrow doping range around $x=1/8$ (Ref. 10). The FI state was also reported for $La_{1-x}Ca_xMnO_3$ below $x=0.2$ (Ref. 11–13). In manganites, the ferromagnetism is usually related to the metallicity according to the double-exchange mechanism. Ferromagnetism can also arise in the insulating state at special types of orbital and charge ordering due to the superexchange mechanism characteristic of magnetic insulators.[14] Although the relation between the FI states and a certain kind of charge ordering seems to be quite evident, the specific type of CO and orbital superstructure is still a subject of controversy.

However, orbital ordering[15] does not seem to be special to the case $x=1/8$, and it may be seen at a broader range of x in a relatively low doping region. A superstructure was indeed observed in the x-ray resonant scattering experiments[16] for samples with $x=0.25$, although it seems to be different from that predicted in Ref. 14. In spite of the interesting physics of the ferromagnetic insulating state, the corresponding concentration range in PCMO $(x<0.3)$ has not received much attention, in contrast to the phase-separated state at $x\geqslant0.3$.

It is a common opinion that PCMO samples are always phase separated for $x=0.3$–0.5 where the ferromagnetic and charge-ordered regions with the CE-type antiferromagnetism coexist.[1] Such a system as whole also can be considered as an inhomogeneous FI. This phase separation is most clearly pronounced in ceramic samples where the intergrain boundaries are additional factors favoring the inhomogeneity.[17] The structure of this phase-separated states including the ferromagnetic component was studied in detail (see Refs. 1, 2, 5, and 18). The cause of the phase separation in the PCMO system can be understood within a simple model showing the instability of the homogeneous checkerboard charge ordering for $x<0.5$ (Ref. 19). The question arises as to what extent this inhomogeneity survives in the FI region of PCMO $(x<0.3)$. Moreover, recent experimental data give an indication that the ferromagnetic regions in the phase-separated state at $x=0.3$ are insulating rather than metallic at least at relatively low magnetic fields.[20,21] At higher fields around 3.5 T, the ferromagnetic droplets are reported to undergo a first-order transition to a metallic state.[22] To clear up the situation with the ferromagnetic insulating state, we undertook a detailed study of the electric and magnetic properties of $Pr_{1-x}Ca_xMnO_3$ for the compositions $x=0.2$, 0.25, 0.27, 0.29, 0.30, 0.33, spanning both the FI and AF insulating regions. We also used in our study the isotope substitution $^{16}O \rightarrow {}^{18}O$. As was shown in Ref. 23, if there exists a competition between the insulating and FM metallic states, the isotope substitution shifts the balance toward the insulator, most probably due to a reduction of the bandwidth. In addition, isotope substitution also reveals the inhomogeneous percolative nature of the samples, if present. Thus, isotope substitution is also a powerful tool to check for the existence of competing phases and to investigate the phase-separated nature of the system. Moreover, a study of the influence of isotope substitution on the Curie temperature allows us to obtain additional information about the magnetic state in $Pr_{1-x}Ca_xMnO_3$. Note that the isotope effect on the Curie temperature of manganites was widely studied starting from a pioneering paper.[24] However, data on this effect for the manganites in the ferromagnetic insulating state are still lacking.

The present study is focused on the behavior of the magnetization and resistivity of $Pr_{1-x}Ca_xMnO_3$ near the crossover concentration $x=0.3$. Special attention is paid to the possible manifestations of phase separation in the FI state. We studied also the effect of oxygen isotope substitution on the properties of the system in order to have an opportunity to shift the phase equilibria. The influence of the calcium content and $^{16}O \rightarrow {}^{18}O$ isotope substitution on the magnetization and Curie temperature was also studied.

The observed behavior of the Pr-Ca manganites is interpreted under the assumption of the formation of inhomogeneous states in different parts of the phase diagram. Within this picture we get a natural explanation of the temperature and magnetic field dependence of the magnetization and resistivity.

