Enhanced giant magnetothermal conductivity in double-layered perovskite manganite La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$

M. Matsukawa, H. Ogasawara, R. Sato, and M. Yoshizawa
Department of Materials Science and Technology, Iwate University, Morioka 020-8551, Japan

R. Suryanarayanan, G. Dhalenne, and A. Revcolevschi
Laboratoire de Chimie des Solides, CNRS, UA446, Bâtiment 414, Université Paris-Sud, 91405 Orsay, France

K. Itoh
National Research Institute for Metals, Tsukuba 305, Japan

The in-plane (κ_{ab}) and out-of-plane (κ_c) thermal conductivity of a double-layered Mn perovskite single-crystal La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ has been studied as a function of temperature ($10 \leq T \leq 300$ K) and magnetic field ($0 \leq H \leq 18$ T). Near the insulating paramagnetic-to-metallic ferromagnetic transition, an anomaly in the value of κ_{ab} was observed, whereas the value of κ_c did not reveal such an anomaly. The observed giant magnetothermal conductivity was enhanced and extended beyond T_c in contrast with the cubic Mn perovskites. Our data seem to indicate the significant role played by the two-dimensional structure and the spin-lattice coupling.

The discovery of colossal magnetoresistance (CMR) in the hole-doped Mn perovskite $Ln_{1-x}D_x$MnO$_3$ (Ln = rare earths; D = Ca, Sr, Ba, Pb) has recently attracted the attention of chemists and physicists alike.[1] Although the double exchange mechanism[2] has been used as a starting point to explain the paramagnetic semiconductor-to-ferromagnetic metal transition and the associated CMR, it is now evident that one has to consider the Jahn-Teller effect and the strong electron-phonon interaction.[3] In this respect, it is important to examine the thermal properties of the perovskites. Such studies should yield crucial information about the various scattering processes of thermal carriers such as electrons and phonons and will eventually aid in the understanding of the complex physical properties of the charge-spin-lattice coupled systems such as Mn perovskites. Whereas there have been several reports on the electronic properties of the perovskites, very few studies[4-7] have been carried out on the thermal transport properties of $Ln_{1-x}D_x$MnO$_3$. It should be noted that the $Ln_{1-x}D_x$MnO$_3$ compounds belong to the Ruddlesden-Popper series generally described as $(Ln,D)_{n+1}$Mn$_n$O$_{3n+1}$ with n = infinity. For $n=2$, one obtains $(Ln,D)_3$Mn$_2$O$_7$, the bilayer Mn perovskite in which two MnO$_6$ layers are stacked with $(Ln,D)_2$O$_2$ layers along the c axis of the structure. The reduced dimensionality has been shown to have interesting consequences on the physical properties of these compounds. Thus the La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ compound exhibits[8,9] a CMR reaching more than 98% near 120 K, the paramagnetic-to-ferromagnetic transition temperature T_c. Furthermore, the CMR is more than 10% even at temperatures distant from T_c. These properties have not yet been well understood. In order to investigate the interplay between the lattice, charge and spin degrees of freedom, we have carried out thermal conductivity measurements of a single-crystal sample of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ as a function of temperature ($10 \leq T \leq 300$ K) and magnetic field ($0 \leq H \leq 18$ T). We observed a giant magnetothermal conductivity in this sample which is strongly correlated with the CMR.

Our data demonstrate the role played by the two-dimensional (2D) structure and the spin-lattice coupling.

