

Suppression of the ferromagnetic-insulating phase in self-doped $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ crystals under pressure

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The effect of hydrostatic pressure P on the magnetic and transport properties of self-doped $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ crystals has been investigated at pressures up to 1 GPa and in the temperature range $15 < T < 300$ K. It was found that the applied pressure enhances the double-exchange coupling, increases the magnetization, and lowers the ferromagnetic-insulator transition temperature. The results obtained here for the self-doped crystals are compared with those observed for lightly doped $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. It is shown that similar mechanisms of ferromagnetic clustering and percolative polarons may account also for the magnetic and transport properties of the self-doped manganites.

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I. INTRODUCTION

The observation of colossal magnetoresistance in hole-doped perovskite-type manganese oxides $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (where $A = \text{Sr}^{2+}$, Ca^{2+} , Ba^{2+} , or Pb^{2+}) has promoted the study of these compounds in recent years. The end compounds with $x=0$ and $x=1$ are antiferromagnetic insulators, whereas those of intermediate compositions ($0.2 < x < 0.5$) and mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ are ferromagnetic and metallic at a certain temperature range below the Curie temperature T_C .^{1,2} Lightly doped manganites have received special attention due to the onset of metallic conductivity at a critical concentration $x = x_c \approx 0.16$, for which percolation of ferromagnetic clusters with metallic conductivity and large polarons may occur.³⁻⁶ According to many investigations,⁵⁻⁸ a highly inhomogeneous state consisting of metallic and insulating magnetic phases may occur in doped manganites. Local Jahn-Teller distortions and polarons, which are characteristic of insulating paramagnetic phases, were found to exist also in the metallic phase.^{5,6} The spatial distribution and temperature evolution of the ferromagnetic phase affects the electrical transport. In other words, a competition between the increasing ferromagnetic fraction (metallic) and the decreasing insulating paramagnetic phase results in a metal-insulator transition. The existence of ferromagnetic clusters below and above the Curie temperature was verified experimentally by NMR (Ref. 7) and Mössbauer spectroscopy.⁸ It has been established that the ferromagnetic state of doped manganites is stabilized by a double-exchange (DE) coupling between the charge carriers and local $3d$ spins. On the other hand, it was argued⁹ that the DE by itself is not sufficient to explain the transport properties of manganites and a strong electron-phonon interaction has to be incorporated in the conduction mechanism. Millis, Littlewood, and Shraiman⁹ have suggested that the above mechanisms may lead to the

generation of dynamic phase separation in the form of magnetic polarons.

Although the effect of pressure on the physical properties of doped manganites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ has been the subject of previous studies,¹⁰⁻¹⁵ no investigations have been carried out, to the best of our knowledge, on self-doped manganites under pressure. A recent publication¹⁶ on $\text{LaMnO}_{3+\delta}$, with a slight cation deficiency, shows that its spin structure below T_C comprises paramagnetic and antiferromagnetic phases in addition to the ferromagnetic one. Measurements of electron-spin resonance¹⁷ on self-doped manganites also provide evidence of coexisting magnetic phases below T_C . The Mn^{4+} content (referred to as hole concentration) in LaMnO_3 may arise not only due to substitution of divalent cations for La, but also due to the nonstoichiometry of La and Mn ions.¹⁸⁻²⁰ For the latter case, the concentration of Mn^{4+} may increase after thermal annealing. For example, it was found²¹ that cation-deficient $\text{La}_{1-x}\text{Mn}_{1-y}\text{O}_3$ ceramics may contain up to 62% Mn^{4+} after an appropriate heat treatment. Self-doped compounds with a high content of Mn^{4+} ions also exhibit ferromagnetism as well as typical metal-insulator transitions at some temperature T_p , close to T_C . Comparing the resistivity and thermopower^{18,19} for doped and self-doped compounds, one finds that holes created by self-doping are more localized in character. This result may be due to a strong on-site binding potential for the holes or a smaller transfer integral due to a relatively larger unit-cell volume.²⁰

As it was noted earlier, no magnetic or transport studies have been carried out on the self-doped parent compound $\text{La}_{1-x}\text{Mn}_{1-y}\text{O}_3$ under pressure. In this paper the effects of hydrostatic pressure on the magnetic and transport properties of a self-doped $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ single crystal near the percolation threshold x_c has been investigated. The data obtained are compared with the corresponding results for doped manganites.