II. SAMPLES AND TECHNIQUES

The measurements were performed on $Pr_{1-x}Ca_xMnO_3$ ceramic samples with $x=0.2$, 0.25, 0.27, 0.29, 0.30, and 0.33. The samples were rectangular bars about $1\times1\times10$ mm^3 in size. The isotope substitution ^{16}O by ^{18}O was performed for the samples with $x=0.2$, 0.25, and 0.30. The magnetization M was determined by vibrating sample and Quantum Design MPMS-7 superconducting quantum interference device (SQUID) magnetometers. The ac magnetic susceptibility χ was measured at a frequency about 10^2 Hz and ac field amplitude of 1 Oe and 10 Oe. The resistivity ρ was measured by the conventional four-probe method at a voltage not higher than 4 V, ensuring the absence of deviations from Ohm's law. The measurements were done in the temperature range $T=4-300$ K, at applied magnetic fields H up to 7 T.

III. EXPERIMENTAL RESULTS

We measured the temperature and magnetic field dependence of the magnetization $M(T,H)$ and electrical resistivity $\rho(T,H)$ for samples of different compositions. First of all, we present the data on the magnetic characteristics of the system under study.

TABLE I. The Curie temperature (K) determined by different methods.

x	Methods of T_C determination				
	χ^{-1}	max χ	M^2_{rem}	M^2	Arrott plot
0.2, ^{16}O	112	106	106	115	111
0.2, ^{18}O	104	99	94	107	101
0.25, ^{16}O	122	115	112	120	117
0.25, ^{18}O	116	111	108	118	115
0.27, ^{16}O	119	115	110	121	-
0.29, ^{16}O	104	100	100	109	-

A. Magnetization and magnetic susceptibility

The preliminary measurements demonstrated a strong temperature dependence of the magnetization for almost all our samples. For samples with $x<0.3$, the behavior of the low-temperature magnetization is characteristic of ferromagnetic materials. Our aim is a detailed study of the dependence of the magnetic characteristics, especially the Curie temperature T_C, on the concentration x and on the isotope composition. As the variations, especially those with the isotope substitution, may be not large, one needs accurate methods to determine T_C. Therefore, we use several methods for that. The results are presented in Table I.

First of all, the temperature dependence of the remanent magnetization was measured in a wide temperature range for all samples with $x<0.3$. The extrapolation of the obtained plots to $M^2=0$ allows us to find the value of T_C. According to the Landau theory of phase transitions, such plots should be linear in the vicinity of T_C. In fact, for these samples, except that with $x=0.29$, we have a rather large linear portion of the curves. The deviations from linearity grow with x approaching the crossover value $x=0.3$.

Another method used to determine T_C was a measurement of the magnetization of the samples at a fixed applied magnetic field H. Similarly to the previous method, the T_C values are determined, extrapolating the linear portions of the $M^2_{FC}(T)$ curves to $M=0$.

We measured also the temperature dependence of the real part of the low-frequency magnetic susceptibility χ'. The peaks in the $\chi'(T)$ curves (see Fig. 1) are related to the transition temperature. In Table I, the corresponding T_C values are the positions of these peaks. The same data can be used in another procedure of finding the T_C values by plotting the temperature dependence of $(\chi')^{-1}$. This dependence is found to be linear, which agrees well with the Curie-Weiss law (some examples of such plots are shown in Fig. 2). The intersection of extrapolated straight lines $(\chi')^{-1} \propto (T-T_C)$ with the horizontal axis gives the T_C value.

At last, to find T_C, we use the well-known Arrott plot technique,[25] measuring the temperature dependence of the magnetization in the geometry with the magnetic field **H**

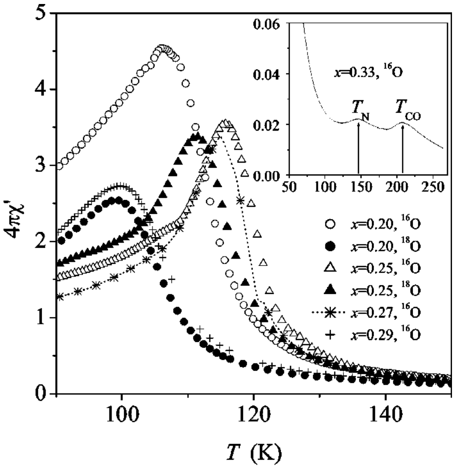

FIG. 1. Real part of the low-frequency magnetic susceptibility χ' vs temperature for the samples with $x<0.3$. The behavior of $\chi'(T)$ for the sample with $x=0.33$ in the expanded scale is shown in the inset.

parallel to the longest axis of the sample. In this geometry, we neglected a relatively small demagnetization factor. The Arrott plots—namely, M^2 vs H/M—are illustrated for samples with $x=0.2$ with different oxygen isotopes in Fig. 3.