Single crystals of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ were grown from sintered rods of the same nominal composition by the floating-zone method using a mirror furnace. Crystals could be easily cleaved, yielding to shiny surfaces. X-ray Laue patterns have indicated the cleaved surface to be the ab plane and therefore, the c axis is perpendicular to it. The x-ray powder pattern obtained by crushing a part of the cleaved crystal did not indicate the presence of any additional phases and the lattice parameters were calculated to be $a = 3.864 \pm 0.002$ Å and $c = 20.130 \pm 0.006$ Å. Energy-dispersive x-ray analyses of the cleaved surface revealed that the composition of the sample was very close to that of the starting rods. The dimensions of the crystals for the present experiment were 3.4×2.8 mm^2 in the ab plane and 1.0 mm along the c axis. The thermal conductivity both in the ab plane (κ_{ab}) and along the c axis (κ_c) of the crystal was measured by means of the steady-state heat-flow method using a Gifford-McMahon-type helium refrigerator in zero field. For the κ_{ab} measurement, a heater (chip resistor) was attached on one end of the crystal using the GE7051 vanish or silver paint to keep a uniform heat current over its cross section perpendicular to the ab-plane surface. The manganine wires were used as thermal resistors to prevent a heat loss from current leads of the heater. Two contacts of differential-type thermocouples were arranged on the ab-plane surface at a separated distance of ~2 mm. The sample was fixed on a copper block using the varnish or silver paint. For the κ_c measurement,[10] the sample was sandwiched between two sapphire substrates of high thermal conductivity and the thermocouples were attached onto the surface of sapphire with varnish or silver paint as shown in the inset of Fig. 1. The measurements as a function of the field were carried out at the National Research Institute for Metals using an 18-T superconducting magnet (Kobe Steel, Ltd.). The generated temperature gradient was directly monitored
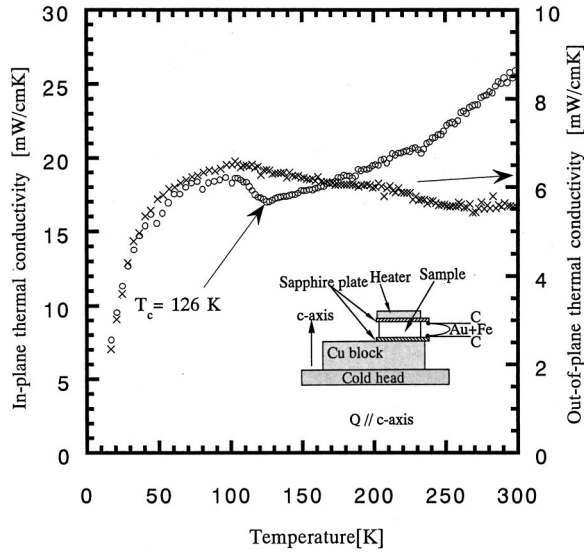
FIG. 1. The in-plane and out-of-plane thermal conductivity of the double-layered perovskite manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ as a function of temperature between 10 and 300 K. The inset shows the experimental configuration for the κ_c measurement.

FIG. 2. The in-plane and out-of-plane electrical resistivity of the double-layered perovskite manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ as a function of temperature between 10 and 300 K. The dashed curve denotes the electron component κ_e estimated from the ab-plane resistivity data using the Wiedemann-Franz (WF) law. The inset shows the configuration of electrical contacts for the ρ_c measurement.

with differential-type thermocouples of Au 0.07 at. % Fe alloy-Chromel and Chromel-Constantan, in zero and applied fields, respectively. The field dependence of the thermopower in Chromel-Constantan thermocouples was calibrated using the Stycast sample. A similar configuration was also used in the cryostat for the thermal conductivity measurement in fields. The estimated error in our measurements was within several percent which mainly arises from the heat radiation loss at high temperatures or the geometrical factor of terminal distances. The resistivity both in the ab plane (ρ_{ab}) and along the c axis (ρ_c) of the crystal was measured on the same crystal. The contact pads were prepared by painting a gold paste on one part of crystal surfaces and annealing it at 200 °C. The electric leads were attached on the contact pads using the silver paint and annealed to reduce contact resistances. For the ρ_{ab} measurement, a conventional four-probe technique was used as follows; the voltage and current contacts were arranged on the ab-plane surface and on both ends of the crystal normal to the ab plane, respectively. For the ρ_c measurement,[11] two contact pads were prepared on each side of the ab plane at a separated distance of ~ 1 mm as shown in the inset of Fig. 2. One pair of contacts across the sample thickness was taken as current electrodes and another pair as voltage. It is considered that this configuration is closer to a direct ρ_c measurement than the Montgomery method. In this configuration, determination of the cross-section area of the sample has some ambiguity but for a highly anisotropic and thick sample along the c axis, it is easily understood that the current along the c axis flows more uniformly over the whole ab plane. It should be noted that in our previous report[12] on a large single crystal of optimum doped $YBa_2Cu_3O_{7-y}$ (Y123), the value of ρ_c measured by the present method became about 10 mΩ m at 300 K, which is comparable with that for thin crystals Y123 (10 ~ 12 mΩ cm at 300 K) by the Montgomery method,[13] where the thickness sizes for the former and latter are ~ 1.7 and ~ 0.1 mm, respectively.