II. EXPERIMENTAL

The dc resistivity measurements under pressure were carried out on a small $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ single crystal, $0.8 \times 1 \times 1.5 \text{ mm}^3$ in size, mounted in a CuBe hydrostatic pressure cell at the interval $77 < T < 300 \text{ K}$. The temperature was measured using a Copper-Constantan thermocouple. The resistivity ρ was measured by a four-point method with silver paint for electrical contacts. Because of the small and irregular dimensions of the crystals, there are relatively large errors (up to 20%) in the absolute values of the reported resistivities. The description of growth of the crystal of $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ was reported previously.²² A mixture of mineral oil and kerosene was used as a pressure transmitting medium. The pressure was measured using a manganin gauge. The decrease in pressure due to the difference in the thermal-expansion coefficients of the pressure transmitting medium and the pressure cell was taken into account. The exact values of pressure were calculated from the temperature dependence of the resistivity of the manganin gauge for each temperature. Such actual values of P 's are used for the plotting of pressure dependencies of the characteristic temperatures of the sample (T_C and T_{FI} vs P). However, the pressures measured at room temperature are marked on the plots of the temperature dependencies of the resistivity and the Hall voltage. Measurements of magnetoresistance were carried out with magnetic fields perpendicular to the current direction. The possible deviation in orientation of the sample and Hall probe with regard to magnetic field at various pressures did not exceed $1-2^\circ$.

The magnetization M of the crystal was probed by a Siemens RHY17 Hall device attached to the sample at temperatures $77 < T < 300 \text{ K}$. The Hall voltage V_H was measured under a relatively low magnetic field of $H = 20 \text{ mT}$. At $T > T_C$, the Hall voltage is proportional to the applied magnetic field H , which for $T < T_C$, $V_H \sim H + 4\pi M$. It should be noted that the experiment described above enables one to perform transport and magnetic measurements under pressure simultaneously. The employment of a Hall device for magnetic measurements will be described in detail elsewhere.²³

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of resistivity $\rho(T)$ observed in a single crystal of $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$. It was found that $\rho(T)$ exhibits an insulatorlike behavior below a temperature $T_{FI} \sim 115 \text{ K}$, and a metallic one in the region of the ferromagnetic phase above this temperature. A comparison between $\rho(T)$ of our self-doped $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ single crystals and samples doped by A^{2+} ions [for example, by Sr^{2+} with $x = 0.16$ (Ref. 16)] shows some resemblance in their temperature-dependent features. In both cases the change in the nature of the electrical conductance may be associated with the percolation effect of conducting clusters and polarons.

The magnetization $M(T, H, P)$ of the crystal probed by the Hall device as a function of temperature at various pressures is shown in Fig. 2. The measurements of M were car-

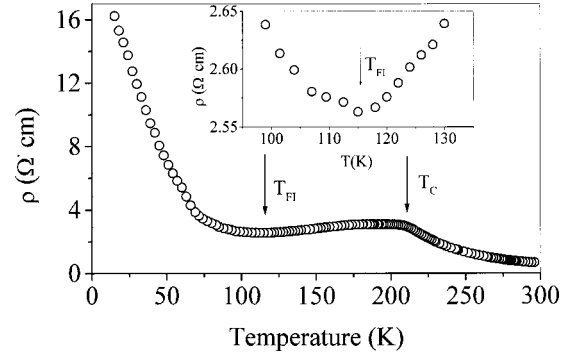


FIG. 1. Temperature dependence of the resistivity of a $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ single crystal. Inset shows resistivity in the vicinity of T_{FI} .