The values of T_C obtained by different methods are presented in Table I. We see a certain scatter in T_C values given by different methods. Let us recall that methods based on the magnetization measurement are more suitable to determine T_C proceeding from the temperature range $T<T_C$, whereas magnetic susceptibility methods work better at $T>T_C$. However, all $T_C(x)$ exhibit a very similar behavior. We found that T_C has a nonmonotonic variation with x. The dependence of T_C on the Ca content x is illustrated in Fig. 4. The curves in this figure correspond to different methods of the determination of T_C. The maximum value of T_C is attained at $x\approx0.25$.

The $^{16}\text{O}\rightarrow{}^{18}\text{O}$ isotope substitution leads to an appreciable decrease of the Curie temperature (see Table I). Although the value of the Curie temperature T_C depends on the procedure of its determination, different methods give close values of the isotope shift for given x: $\Delta T_C\approx3\pm1$ K for $x=0.25$ and $\Delta T_C\approx10\pm2$ K for $x=0.20$. This means that the isotope effect on T_C is an intrinsic property of the ferromagnetic insulator state. This effect was observed earlier only for the metallic state of manganites.

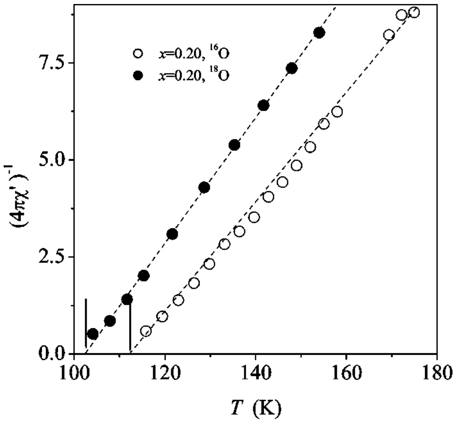

FIG. 2. Temperature dependence of the inverse ac magnetic susceptibility $(4\pi\chi')^{-1}$ for the samples with $x=0.20$ and different oxygen isotopes.

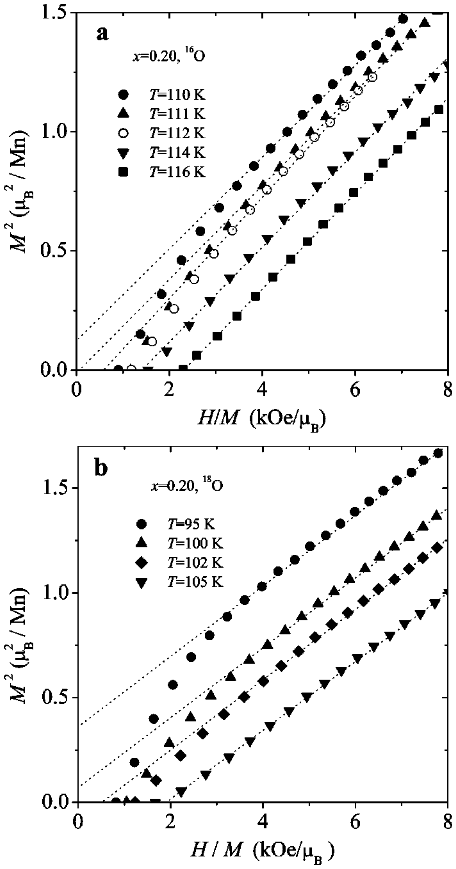

FIG. 3. The Arrott plots for samples with $x=0.2$ and oxygen isotopes (a) ^{16}O and (b) ^{18}O. The dashed lines are the extrapolations of linear portions of the experimental curves to low magnetic fields. The Curie temperature T_C is determined by the dashed line passing through the coordinate origin.