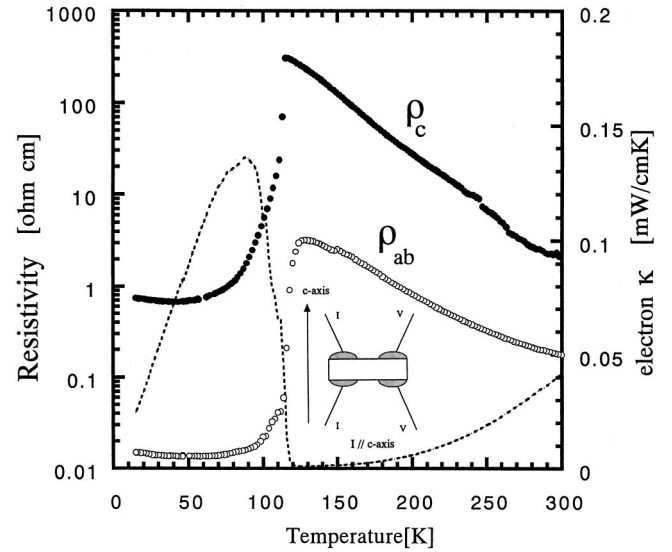The in-plane and out-of-plane thermal conductivity of the

double-layered perovskite manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ as a function of temperature, between 10 and 300 K, is shown in Fig. 1. Moreover, the in-plane and out-of-plane electrical resistivity of the double-layered perovskite manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ as a function of temperature is also shown in Fig. 2, where the dashed curve denotes the electron component κ_e estimated from the ab-plane resistivity data using the Wiedemann-Franz (WF) law. The value of κ_{ab} decreased monotonically from 300 K to around 126 K which is close to T_c of the sample and then increased slowly with a broad maximum at ~ 100 K. A similar anomaly was observed near the paramagnetic-ferromagnetic transition in the case of the cubic perovskite.[4] The positive curvature in κ_{ab} above T_c is a common feature to both the cubic and the double-layered perovskites. In contrast to the behavior of κ_{ab}, no obvious anomaly was observed in the temperature dependence of κ_c. Below 100 K, however, the temperature dependence of κ_c closely resembled that of κ_{ab}. The observed anomaly in κ_{ab} is closely associated with the complex phase transition at T_c, where both the semiconductor-metal and the paramagnetic-ferromagnetic transitions occur as indicated by the resistivity and magnetic measurements as shown in Fig. 2.[8,9] The κ anomaly, $\Delta\kappa[=\kappa(100\,\text{K})-\kappa(T_c)]=1.6\,\text{mW/cm K}$, around T_c is separated into electron, magnon, and phonon components such as $\Delta\kappa=\Delta\kappa_e+\Delta\kappa_m+\Delta\kappa_{ph}$. The electron thermal conductivity associated with the semiconducting-to-metal transition is estimated from resistivity data using the WF law to be 0.13 mW/cm K at 100 K as shown in Fig. 2. Next, the magnon thermal conductivity associated the paramagnetic-to-ferromagnetic transition is calculated from the specific-heat data[14] of double-layered perovskite manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ on the basis of the 2D kinetic expression, $\Delta\kappa_m=(\frac{1}{2})\Delta C_{mag}\nu_m^2\tau_m$, where ΔC_{mag}, ν_m, and τ_m represent the specific heat anomaly, the velocity, and lifetime of long-wavelength spin wave, respectively. Recently, inelastic