ried out under an applied magnetic field $H = 20 \text{ mT}$; therefore, V_H results from both M and H . At $P = 0$ we carried out the measurement of genuine magnetization of our sample in a magnetic field 20 mT using a commercial superconducting quantum interference device (SQUID). These results are shown on the inset to Fig. 2. One can note a good correlation between the data obtained by the Hall device and the SQUID at $P = 0$. The correspondence of $V_H = 1 \mu\text{V}$ to $M = 0.07 \text{ emu/mol}$ can be also evaluated from the comparison of the above data. The Curie temperature is defined as the midpoint temperature of the transition curve, corresponding to an average transition temperature. As expected, the Curie temperature increases under pressure (see Fig. 3) due to a bandwidth broadening and strengthening of DE ferromagnetic coupling.¹³⁻¹⁵ Since V_H depends on both T and P , it is quite difficult to derive an exact value of magnetization for the entire temperature region. However, with the specific Hall device used here, V_H is almost independent of T in the region $200 < T < 300 \text{ K}$. Therefore one may estimate the change in M in the vicinity of T_C as resulting solely from the change in P . It was found that the Hall voltage V_H in the vicinity of T_C increases under a pressure of 0.91 GPa by $\sim 44\%$ (see Fig. 2). However, the sensitivity of the present

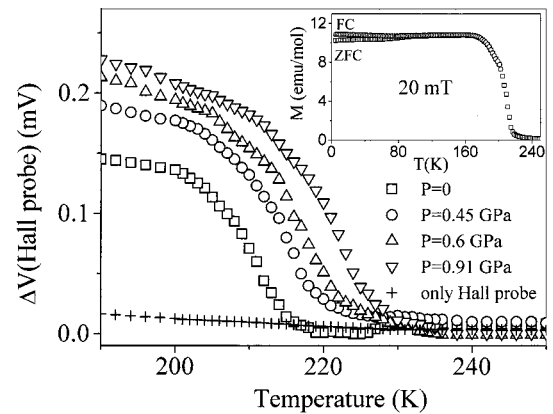


FIG. 2. The Hall voltage V_H of the Hall probe attached to a $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ single crystal under various pressures. The inset shows the temperature dependence of magnetization measured by SQUID at $P = 0$.

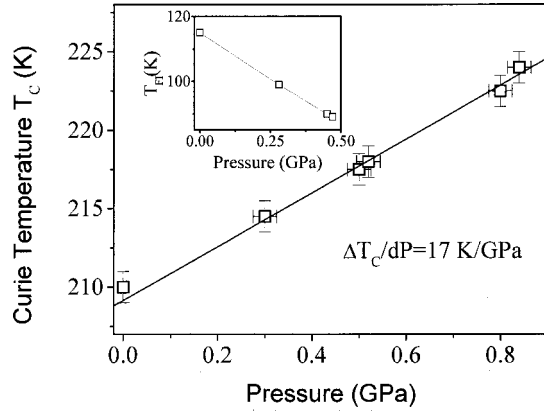


FIG. 3. The Curie temperature T_C of a $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ single crystal as a function of pressure. The inset shows the pressure dependence of T_{FI} .

Hall device increases at the same interval of pressures by only 12%. It appears therefore that an applied pressure tends to increase the volume of the ferromagnetic (FM) clusters at the expense of other paramagnetic and antiferromagnetic phases. No hysteresis was found in our magnetization and resistivity measurements. A reversible nonhysteretic magnetization and resistivity was also found in the vicinity of T_{FI} for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with a doping of $x=0.14$. Hysteretic resistivity has been observed around T_{FI} only for $x < 0.14$. The above observations may indicate that the FI transition changes from a first- to a second-order transition¹⁵ upon increasing the doping level.