The dependence of the magnetization on the applied magnetic field H was measured for all our samples at $T<T_C$. The results are shown in Fig. 5. The behavior of the magne-

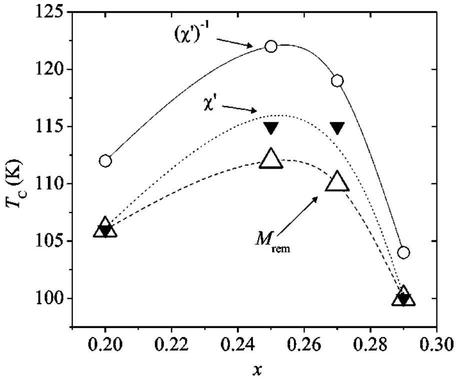

FIG. 4. The dependence of T_C determined by different methods on the Ca content x. Lines are guide for the eye.

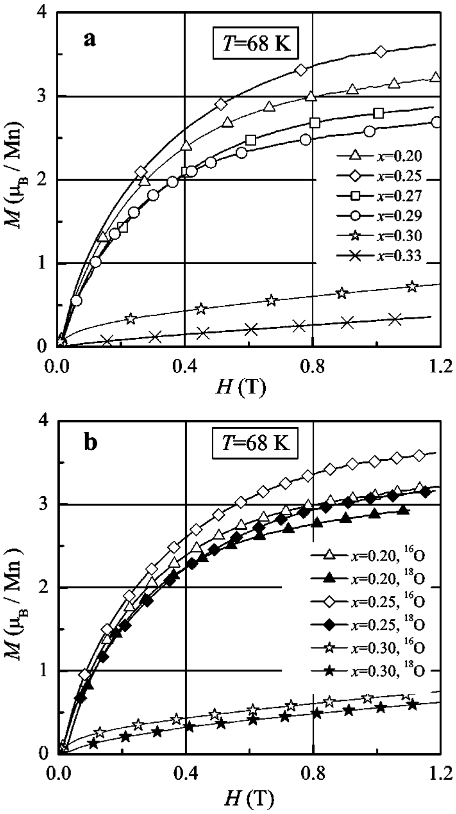

FIG. 5. The dependence of the magnetization on the applied magnetic field (a) for the samples with ^{16}O and (b) comparison of the data for the samples with ^{16}O and ^{18}O.

tization depends strongly on x. For $x < 0.30$, $M(T,H)$ curves are typical for ferromagnets: at low H the magnetization $M(H)$ increases fast and nearly saturates at $H > 1$ T. In this range of x, the magnetization value at $H > 1$ T is maximum at $x = 0.25$ and gradually decreases with a growth of x. At the threshold value $x = 0.3$ the magnetization undergoes a pronounced drop and continues to decrease at a further growth of x. The behavior of the magnetization at higher magnetic field at 5 K is shown in Fig. 6. The characteristic feature of all curves is the absence of a complete saturation even at fields as high as 7 T. All curves attain a near-saturation limit at about 1.2 T but the magnetization continues to increase slowly. This increase is close to linear and the slope of all curves is almost the same for all samples in a wide field range. Such a feature was also observed[26] in pulsed magnetic fields up to 30 T for the same compound with $x = 0.3$ and oxygen isotope ^{18}O. It is natural to suppose that the slow growth of the magnetization independent of x is determined by the contribution due to canting of antiferromagnetic sublattices and/or to rare earth spins. The rare earth ions can give a noticeable contribution to the magnetization especially at low temperatures (see, e.g., Ref. 27).

The quasisaturation value of M is noticeably lower than the expected value of magnetization for our compositions. Indeed, the maximum quasisaturation value of magnetization which is observed for the sample with $x = 0.2$ at 5 K is about of $(3.3\text{–}3.5)\mu_B$, which is significantly less than the spin-only manganese magnetization $M_s = 3.8\mu_B$. Such a behavior is an indication of certain inhomogeneity inherent to the ferromagnetic insulator state. Another signature of the phase separation is the hysteresis of all magnetization curves at high fields (exceeding the quasisaturation field $H \approx 1.2$ T).

