Observation of itinerant ferromagnetism in layered $Sr_3Ru_2O_7$ single crystals

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$Sr_3Ru_2O_7$ is a layered compound and a member of the Ruddlesden-Popper-type compound series of $Sr_{n+1}Ru_nO_{3n+1}$ ($n=1$, 2, and $n=\infty$) with $n=2$. Single crystals of $Sr_3Ru_2O_7$ were grown and characterized, providing an unambiguous indication of a rich ferromagnetic state with $T_c=104$ K and a saturated moment of $1.30\pm0.05\mu_B$/Ru at $T=5$ K. Among many interesting features, a magnetic spin reorientation transition is observed, suggesting that moments in the ordered state order ferromagnetically with a slight canting on adjacent spins. Negative magnetoresistance, commonly occurring in ferromagnets, is relatively large (19% at 10 T and $T=30$ K), suggesting a significant suppression of spin-flip scattering by the applied magnetic field. The results are discussed with comparisons drawn with sister compounds Sr_2RuO_4, $SrRuO_3$ and other related systems. [S0163-1829(97)51102-7]

In this paper, the results of measurements of the magnetic and transport properties of $Sr_3Ru_2O_7$ single crystals are reported. $Sr_3Ru_2O_7$, isostructural with $Sr_3Ti_2O_7$, is a layered compound with a body-centered tetragonal unit cell.[1–3] It is a member of the Ruddlesden-Popper-type compound series, $Sr_{n+1}Ru_nO_{3n+1}$ ($n=1$, 2, and ∞). The series includes the well studied Sr_2RuO_4 ($n=1$) and $SrRuO_3$ ($n=\infty$).[4–7] There are a few reports on $Sr_3Ru_2O_7$ ($n=2$);[2] however, these studies have focused on polycrystalline samples where second phases and, possibly, the polycrystalline nature of the samples obscured a wide range of magnetic properties revealed by this single-crystal study.

This study of $Sr_3Ru_2O_7$ displays a rich ferromagnetic state with a Curie temperature T_C equal to 104 K followed by another magnetic transition, T^*, at 66 K. Below T^*, isothermal magnetization $M(H,T=\text{const})$ data with the applied magnetic field in the basal plane, i.e., $H\perp(001)$, exhibits a sharp spin reorientation transition or a possible metamagnetic transition followed by a saturation of the magnetization. It may be inferred that along (001) the magnetic spins of adjacent neighbors align ferromagnetically with a slight canting away from the (001). The extrapolation of the high-field linear dependence of $M(H,T=\text{const})$ to $H=0$ leads to an estimate of the saturation moment, μ_0, equal to $1.30\pm0.05\mu_B$/Ru, independent of the applied field direction. The resistivity $\rho(T)$ along (001) displays a weak Fisher-Langer anomaly[8] at 104 K and a rapid decrease below 66 K. Large negative magnetoresistance effects are observed, and reach 19% at 10 T. Based on this study, it may be plausible to associate the different properties of members of the $Sr_{n+1}Ru_nO_{3n+1}$ series with the difference in the number of Ru-O layers, n, in the unit cell. This is particularly true for magnetic properties where the series evolves from a paramagnet at $T>1$ K ($n=1$) to a canted ferromagnet ($n=2$) to a collinear spin ferromagnet ($n=\infty$) as n increases.