Figure 4 presents curves of $\rho(T)$ measured under pressure. It seems that the applied pressure enhances the carrier itinerancy and converts the FI phase to a metallic FM phase at $P=0.94$ GPa. There is a similarity in the effect of pressure on lightly doped and self-doped manganites, which is manifested by the shift of their metal-insulator transition. In both $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x=0.16$ and $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ single crystals, the pressure-effect coefficient of T_{FI} is ~ -40 K/GPa up to a pressure of 1 GPa.¹⁴ The transition temperature T_{FI} of our crystal is also slightly affected by magnetic fields, e.g., an applied magnetic field of 1.5 T increases T_{FI} by only ~ 2 K, for both $P=0$ and $P=0.63$ GPa. A similar field depen-

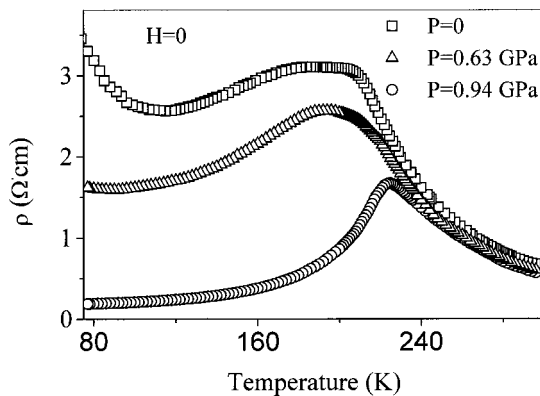


FIG. 4. Temperature dependence of the resistivity of a $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ single crystal at various applied pressures.

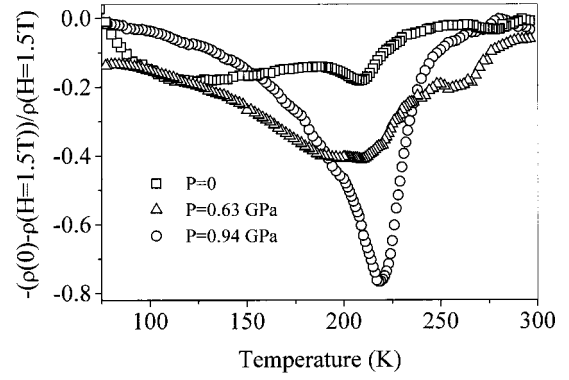


FIG. 5. Magnetoresistance (MR) at an applied magnetic field $H=1.5$ T as a function of temperature. The MR's are given for various pressures.

dence of T_{FI} was observed for lightly doped samples.¹⁵

The effect of pressure on the magnetoresistance (MR) of a $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ single crystal is presented in Fig. 5. It is clearly seen that at $P=0$ the MR exhibits a minimum of $\sim 18\%$ in the vicinity of T_C and a broad minimum at lower temperatures. An applied pressure causes a drastic change in the shape of the MR. At $P=0.94$ GPa the minimum of the MR observed near T_C is $\sim 80\%$, resembling the results observed for doped manganites, which exhibit a metal-insulator transition near T_C .²

Let us compare some of the following pressure effects on self-doped $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ with that of a lightly doped $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ compound: (i) In both systems T_{FI} shifts towards lower temperatures under pressure and disappears at a strong enough pressure; (ii) At high pressure, $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ ($P=0.94$ GPa) and $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ [$P=1.4$ GPa (Ref. 14)] exhibit metallic behavior; (iii) The pressure coefficients of T_C for both compounds $d \ln T_C/dP \approx 0.077$ K/GPa for $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ and $d \ln T_C/dP \approx 0.08$ K/GPa for $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ (Ref. 14) are remarkably close. It should be noted that the pressure coefficient is extremely sensitive to the concentration of the dopant, for example, in the case of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ the value obtained¹³ for $d \ln T_C/dP$ is 0.053 K/GPa. On the other hand, a pronounced difference occurs in the resistivity of self-doped $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ and $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$.¹⁴ The resistivity of $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ under a pressure of $P=0.94$ GPa ("metallic" state) was found to be two to three orders of magnitudes higher than that of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.15, 0.16$).¹⁴ The value of the resistivity of the $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ crystal as well as that of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (for $0.1 < x \leq 0.14$)^{14,15} is hardly reconciled with a metallic conduction expected for itinerant carriers in a homogeneous single-phase crystal.