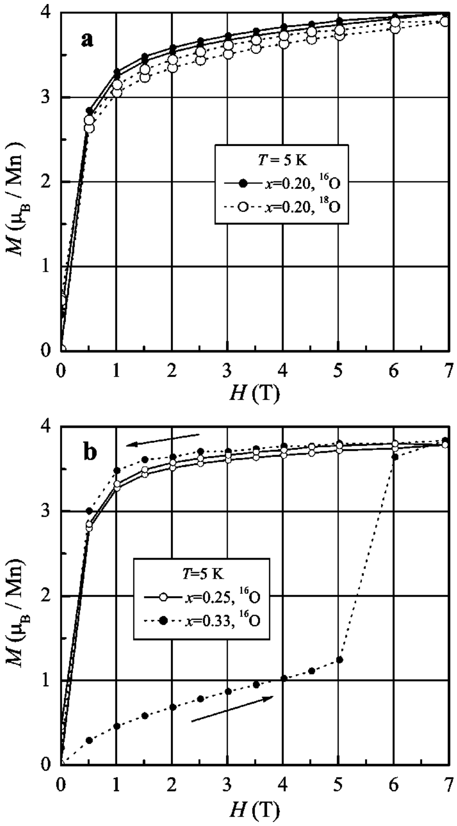

FIG. 6. The behavior of the magnetization at magnetic fields up to 7 T at 5 K (a) for the samples with ^{16}O and ^{18}O, $x = 0.2$, and (b) for the samples with $x = 0.25$ and 0.33.

For the samples with $x \geqslant 0.3$, we observed in a certain temperature range a steep growth of the magnetization at fields above 5 T. Such a behavior of the virgin curve is illustrated by the solid curve in Fig. 7 for samples with $x = 0.3$ at $T = 30$ K and by the dashed curve in Fig. 6(b) for the sample

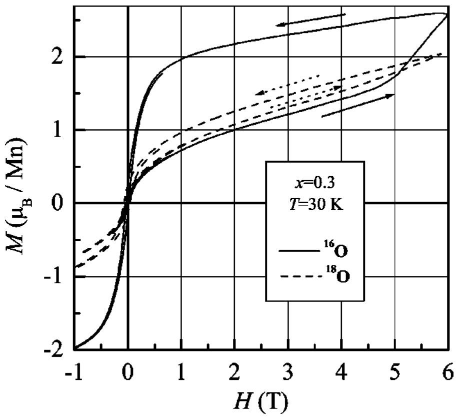

FIG. 7. The behavior of the magnetization at magnetic fields up to 6 T at 30 K for the samples with $x = 0.3$ and ^{16}O (solid line) and ^{18}O (dashed line).

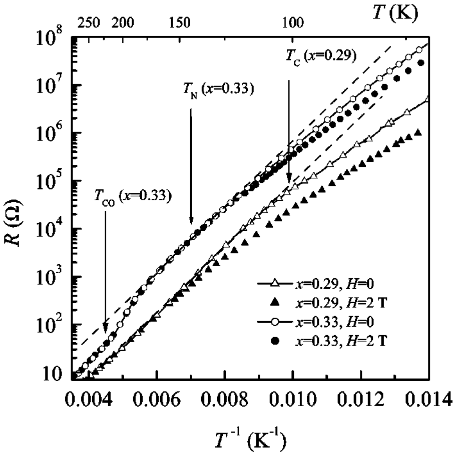

FIG. 8. The temperature dependence of resistance for samples with $x=0.29$ and $x=0.33$ at different values of the applied magnetic field. Dashed lines extrapolate the high-temperature portions of curves at $H=0$.

with $x=0.33$ at $T=5$ K. After this steep growth of M, the magnetization continues to increase slowly. All curves with the steep growth are characterized by a pronounced hysteresis. For the next sweeps the magnetization becomes typical for a ferromagnet and $M(H)$ varies in a nearly reversible manner. Such a behavior is similar to that observed in (LaPr)Ca manganites.[28] The sharp growth of $M(H)$ is an indication of the increasing content of the ferromagnetic phase in a phase-separated system.

The magnetization of the samples with different oxygen isotopes^{16}O and ^{18}O is shown in Figs. 5(b), 6(a), and 7. Isotope substitution leads to an appreciable decrease of the magnetization. Note that the width of the high-field hysteresis loop is larger for the samples with ^{18}O [see Fig. 6(a)]. This shows that $^{16}\mathrm{O}\rightarrow{}^{18}\mathrm{O}$ isotope substitution favors the antiferromagnetism and enhances the phase separation. On the other hand, the increased tendency to antiferromagnetism is accompanied by the disappearance of the steep growth feature in the magnetization curve; compare the solid and dashed lines in Fig. 7.