Most itinerant transition-metal oxides are not ferromagnetic because the superexchange between the magnetic cations via the anion typically favors antiferromagnetic correlations. The strong antiferromagnetic correlations and long-range antiferromagnetic order displayed by most of the parent compounds of the high-T_c superconductors are classic examples of this tendency. Qualitatively, ferromagnetism is favored over antiferromagnetism in most conducting systems. Of these oxides, $SrRuO_3$ with $T_c=165$ K, the $n=\infty$ member of $Sr_{n+1}Ru_nO_{3n+1}$, has been the only known itinerant $4d$ transition-metal oxide ferromagnet. $SrRuO_3$ is a perovskite composed of infinite layers of RuO_6 octahedra. This compound with a $4d^4$ low-spin configuration ($S=1$) is believed to have a very narrow π^* band that is two-thirds filled.[4,5] The nature of the magnetism in this compound and other ruthenates with narrow $4d$ bands depends in an extremely sensitive way on the degree of band filling and band width. Differences reflected in the magnetic properties of $SrRuO_3$, $CaRuO_3$ and these compounds with slight impurity doping illustrate the subtlety.[9] Attention to the ruthenates has recently been heightened by the report of superconductivity with a superconducting transition temperature T_s of 0.93 K in the $n=1$ member of $Sr_{n+1}Ru_nO_{3n+1}$, Sr_2RuO_4 (Ref. 10). This compound possesses the K_2NiF_4 structure composed of RuO_6 planes offset along the c axis and with an intervening layer of Sr ions. The structure of $Sr_3Ru_2O_7$, the $n=2$ member of $Sr_{n+1}Ru_nO_{3n+1}$, is composed of pairs of closely coupled RuO_6 planes offset along the c axis and with the pairs separated by a layer of Sr ions. The rich superconducting and magnetic properties of the $n=1$ and $n=\infty$ compounds of the $Sr_{n+1}Ru_nO_{3n+1}$ and their relevance to the high-T_c cuprates and the colossal magnetoresistivity in Mn-based oxides[11] have driven this study of the closely related $n=2$ compound.

Single crystals were grown in Pt crucibles using flux techniques from off-stoichiometric quantities of RuO_2, $SrCO_3$, and $SrCl_2$ (a self-flux). These mixtures were heated to 1500 °C in partially capped Pt crucibles, soaked for 25 h, cooled at 2 °C/h to 1350 °C, and then rapidly cooled to room temperature. The resulting shapes of $Sr_3Ru_2O_7$ tend to be platelike. The average size of single crystals is $1\times1\times0.5$ mm^3 with the c axis along the shortest dimension. The starting ratio of Sr:Ru has a large influence not only on the form of crystals but also on the ratio of Sr:Ru in grown crystals. Thus, by slightly changing the starting Sr to Ru ratio, we have successfully grown crystals of $Sr_{n+1}Ru_nO_{3n+1}$ with

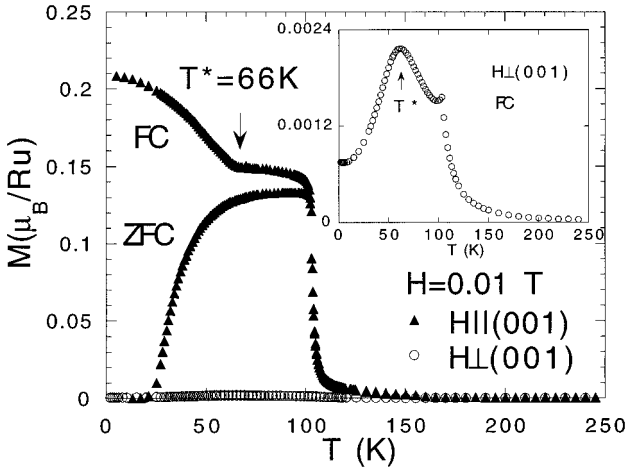

FIG. 1. Magnetization M vs temperature T at $H=0.01$ T for $Sr_3Ru_2O_7$; solid triangles: M vs T with $H\|(001)$ measured in a zero-field-cooled (ZFC) and field-cooled (FC) sequence. Open circles: M vs T with $H\perp(001)$ after FC. Inset: M vs T for FC at $H\perp(001)$.