According to recent models and experimental results,^{3-6,24,25} percolation of polarons or ferromagnetic clusters play an important role in the lightly doped metallic state of manganites. It was suggested by the various groups that polarons could form clusters in which holes move freely. An extended polaron network and metallic conductivity appears at the percolation limit $x_c=0.16$. Such a mechanism is likely to take place also in the self-doped manganite studied here. The role of the applied pressure is probably to reinforce the

overlapping of large polaron clusters, which results in metalliclike conductivity.

Two different magnetically ordered phases have been realized for lightly doped manganites at $T < T_C$: (i) At $T_{FI} < T < T_C$, the transport and magnetic properties are affected by a dominant DE mechanism; (ii) for temperatures lower than T_{FI} one should take into account superexchange (SE) interactions.^{15,26} Endoh *et al.*²⁶ considered a microscopic model for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ that involves both SE and antiferromagnetic interactions and obtained a qualitative phase diagram for various hole concentrations. In this model an orbital ordering sets in at T_{FI} and accompanies charge localization. Martinez *et al.*¹⁵ assumed that the shift of T_{FI} for lightly doped $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ under pressure is caused by an increase of orbital overlapping integrals and therefore an increase of SE interactions. Since many structural and electronic parameters are involved in the exchange coupling, it is almost impossible to predict uniquely the behavior of SE under pressure. For example, in a series of isostructural dielectric compounds $\text{CuM}_2\text{X}_4 \cdot 2\text{H}_2\text{O}$ ($M = \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$; $X = \text{Cl}, \text{Br}$) the SE interaction between Cu^{2+} ions under pressure leads to an increase of T_C for four compounds and to a decrease in two others.²⁷ In our self-doped crystals the resistivity is higher, and as a consequence carriers are more lo-

calized, and the SE interactions can play an essential role in its magnetic and transport behavior.

In summary, the magnetization and electrical conductance of a single crystal $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ were studied under applied hydrostatic pressure and magnetic field. It was found that this crystal exhibits features similar to those observed in lightly doped manganites $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.15, 0.16$). An increase in pressure leads to a decrease and finally to a suppression of the low-temperature insulating phase, at $P = 0.94$ GPa. On the other hand, it shifts the Curie temperature T_C toward higher temperatures. The suppression of an insulating phase transition under pressure is considered as a result of percolating polarons. A strong rise of MR at $P = 0.94$ GPa and in the vicinity of T_C also reflects the high sensitivity of transport properties to external pressure.