neutron-scattering measurements[15] strongly support that the perovskite manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ is a quasi-two-dimensional ferromagnet with weak coupling between different ferromagnetic bilayers. Thus we take the 2D kinetic expression as an upper limit of the ab-plane magnon contribution. Taking $\Delta C_{mag} = 0.25\, J\, cm^3\, K$,[14] $\nu_m = 6 \times 10^4\, cm/s^5$ and $\tau_m = 2 \times 10^{-12}\, s^5$, we obtain $\Delta\kappa_m = 0.9\, mW/cm\, K$. Finally, the phonon component $\Delta\kappa_{ph}$ becomes $0.6\, mW/cm\, K$, which is probably associated with the freezing of phonon scattering due to spin fluctuation. Thus from this rough estimation it is made clear that the κ enhancement is caused by the main contributions of both phonons and magnons, and partially by electron contribution. Above T_c, the electronic contribution is negligible from the WF estimation. Separating the measured κ_{ab} above T_c into both phonon and magnon contributions using the magnetic specific-heat data, we found that κ_m reaches at most a few percent of the measured thermal conductivity and thermal carriers become phonons. We make some comparison to thermal conductivity anisotropies of manganites and high-T_c cuprates since the $Bi_2Sr_2CaCu_2O_8$ (Bi2212) and Y123 compounds have double-layered perovskite structures of the CuO_2 planes per the unit cell as well as the double-layered $La_{1.2}Sr_{1.8}Mn_2O_7$. Of course, for both Bi2212 and Y123, there are some differences in the detailed atom positions except for the CuO_2 double-layered structures. In the Bi2212 compound,[16] a room-temperature anisotropy of the measured thermal conductivity κ_{ab}/κ_c reaches ~ 6 and subtracting from the measured value electronic contribution, we obtained that the value of $\kappa_{ab,ph}/\kappa_{c,ph}$ becomes ~ 4 at room temperatures. In insulating YBCO,[10] the ratio of $\kappa_{ab,ph}/\kappa_{c,ph}$ attained a factor of about 4–5. Thus it is found that the anisotropy of the phonon thermal conductivity in double-layered cuprates is very similar to κ_{ab}/κ_c (~ 4 at 300 K) in the double-layered manganite. The mean free path of phonons near T_c is also evaluated from the specific-heat data using the kinetic expression, $\kappa_{ph} = (\frac{1}{3})C_{ph}\nu_{ph}l_{ph}$. Taking $\kappa_{ab} = 17\, mW/cm\, K$, $C_{ph} = 0.69\, J/cm^3\, K$[14] and $\nu_{ph} = 4.3 \times 10^5\, cm/s$,[17] we obtained the value of l_{ph} as ~ 17 Å in the ab plane, which is at most several times larger than the lattice parameter of a axis (for the value of $\kappa_c = 6.3\, mW/cm\, K$, $l_{ph} \sim 6.3$ Å). Because of small anisotropy of phonon transport in comparison with large anisotropy of the low-field magnetization (~ 10) and electrical transport (~ 100), we assumed a dimensional factor of $\frac{1}{3}$ (in the case of 3D) in the kinetic expression of phonon gas. Here, the value of sound velocity estimated from the longitudinal elastic constant data[17] of the cubic $La_{1-x}Sr_xMnO_3$ single crystal ($x = 0.165$) was used as the value of ν_{ph} because we have no published data on the sound velocity of double-layered perovskite manganite $La_{1.2}Sr_{1.8}Mn_2O_7$.

Next, we consider the magnetic-field dependence of the normalized magnetothermal conductivity (NMTC) $[\kappa_{ab}(H)/\kappa_{ab}(0)]$ of our sample (Fig. 3). The field was applied parallel to the ab plane whether a thermal current was directed to in the ab plane or along the c axis. The $\kappa_c(H)/\kappa_c(0)$ data around T_c are also listed in Fig. 3. The value of the NMTC in the ab plane showed a rapid increase at low fields, gradually increased at high fields and finally saturated to a constant value at all measured temperatures.
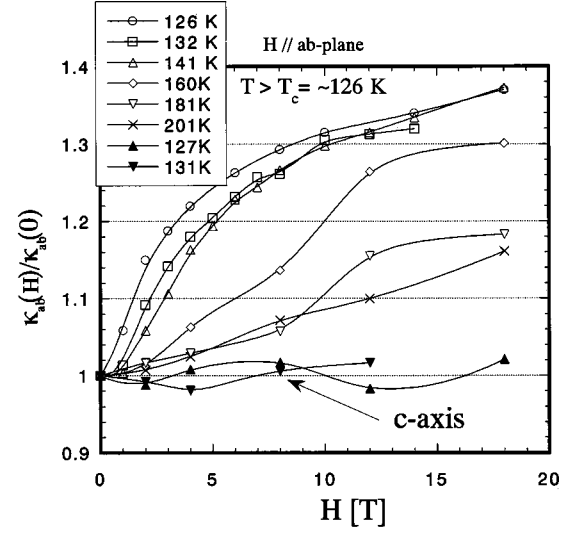
(a)
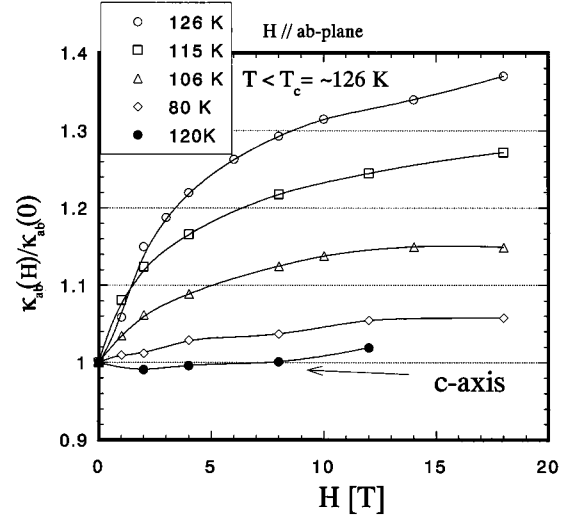
(b)