$n=1$, 2, and ∞. X-ray diffraction patterns from powdered $Sr_3Ru_2O_7$ single crystals show no impurity peaks from either $SrRuO_3$ or Sr_2RuO_4. The refinement of a body-centered tetragonal cell using 21 reflections yielded $a=3.901$ Å and $c=20.501$ Å. These values are in good agreement with those reported previously.[1] Results of scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) indicate that crystals studied are of high quality. The temperature and field dependence of the resistivity were measured using a standard four-probe technique and the magnetization was measured with a commercial superconducting quantum interference device magnetometer (Quantum Design).

Shown in Fig. 1 is magnetization $M(T)$ vs temperature T measured in a zero-field-cooled (ZFC) and field-cooled (FC) sequence with $H\|(001)$ and $H\perp(001)$ ($H=0.01$ T). The inset in Fig. 1 shows M vs T for $H\perp(001)$ on an expanded scale. For $H\|(001)$, a clear transition into a ferromagnetic state is seen at 104 K with an additional transition occurring at $T^*=66$ K. In addition, the system exhibits a large irreversibility at $T<104$ K in $M(T)$ when measured ZFC or FC. Such irreversibility is typical of the movement of domains in ferromagnets.

The temperature dependence of the magnetic susceptibility $\chi(T)$ defined by M/H for $170\leqslant T\leqslant 370$ K obeys a Curie-Weiss law given by $\chi(T)=\chi_0+c/(T-\theta)$. (We determined that a field of 0.01 T was low enough to define ''zero-field'' susceptibility.) The parameters obtained by fitting the $\chi(T)$

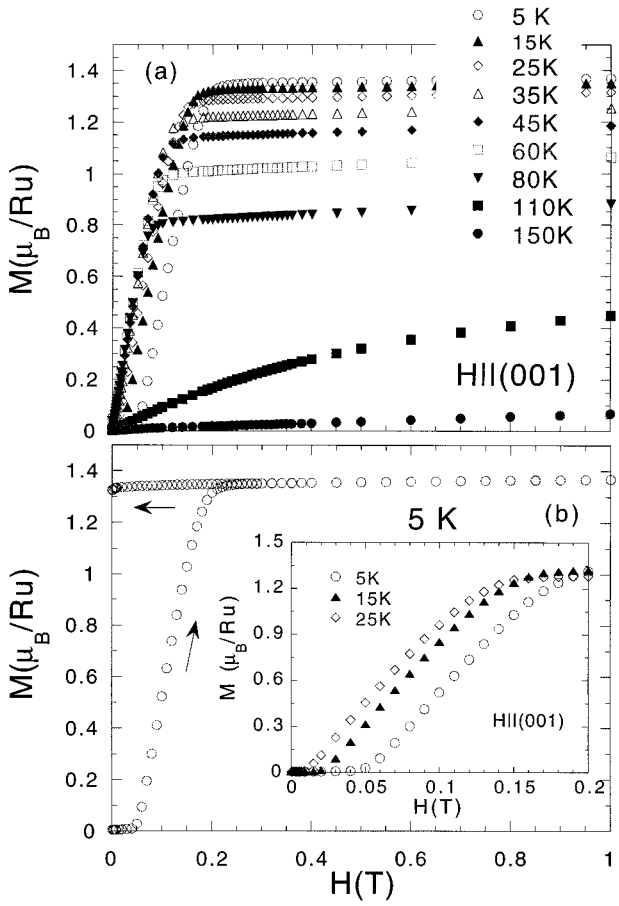

FIG. 2. Magnetization M vs applied field H with $H\|(001)$; (a) M vs T for various temperatures; (b) hysteresis of M at $T=5$ K. Inset: M vs H at low fields for $T=5$, 15, and 25 K.