Additional information on the magnetic state of samples with $x\geqslant 0.3$ can be obtained from measurement of the magnetic susceptibility. We analyzed, in particular, the temperature dependence of the real part of the magnetic susceptibility $\chi'(T)$ for the sample with $x=0.33$. The results of our measurement are shown in the inset to Fig. 1. This $\chi'(T)$ curve exhibits two peaks. The position of the high-temperature peak correlates with the charge-ordering temperature, whereas the low-temperature peak can be related to the Neél temperature.[1]

B. Resistivity

The behavior of the resistivity is shown in Fig. 8. It is convenient to represent the resistivity in a semilogarithmic scale as a function of inverse temperature. At temperatures higher than the magnetic transition point, the resistivity obeys the Arrhenius law with the activation energy E_a about 0.1 eV, which agrees with the data of Ref. 29. The curves with $x<0.3$ exhibit a kink near the Curie temperature, at which E_a decreases by about a factor of 2. An applied magnetic field shifts this jump to higher temperature and makes it smoother. Figure 8 shows the behavior of resistivity for $x=0.29$ and $x=0.33$. Here E_a changes from 0.13 eV to 0.08 eV for $x=0.29$. In contrast to the ferromagnetic insulator $x<0.3$, the magnetic ordering transition for a sample with $x=0.33$ corresponds only to a slight change in a slope of the experimental curve $(H=0)$. However, the charge-ordering transition in this case gives a steep change in the resistivity. It should be mentioned that the activation energy E_a is nearly the same for all samples at high temperatures where the samples are paramagnetic.

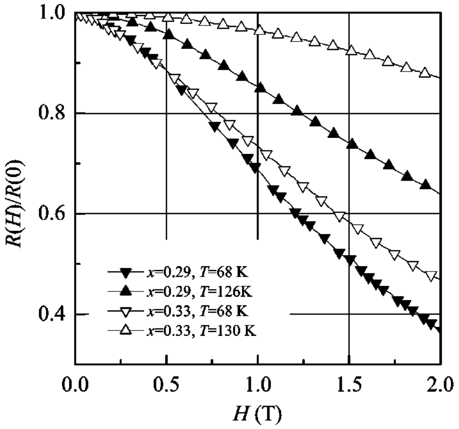

FIG. 9. The magnetic field dependence of the resistivity for samples with $x=0.29$ (solid symbols) and $x=0.33$ (open symbols).

The magnetic field dependence of resistivity is shown in Fig. 9 for different temperatures. Both ferromagnetic and antiferromagnetic samples exhibit a negative magnetoresistance. The magnetoresistance $[R(0)-R(H)]/R(0)$ increases as the temperature decreases and attains a value of about 50% at $H=2$ T. The temperature dependence of the magnetoresistance is illustrated in Fig. 10. For the temperature range corresponding to the paramagnetic phase, the magne-

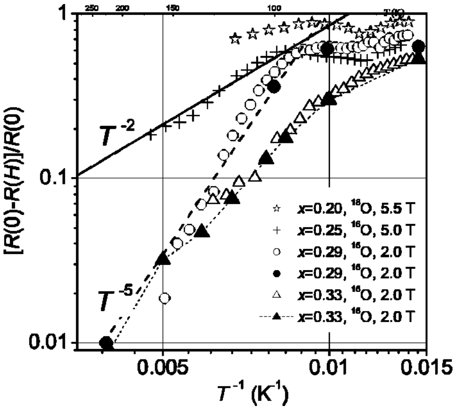

FIG. 10. The temperature dependence of the magnetoresistance for different samples. The solid symbols correspond to the zero-field cooling and other ones correspond to the field cooling regime.

toresistance obeys the power law T^{-n} with $n=2$–5. Such a decrease of the magnetoresistance with temperature is an indication of the magnetic inhomogeneity of our samples even in the paramagnetic state; this problem is discussed in detail in Ref. 31. In particular, it is shown that the T^{-5} power law corresponds to a spin-dependent electron transport between anisotropic ferromagnetic clusters via a nonmagnetic medium. The existence of such behavior for the sample with $x=0.29$ is an additional indication of the phase inhomogeneity of the ferromagnetic insulator near the crossover to the antiferromagnetic state.