FIG. 3. The magnetic-field dependence of the normalized magnetothermal conductivity (NMTC) $[\kappa_{ab}(H)/\kappa_{ab}(0)]$ of the double-layered manganite $La_{1.2}Sr_{1.8}Mn_2O_7$. The field was applied parallel to the ab plane at several temperatures near T_c. (a) $T > T_c$ and (b) $T < T_c$. The closed marks denote the $\kappa_c(H)/\kappa_c(0)$ data just around T_c.

The effect of the magnetic field on κ_{ab} was marked just above T_c and the NMTC showed a large increase of $\sim 32\%$ at 10 T, which we term a giant magnetothermal conductivity (GMTC). However, the value of κ_c did not display such a remarkable increase and was almost independent of the field up to 18 T. This behavior along the c axis is consistent with the temperature variation of κ_c with no anomaly near T_c, as shown in Fig. 1. This finding indicates that thermal carrier scattering processes associated with the semiconductor-metal and the paramagnetic-ferromagnetic transitions become ineffective along the c axis and as the phonon scattering centers, structural disorders such as stacking faults are more dominant over the field-dependent scattering center such as spin-fluctuation scattering.

We also show in Fig. 4 the NMTC under several fields as a function of the reduced temperature $t = (T - T_c)/T_c$. For
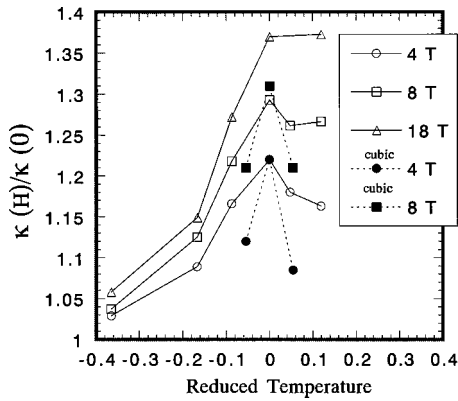
FIG. 4. The normalized magnetothermal conductivity under several fields as a function of the reduced temperature $t=(T-T_c)/T_c$. For comparison, the data points in the case of the cubic perovskite $La_{0.83}Sr_{0.17}MnO_3$ (LSMO) with $T_c=275$ K, reported by Cohn et al. (Ref. 5), are also shown.

comparison, the data points in the case of the cubic perovskite $La_{0.83}Sr_{0.17}MnO_3$ (LSMO) with $T_c=275$ K, reported by Cohn et al.,[5] are also shown. If we assume that the thermal carrier (charge/and/or phonon) scattering due to spin fluctuation is dominant over other carrier scattering processes such as the electron-phonon interaction and the phonon-phonon Umklapp process, it then follows that the maked rise in κ_{ab} in the presence of the magnetic field is mainly caused by the freezing out of the spin-fluctuation scattering. Comparing our data with those reported for the cubic LSMO, it is important to note that the giant field effect on the thermal conductivity for the layered manganites is not limited to the narrow region just above T_c but exists over a wide temperature range up to $t=0.1$. Furthermore, it should be noted that the thermal fluctuation effect for the cubic LSMO with a higher value of $T_c\sim275$ K is more important compared to that for our sample, whose T_c is less than half of that for the cubic compound. Hence the reason for the strong enhancement of the spin-fluctuation scattering observed in the present double-layered compound may be attributed to the two-dimensional layered structure. This finding is also consistent with the enhanced magnetoresistance of the double perovskite[8,9] in contrast with that of the cubic compound.