are displayed in Table I along with similar information for Sr_2RuO_4 and $SrRuO_3$. For $H\|(001)$, the effective paramagnetic moment μ_{eff} for $Sr_3Ru_2O_7$ estimated from the Curie constant C is $2.63\mu_B$/Ru as compared to the predicated paramagnetic moment $2.83\mu_B$/Ru for the low-spin $S=1$ configuration. This value of μ_{eff} is close to the value measured for $SrRuO_3$ but is somewhat larger than μ_{eff} for $H\perp(001)$. $\chi_0(H\|(001))$ is 3.2×10^{-3} (emu/mole), comparable to that for $SrRuO_3$, but almost an order of magnitude larger than that reported for Sr_2RuO_4 (see Table I). Our studies of low-temperature heat capacity ($1.5<T<15$ K) of $Sr_3Ru_2O_7$ single crystals yield an electronic contribution $\gamma=77.6$ mJ/mole K^2.[12] The large value of χ_0 and γ for $Sr_3Ru_2O_7$ indicates a largely enhanced density of states at the Fermi level, implying highly correlated electron behavior

TABLE I. Relevant parameters for $Sr_{n+1}Ru_nO_{3n+1}$. ($\perp$) or ($\|$) indicates $H\perp$ or $\|(001)$. T_C is defined as the Curie temperature, and T_s the superconducting transition temperature.

	Sr_2RuO_4 ($n=1$)	$Sr_3Ru_2O_7$ ($n=2$)	$SrRuO_3$ ($n=\infty$)
$\mu_{\text{eff}}(\mu_B)$	4.95 (Ref. 2), 1.04 (Ref. 13)	2.63($\|$), 1.35($\perp$)	2.76($\|$), 2.83($\perp$)
$\mu_0(\mu_B)$		1.34($\|$), 1.27($\perp$)	1.1 (Refs. 14,15), 1.4
χ_0 (memu/mole)	0.47 (Ref. 13)	3.2($\|$), 0.16($\perp$)	3.9 (Ref. 9)
T_C or T_s (K)	0.93	104	165 (Refs. 9,15)
θ (K)	−219 (Ref. 13)	136($\|$), 126($\perp$)	166 (Ref. 9)

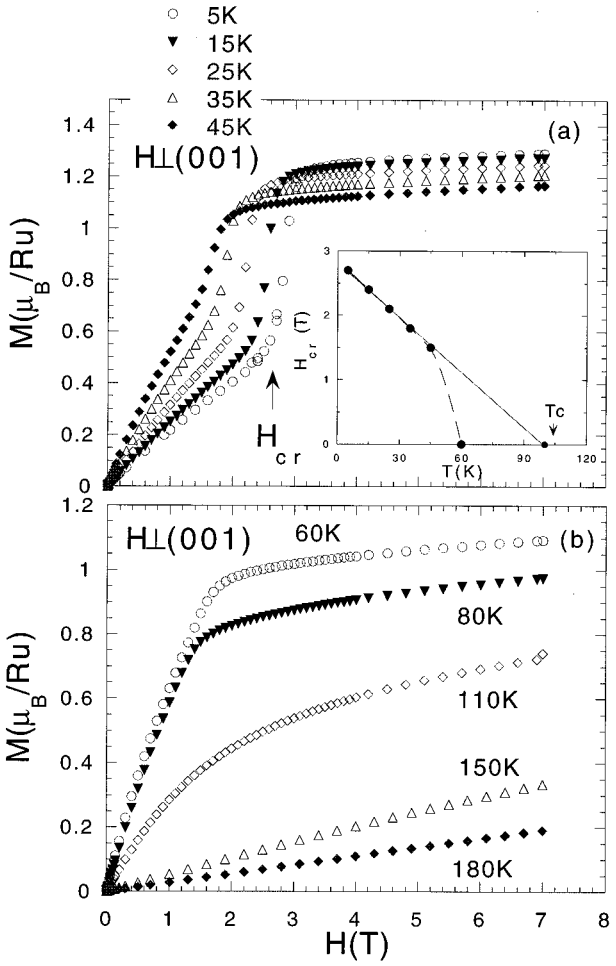

FIG. 3. Magnetization M vs applied field $H\perp(001)$ for various temperatures; (a) M vs H for $5\leqslant T\leqslant 45$ K; (b) M vs T for $60\leqslant T\leqslant 180$ K. Inset: critical field $H_{\rm cr}$ vs T.