IV. DISCUSSION

The most spectacular results of our measurement concern the dependence of the Curie temperature in the ferromagnetic insulating state on the doping level x and the oxygen isotope substitution. The Curie temperature attains the maximum value at $x=0.25$. Earlier it was suggested that the composition with $x=0.25$ favors a special type of charge and orbital ordering corresponding to the ferromagnetic insulating state.[14] Therefore, it is natural to expect that the ferromagnetic insulating state is the most stable just for this commensurate composition. In fact, our experiment shows that the $x=0.25$ composition is singled out by its specific characteristics. In principle, the existence of the T_C peak at $x=0.25$ is quite natural. Nevertheless, up to now there has been no direct experimental proof of this fact. Note that in a widely cited phase diagram from Ref. 1 (see also Ref. 30) there was only one experimental point between $x=0.2$ and $x=0.3$, so it was difficult to identify the maximum in $T_C(x)$ near $x=0.25$. In addition to the highest T_C it exhibits the highest magnetization value and demonstrates the minimum T_C shift induced by the oxygen isotope substitution. The latter is an additional indication of the enhanced homogeneity of the ferromagnetic insulator state for the sample with $x=0.25$ since the isotope effect is more pronounced under the conditions of the phase separation (see, e.g., Ref. 31).

The substitution of ^{16}O by ^{18}O leads to the lowering of both the Curie temperature and the saturation magnetization. This shows that the heavier isotope causes a suppression of the ferromagnetism even in the insulating state. This result is in certain contrast to the usual interpretation of the pronounced isotope effect in the (LaPr)Ca manganites as a manifestation of the metal-insulator crossover, which uses the picture of the isotope-induced shift of the phase equilibrium from a ferromagnetic metal to an antiferromagnetic insulator.[23,28,32] Here both phases, antiferromagnetic and ferromagnetic, are insulators. Thus, the nature of the isotope effect in insulators requires a special discussion.

Usually, the electron localization is accompanied by some type of orbital and charge ordering, favoring in our case the ferromagnetic ground state. In conventional Mott insulators with integer occupation of the d shell, ferromagnetism may appear for a certain orbital ordering. In this case, the corresponding exchange interaction is caused by the virtual hopping of an electron from one site to another and back, and k_BT_C is of the order of $(t^2/U)J_H/U$ (t is the electron hopping integral, U is the on-site Coulomb repulsion energy, and J_H is the Hund's rule coupling). The U value here is assumed to be larger than the hopping integral t $(U \gg t)$. In this case, the hopping time $\tau \sim \hbar/U$ is too short for the lattice to respond.[33] This means that the isotope effect should be suppressed. On the other hand, the real electron hopping t determining the double-exchange ferromagnetism in metallic systems is characterized by polaron narrowing,[34] which may lead to an appreciable isotope effect enhanced by the Jahn-Teller nature of the Mn^{3+} ion. Thus, the very existence of the strong isotope effect in the FM insulating of (PrCa)MnO$_3$ is an indication that the mechanism of ferromagnetism in this case cannot be simply reduced to that of well-defined Mott insulators like K$_2$CuF$_4$ (Ref. 35).

In contrast to Mott insulators with integer occupation of d sites, here we formally have ions of different valence Mn^{3+} and Mn^{4+}. In such a situation, one can get an insulating state in two situations.

We may have a phase-separated state with possibly even metallic (and ferromagnetic) droplets, which is, however, below the percolation threshold. In this case, the state inside these droplets would be the same as in the FM phase of metallic manganites, and one would also expect a strong isotope effect.