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- ¹P. Schiffer, A. P. Ramirez, W. Bao, and S.-W. Cheong, *Phys. Rev. Lett.* **75**, 3336 (1995).
- ²A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, *Phys. Rev. B* **51**, 14 103 (1995).
- ³L. P. Gorkov, *Phys. Usp.* **41**, 589 (1998).
- ⁴L. P. Gor'kov and V. Z. Kresin, *J. Supercond.* **12**, 243 (1999).
- ⁵D. Louca and T. Egami, *Phys. Rev. B* **59**, 6193 (1999).
- ⁶D. Louca, T. Egami, E. L. Brosha, H. Roder, and A. R. Bishop, *Phys. Rev. B* **56**, R8475 (1997).
- ⁷J. Dho, I. Kim, S. Lee, K. H. Kim, H. J. Lee, J. H. Jung, and T. W. Noh, *Phys. Rev. B* **59**, 492 (1999).
- ⁸V. Chechersky, A. Nath, I. Isaak, J. P. Franck, K. Ghosh, H. Ju, and R. L. Greene, *Phys. Rev. B* **59**, 497 (1999).
- ⁹A. J. Millis, P. B. Littlewood, and B. I. Shraiman, *Phys. Rev. Lett.* **74**, 5144 (1995).
- ¹⁰J. M. De Teresa, M. R. Ibarra, J. Blasco, J. Garcia, C. Marquina, P. A. Algarabel, Z. Arnold, K. Kamenev, C. Ritter, and R. von Helmolt, *Phys. Rev. B* **54**, 1187 (1996).
- ¹¹J. J. Neumeier, M. F. Hundley, J. D. Thompson, and R. H. Heffner, *Phys. Rev. B* **52**, R7006 (1995).
- ¹²J. S. Zhou, J. B. Goodenough, A. Asamitsu, and Y. Tokura, *Phys. Rev. Lett.* **79**, 3234 (1997).
- ¹³M. Itoh, K. Nishi, J. D. Yu, and Y. Inaguma, *Phys. Rev. B* **55**, 14 408 (1997).
- ¹⁴Y. Moritomo, A. Asamitsu, and Y. Tokura, *Phys. Rev. B* **56**, 12 190 (1997).
- ¹⁵B. Martinez, R. Senis, L. Balcells, V. Laukhin, J. Fontcuberta, L. Pinsard, and A. Revcolevschi, *Phys. Rev. B* **61**, 8643 (2000).
- ¹⁶R. De Renzi, G. Allodi, G. Amoretti, M. C. Guidi, S. Fanesi, G. Guidi, F. Licci, A. Caneiro, F. Prado, R. Sanches, S. Oseroff, and A. Amato, *Physica B* **289–290**, 85 (2000).
- ¹⁷A. I. Shames, E. Rozenberg, G. Gorodetsky, and M. Greenblat (unpublished).
- ¹⁸R. Mahendiran, S. K. Tiwary, A. K. Raychaudhuri, R. Malesh, and C. N. R. Rao, *Phys. Rev. B* **54**, R9604 (1996).
- ¹⁹R. Mahendiran, S. K. Tiwary, A. K. Raychaudhuri, R. Malesh, N. Rangavittal, and C. N. R. Rao, *Phys. Rev. B* **53**, 3348 (1996).
- ²⁰J. A. Alonso, M. J. Martinez-Lope, M. T. Casias, and A. Munoz, *Solid State Commun.* **102**, 7 (1997).
- ²¹P. S. I. P. N. de Silva, F. M. Richards, L. F. Cohen, J. A. Alonso, M. J. Martinez-Lope, M. T. Casais, K. A. Thomas, and J. L. MacManus-Driscoll, *J. Appl. Phys.* **83**, 394 (1998).
- ²²W. H. McCarroll, K. V. Ramanujachary, M. Greenblatt, and F. Cosandey, *J. Solid State Chem.* **136**, 322 (1998).
- ²³V. Markovich, G. Gorodetsky, and S. Strikman (unpublished).
- ²⁴D. Khomskii, *Physica B* **280**, 325 (2000).
- ²⁵G. Biotteau, F. Moussa, M. Hennion, J. Rodrigues-Carvajal, A. Wildes, L. Pinsard, and A. Revcolevschi, *Physica B* **276**, 562 (2000).
- ²⁶Y. Endoh, K. Hirota, S. Ishihara, S. Okamoto, Y. Murakami, A. Nishizawa, T. Fukuda, H. Kimura, H. Nojiri, K. Kaneko, and S. Maekawa, *Phys. Rev. Lett.* **82**, 4328 (1999).
- ²⁷V. P. Dyakonov, E. V. Zaroquentsev, G. G. Levchenko, and V. I. Markovich, *Fiz. Tverd. Tela (Leningrad)* **29**, 2894 (1987) [*Sov. Phys. Solid State* **29**, 1664 (1987)].