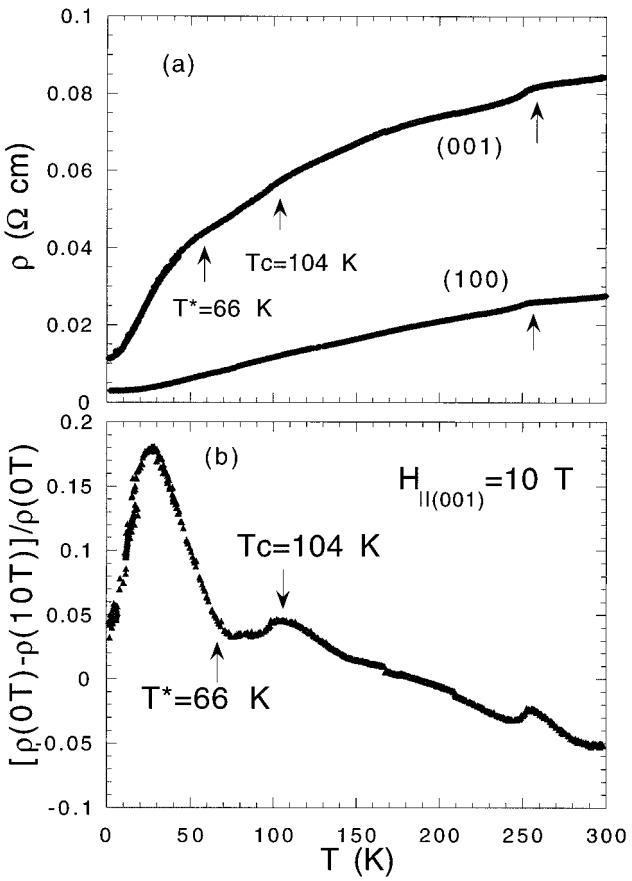

FIG. 4. (a) Electrical resistivity $\rho(T)$ for (001) and (100) directions vs T. (b) $\rho(0\ \mathrm{T})-\rho(10\ \mathrm{T})/\rho(0\ \mathrm{T})$ vs T.

due to the narrow $4d$ band. The value of θ obtained for the two directions of the magnetic field are 130 K$\pm$5 K, which is considerably higher than T_C, possibly indicative of spin fluctuations persisting above T_C (see Table I).

The magnetic anisotropy in $M(T)$ below T_C at low fields is anomalously large. Such an anisotropy indicates that (001) or near (001) is the easy axis. The broad maximum seen below T_C at $H\perp(001)$, on the other hand, resembles antiferromagnetic behavior, signaling a possible noncollinear spin structure existing in the ferromagnet phase (see inset in Fig. 1). Although the exact spin structure is yet to be determined, we believe that adjacent spins align with a finite angle between them due to antiferromagnetic correlations within *ab* planes, while perpendicular to these planes, the spins are ferromagnetically coupled. Such a spin configuration results in spin canting, and thus, the spin reorientation transition.