It is also possible (and probably more plausible in the Pr-Ca system) that we are dealing with a genuine insulating state. Such a state with localized electrons should necessarily have some superstructure, e.g., due to charge and/or orbital ordering. This is indeed the case in La$_{1-x}$Sr$_x$MnO$_3$ close to $x\simeq 1/8$ (Ref. 10) and it can be also the case for $x\simeq 1/4$ (Ref. 14). However, the energy gap would be determined not by the very large Hubbard on-site interaction U but rather by the intersite Coulomb repulsion V, which would be of the order or even less than the electron hopping t integral. Indeed the energy gap in charge-ordered manganites is rather small, typically about 0.2–0.4 eV. This means that the virtual hopping leading to an exchange would occur mostly between Mn^{3+} and Mn^{4+} and would cost an energy V rather than U. Thus, even if $t<V$, the corresponding exchange constant would contain t^2/V instead of t^2/U (in contrast to the usual Mott insulators). Hopping processes are then much slower $(\tau \sim \hbar/V)$, and the polaronic band narrowing leading to the isotope effect can come into play.

However, it is possible that $V \lesssim t$, and we cannot use the perturbation theory in t/V at all. Then an insulating state can appear due to the formation of a charge density wave and orbital density wave caused by the nesting of the Fermi surface. The corresponding energy gap here would be $\Delta_{CO} \propto t\exp[-1/VN(0)] \sim t\exp(-t/V)$ and may be much smaller than the bandwidth $W=2zt$ (z is the number of nearest neighbors). This seems to be indeed the case in our system, in which the measured value of the activation energy $E_a \sim 0.1$ eV is much less than the bandwidth $W \simeq 1$–2 eV. The mechanism of ferromagnetism in this case may be then quite similar to that in double-exchange metals (electron hopping between Mn^{3+} and Mn^{4+} leading to a decrease of the total kinetic energy of a conduction electron in a ferromagnetically ordered state). The presence of a relatively small gap at the Fermi surface $\Delta < W$ would not significantly modify the picture. Thus, we can also expect a significant isotope effect. The observation of such an effect in our system may thus be considered as an indication that the origin of ferromagnetism here is rather similar to the double exchange, despite the fact that we are dealing with insulators.

The transport and magnetic properties of $Pr_{1-x}Ca_xMnO_3$ depend strongly on the doping level x. Note that the saturation value of the magnetization in the ferromagnetic phase decreases with x approaching the crossover Ca content $x=0.3$. This may be an indication of certain inhomogeneities inherent already to the concentration range $x<0.3$. The substitution of ^{16}O by the heavier isotope ^{18}O usually favors electron localization and antiferromagnetism.[23] Here we also observe an appreciable lowering of the saturation magnetization in the samples with ^{18}O, which can be a signature of the magnetic inhomogeneity. The data at $x=0.3$, especially the steep increase of the magnetization in high fields accompanied by the pronounced hysteresis, agree with the commonly used treatment of the Pr-Ca manganites as a phase-separated system, being a mixture of the charge-ordered antiferromagnetic insulator and the ferromagnetic metal. The data of resistivity correlate with the behavior of magnetization. A pronounced drop in the activation energy E_a below the Curie temperature and a decrease of resistivity in the magnetic field both in the ferromagnetic insulator phase and in the phase-separated region at $x>0.3$ demonstrates that the increase of the magnetization of a sample is closely related to the decrease of E_a. Such a behavior of E_a is natural for magnetic semiconductors[36] and materials with an appreciable contribution of the double-exchange mechanism to magnetic ordering. In such materials, the alignment of atomic magnetic moments enhances the probability of electron transfer between lattice sites.

In summary, we studied the dependence of the magnetic and transport properties of $Pr_{1-x}Ca_xMnO_3$ at different concentrations, spanning both the ferromagnetic insulating region $x<0.3$ and the antiferromagnetic region $x\geqslant 0.3$, and also investigated the effect of the $^{16}O\rightarrow{}^{18}O$ isotope substitution. We found that the value of T_C is maximum at the concentration $x=0.25$. The magnetoresistance turned out to be negative even in case of an insulating ferromagnetic ground state. Many features of $Pr_{1-x}Ca_xMnO_3$ can be interpreted under the assumption of the existence of inhomogeneous states in different parts of the phase diagram. The observation of a noticeable isotope effect in our system may be an indication that the origin of ferromagnetism in the $Pr_{1-x}Ca_xMnO_3$ system with $x<0.3$ has a certain relation to the double exchange despite the fact that the system in this regime is an insulator.

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