Now, considering certain models which go beyond the double exchange mechanism, we note that in the case of $LaSrMnO_3$, Millis et al.[3] proposed that the strong electron-phonon interaction arising from the Jahn-Teller effect played a significant role in the CMR effect. From the standpoint of competition between the double exchange and the strong electron-phonon interactions, our present data concerning the anomaly near T_c, the positive curvature of κ_{ab} at high temperatures and the field-induced enhancement in κ_{ab} need to be examined. The temperature dependence of κ_{ab} at high temperatures above 200 K far from T_c showed thermally activated type behavior which is not described by the spin-fluctuation scattering mechanism. In the case of the transition metal oxides for which strong electron-phonon couplings are known to exist, it is well established that polaronlike excitations lead to a hopping-type dependence of electrical conductivity for temperatures greater than one-half of the Debye temperature.[18] Thus, the positive curvature of κ_{ab} or the exponential temperature dependence of κ_{ab} above T_c, in contrast to the negative one of κ_c, is likely related to the polaron transport in the MnO_2 planes. A detailed resistivity analysis of $La_{0.67}Ca_{0.33}MnO_3$ films, for example, has been explained by a small polaron hopping model.[19] Thus, above T_c, in the semiconducting state, the carriers are localized as small polarons but, below T_c, there is a considerable increase in mobile carriers. This increase causes a large enhancement in κ_{ab} in addition to the role played by the suppression of the spin-fluctuation scattering rate or magnon contribution. Recent Raman data obtained[20] as a function of magnetic field on a single crystal of $La_{1.2}Sr_{1.8}Mn_2O_7$ have been interpreted on the basis of the formation of small polarons at $T>T_c$ and a crossover from small to large polarons as the system undergoes the paramagnetic-ferromagnetic transition.

In summary, we have measured the in-plane and out-of-plane thermal conductivity of the double-layered perovskite $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal as a function of the temperature and magnetic field. The thermal behavior of κ_{ab} displayed a clear anomaly near T_c, similar to that of the cubic manganites $LaMnO_3$ whereas no such anomaly was observed in the behavior of κ_c. The observed giant magnetothermal conductivity in this layered compound is more enhanced in comparison with that of the cubic systems; this is probably related to the stronger spin-fluctuation scattering due to the 2D layered structure of the double perovskite.

[1] For a detailed discussion and extensive references, see *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides*, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1988); A. P. Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1997).

[2] C. Zener, Phys. Rev. **82**, 403 (1951); P. G. de Gennes *ibid.* **118**, 141 (1960).

[3] A. J. Millis et al., Phys. Rev. Lett. **74**, 5144 (1995); A. J. Millis et al., *ibid.* **77**, 175 (1996).

[4] D. W. Visser et al., Phys. Rev. Lett. **78**, 3947 (1997).

[5] J. L. Cohn et al., Phys. Rev. B **56**, R8495 (1997).

[6] Baoxing Chen et al., Phys. Rev. B **55**, 15 471 (1997).

[7] S. Uhlenbruck et al., Phys. Rev. B **57**, R5571 (1998).

[8] Y. Moritomo et al., Nature (London) **380**, 141 (1996).

[9] W. Prellier et al., Physica B **259-261**, 833 (1999).

[10] S. Hagen et al., Phys. Rev. B **40**, 9389 (1989).

[11] A. Odagawa et al., Physica C **217**, 222 (1993).

[12] M. Matsukawa et al., Phys. Rev. B **53**, R6034 (1996).

[13] S. J. Hagen et al., Phys. Rev. B **37**, 7928 (1988).

[14] J. E. Gordon et al., Phys. Rev. B **60**, 6258 (1999).

[15] Tapan Chatterji et al., Phys. Rev. B **60**, R6965 (1999).

[16] M. F. Crommie and A. Zettl, Phys. Rev. B **43**, 408 (1991).

[17] H. Hazawa et al., Physica B (to be published).

[18] N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1990).

[19] G. Jakob et al., Phys. Rev. B **58**, R14 966 (1998).

[20] D. B. Romero et al., Phys. Rev. B **58**, R14 737 (1998).