The spin canting and magnetization saturated in relatively low applied field are striking features of this compound. Shown in Fig. 2(a) is isothermal magnetization M vs $H\|(001)$ at various temperatures. The magnetic behavior shown is typical of a ferromagnet. The hysteresis in M vs H for $T=5$ K expected for ferromagnets is obvious in Fig. 2(b). As indicated in the inset, the spins undergo a reorientation characterized by an initial plateau in M at low fields ($H<0.05$ T). This plateau disappears when $T>25$ K. More importantly, the saturation field H_s is in the vicinity of 0.2 T at 5 K and decreases with increasing temperature [see Fig. 2(a)]. Such a H_s is uncharacteristically low and in sharp contrast to the case of $SrRuO_3$ where magnetization does not seem to be saturated at $H=12$ T and $T=4.2$ K.[5] This strongly suggests that the easy magnetization in $Sr_3Ru_2O_7$ is (001). The saturation moment μ_0 obtained by extrapolating the high-field linear portion of M vs H to $H=0$ is $1.34\mu_B$/Ru at 5 K. This value is close to that for $SrRuO_3$ but smaller than the fully saturated moment of $2\mu_B$/Ru expected for low-spin state Ru^{4+}, i.e., $g\mu_B S$ for $g=2$ and $S=1$. The slightly depressed saturation moment μ_0 compared to that expected for a full $S=1$ is not unexpected and can be attributed to hybridization and/or a slight orbital and crystal electric field contributions to the free ion angular momentum.

In Fig. 3, we display M vs H at various temperatures for $H\perp(001)$. A large jump of M occurs at a critical field $H_{\rm cr}$, $H_{\rm cr}=2.7$ T at $T=5$ K, for instance, and is then followed by a nearly saturated M as H increases. There is no doubt that at $H=H_{\rm cr}$ the spin system undergoes a transition to a state where all the spin directions are parallel to the field. Remarkably, the saturated moment extrapolated is $1.27\mu_B$/Ru at 5 K and nearly identical to that when $H\|(001)$ ($1.34\mu_B$/Ru). Such behavior along with the relatively low $H_{\rm cr}$ (<3 T at 5 K) implies a low-magnetic anisotropy energy or exchange stiffness in the ferromagnetic system although there is a large magnetic anisotropy at very low fields characterized by $M(T)$ in Fig. 1. In addition, $H_{\rm cr}$ decreases with temperature,

and rapidly disappears as $T \rightarrow 60$ K. A linear extrapolation of H_{cr} for $0<T<50$ K intercepts at $T=100$ K, nearly identical to T_C, see the inset in Fig. 3(a). The disappearance of the reorientation transition near 66 K together with the anomaly observed in the same temperature range in $M(T)$ (Fig. 1) may result from a canting of the spins away from the (001) direction for $T<66$ K. Measurements of $M(T,H)$ with $H \perp (001)$ indicate no magnetic anisotropy between (100) and (010).

Shown in Fig. 4(a) is temperature dependence of the resistivity $\rho(T)$ for current parallel to (001) and (100). Consistent with the anisotropic behavior observed in magnetic properties, $\rho(T)$ also exhibits a considerably large anisotropy ($\rho_c/\rho_{ab}=3.1$ at 300 K). Indeed, the higher $\rho(T)$ along (001) is in accordance with the crystal structure where the ratio of the c axis to a axis, c/a, is approximately 5.2, leading to a much weaker overlap along (001). $\rho(T)$ in the basal plane is about two orders of magnitude larger than that for $SrRuO_3$.[15] While $\rho(T)$ displays a characteristic saturation due to the elastic scattering at low temperatures, the temperature dependence of $\rho(T)$ for both directions in the temperature range measured does not seem to show T^2 behavior which is normally characteristic of Baber scattering. More markedly, a rapid decrease in $\rho(T)$ for (001) seen in the vicinity of T^* indicates a significant reduction of spin scattering. There appears to be a weak Fisher-Langer feature below $T=104$ K, which is characteristic of most metallic ferromagnets. No corresponding anomaly is discerned in $\rho(T)$ perpendicular to (001). In addition, a discontinuity of $\rho(T)$ near 260 K is observed, and then followed by a less temperature-dependent $\rho(T)$ above 260 K. The origin of this anomaly is puzzling since there are no corresponding anomalies in the $M(T,H)$ at this temperature.

Negative magnetoresistance effects are observed. There is no significant difference in magnetoresistance effects for longitudinal (current density $J \| H$) and transverse ($J \perp H$) configurations. Shown in Fig. 4(b) is $\rho[(0\text{ T})-\rho(10\text{ T})]/\rho(0\text{ T})$ vs T along (001). Three peaks are seen. The peak near 260 K is associated the unknown anomaly. A small peak seen near T_c indicates a slight suppression of spin-flip scattering common to most ferromagnets. A much larger peak (19%) is observed at 30 K strongly suggesting that the electron scattering below T^* depends in a very sensitive way on the spin reorientation. In contrast, $SrRuO_3$ under the similar conditions shows a magnetoresistance ratio of 10% which is peaked in the vicinity of T_c.[9] The larger negative magnetoresistance effects imply that in an applied field the increase in energy needed to flip a spin is larger in $Sr_3Ru_2O_7$ than in $SrRuO_3$, resulting in a sharper decrease in spin-flip scattering in $Sr_3Ru_2O_7$ than in $SrRuO_3$.

Some theoretical efforts have been made to understand itinerant ferromagnetism in oxides[4,5] and spin reorientation or metamagnetism in metallic compounds.[16,17] A localized spin model is not applicable since the magnetic properties in these materials depends critically on hybridization and the details of the band structure in the vicinity of the Fermi energy. While some of these theoretical results for systems similar to those discussed here give some glimpses at the sensitivity of properties to band filling, discrepancies remain and further analysis is required. This identified canted itinerant ferromagnet not only reveals fascinating phenomena but also poses a challenge to explore the nature of this kind of itinerant ferromagnetic oxides.

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[1] H. K. Muller-Buschbaum and J. Wilkens, Z. Anorg. Allg. Chem. **591**, 161 (1990).
[2] M. Itoh, M. Shikano, and T. Shimura, Phys. Rev. B **51**, 16 432 (1995).
[3] S. N. Ruddlesden and P. Popper, Acta Crystallogr. **11**, 54 (1958).
[4] J. B. Goodenough, Czech. J. Phys. B **17**, 304 (1967).
[5] J. M. Longo, P. M. Raccah, and J. B. Goodenough, J. Appl. Phys. **39**, 1327 (1968).
[6] J. J. Randall and R. Ward, J. Am. Chem. Soc. **81**, 2629 (1959).
[7] R. J. Cava, B. Batlogg, K. Kiyono, H. Takagi, J. J. Jrajewski, W. F. Peck, Jr., L. W. Rupp, Jr., and C. H. Chen, Phys. Rev. B **49**, 11 890 (1994).
[8] M. F. Fisher and J. S. Langer, Phys. Rev. Lett. **20**, 665 (1968).
[9] G. Cao, S. McCall, J. Bolivar, M. Shepard, F. Freibert, P. Henning, and J. E. Crow, Phys. Rev. B **54**, 15 144 (1996); M. Shepard, G. Cao, S. McCall, F. Freibert, and J. E. Crow, J. Appl. Phys. **79**, 4821 (1996).
[10] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994).
[11] R. von Helmholt *et al.*, Phys. Rev. Lett. **71**, 2331 (1993); S. Jin *et al.*, Science **264**, 413 (1994).
[12] S. McCall, G. Cao, and J. E. Crow (unpublished).
[13] J. J. Neumeier, M. F. Hundley, M. G. Smith, J. D. Thompson, C. Allgeier, H. Xie, W. Yelon, and J. S. Kim, Phys. Rev. B **50**, 17 910 (1994).
[14] J. Lynn *et al.* (private communications).
[15] P. B. Allen, H. Berger, O. Chauvet, L. Forro, T. Jarlborg, A. Junod, B. Revaz, and G. Santi, Phys. Rev. B **53**, 4393 (1996).
[16] E. P. Wohlfarth, Philos. Mag. **7**, 1817 (1962).
[17] Y. Takahashi and M. Tano, J. Phys. Soc. Jpn. **51**, 1792 (1982).