Giant Room-Temperature Magnetoresistance in Polycrystalline $Zn_{0.41}Fe_{2.59}O_4$ with α-Fe_2O_3 Grain Boundaries

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A tunneling-type magnetoresistance (MR) as large as 158% is observed at $T = 300$ K in a polycrystalline $Zn_{0.41}Fe_{2.59}O_4$ sample, in which the $Zn_{0.41}Fe_{2.59}O_4$ grains are separated by insulating α-Fe_2O_3 boundaries. The huge room-temperature MR is attributed to the high spin polarization of $Zn_{0.41}Fe_{2.59}O_4$ grains and antiferromagnetic correlations between magnetic domains on both sides of the insulating α-Fe_2O_3 boundary. The MR exhibits strong temperature dependence below 100 K and its magnitude is enhanced to reach 1280% at 4.2 K, which may arise from the Coulomb blockade effect.

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There has been a growing interest in the tunneling magnetoresistance (MR) effect in materials which combine ferromagnetic metals (FMs) and insulators (Is) due to their potential applications for magnetoresistive devices. Although this effect was discovered by Julliere [1] in FM/I/FM junctions early in 1975, large and reproducible tunneling MR ratios have been found only recently. Large tunneling MR can also be observed in a different class of tunnel-type nanostructures, such as granular FMs embedded in an insulating matrix as well as polycrystalline FMs. In this class of granular materials, electron tunneling from one FM grain to another depends on the relative orientation between magnetic moments of the grains. The tunnel resistance decreases when the magnetic moments of the grains are aligned in parallel in an applied magnetic field H, resulting in a large negative MR.

The fundamental quantity which determines the tunneling MR ratio in the magnetic granular system is the spin polarization in FM granules. The most popular definition of the spin polarization for a FM is $P = (N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$ where N_s ($s = \uparrow$ or $\downarrow$) is the density of states at the Fermi energy for electrons with spin s. $P = 0$ corresponds to a paramagnetic metal and $P = 1$ to a half metal in which only one spin subband makes a contribution to the tunneling conduction of electrons. The tunneling MR ratio is proportional to P^2 either in FM/I/FM junctions or in magnetic granular materials, reaching its maximum for $P = 1$. As a result, a straightforward way of enhancing the tunneling MR is to use the high spin-polarization or half-metallic FMs in the tunnel-type nanostructures. Doped manganites [2–4], CrO_2 [5], and Fe_3O_4 [6] have been used as the FM electrodes of the FM/I/FM tunnel junctions. At the same time, other tunnel-type nanostructures such as layered manganites [7], granular CrO_2 film [8], as well as polycrystalline manganites [9], $Tl_2Mn_2O_7$ [10] and Sr_2FeMoO_6 [11] have also been reported. In these materials, large tunneling MR ratios have been observed at low temperatures. For example, 450% at 14 K and 1% at 300 K observed in $La_{1-x}Sr_xMnO_3/CaTiO_3/La_{1-x}Sr_xMnO_3$ junctions [4], 100% at 5 K and 0.1% at 300 K in CrO_2-Cr_2O_3 granular systems [8], 32% at 5 K and 1.1% at 300 K in polycrystalline $La_{2/3}Sr_{1/3}MnO_3$ [9], 43% at 5 K and 0 at 300 K in polycrystalline $Tl_2Mn_2O_7$ [10], and 45% at 4.2 K and 11.5% at 300 K in Sr_2FeMoO_6 [11]. However, the observed MRs are much lower than would be expected for these highly spin-polarized systems, especially at room temperature. The small tunneling MR at room temperature may be attributed to the decrease of P and the increase of spin-flip tunneling with temperature increased, while enhanced MR at low temperatures may arise from the Coulomb blockade effect.

The very small room-temperature MR is an unfavorable factor of the application for magnetoresistive devices. It is highly desirable to find a tunnel-type material with high spin polarization and large MR at room temperature. In this Letter we report a new class of nanostructured material, polycrystalline $Zn_{0.41}Fe_{2.59}O_4$, exhibiting an intrinsic tunneling-type MR as large as 158% at $T = 300$ K and $H = 5$ kOe. The single-phase system of cubic $Zn_xFe_{3-x}O_4$ ($0.4 < x < 0.8$) is an FM with the Curie temperature $T_c = 300$–350 K and shows comparatively low resistivity at room temperature [12]. The polycrystalline material reported here is a two-phase system in which the $Zn_{0.41}Fe_{2.59}O_4$ grains are separated by uniform α-Fe_2O_3 grain boundaries. The rhombohedral α-Fe_2O_3 is an antiferromagnetic insulator with the Néel temperature of 958 K and room-temperature resistivity of about 10^{10} Ω cm. Such a huge room-temperature tunneling MR indicates that $Zn_{0.41}Fe_{2.59}O_4$ is a highly spin-polarized FM. As the temperature is lowered from room temperature, the tunneling MR first increases slowly and then has a big enhancement below 100 K, reaching 1280% at 4.2 K.

Sample was prepared by a sol-gel method using mix ingredients ZnO and $Fe(NO_3)_3 \cdot 9H_2O$ in the mole proportion of 1:5. First, the gel was precalcined at 1100 °C for 4 h in air. Then, the powder was cold-pressed into pellets under a pressure of 1000 kg/cm^2. Finally, these disks were sintered at 1400 °C for 2.5 h in air. Resistivity and MR were measured using a standard four-probe method in the

range of 4.2 to 350 K. From its XRD pattern, the sample was found to consist of two phases: $(Zn_xFe_{3-x}O_4)_{1-y}$ and $(\alpha\text{-}Fe_2O_3)_y$. The Zn^{2+} content of $x = 0.41$ and the mole percentage of $y = 0.11$ for α-Fe_2O_3 were determined from inductively coupled plasma (ICP) results. The major phase of $Zn_xFe_{3-x}O_4$ constitutes FM grains in the polycrystalline sample, while the minor phase of α-Fe_2O_3 surrounds the $Zn_xFe_{3-x}O_4$ grains, forming grain boundaries. The appearance of the α-Fe_2O_3 phase at the grain boundaries should be attributed to preferential volatilization of Zn there and further oxygenation of Fe^{2+} at $T = 1400\,^{\circ}C$ in air. As a result, the present polycrystalline sample is composed of many $Zn_xFe_{3-x}O_4$ grains separated by insulating α-Fe_2O_3 grain boundaries, as shown in the left inset of Fig. 1. This picture has been confirmed by TEM and high-resolution TEM. Figure 1 is a high resolution TEM picture of the present sample. It can be seen that two dark $Zn_xFe_{3-x}O_4$ grains are separated by a light α-Fe_2O_3 boundary. It was found that the size of a $Zn_xFe_{3-x}O_4$ grain is about 150 nm and the α-Fe_2O_3 boundary has uniform thickness of about 7 nm. The Curie temperature of the sample was obtained to be $T_c = 318$ K by magnetization measurements using the vibrating sample magnetometer (VSM).

The field dependence of the room-temperature resistivity for the sample are shown in Fig. 2, from which a huge negative MR was observed. The MR magnitude is defined as $\Delta\rho/\rho_H = [\rho_0 - \rho_H]/\rho_H$ where ρ_0 and ρ_H are the resistivities at zero field and an applied field H, respectively. We obtain a value of room-temperature MR as large as 158% at $H = 5$ kOe. The MR magnitude decreases with H decreased, equal to 143% at $H = 2.5$ kOe. For comparison, a single-phase sample of $Zn_{0.41}Fe_{2.59}O_4$ was prepared in pilot atmosphere at $T = 1400\,^{\circ}C$. The right inset of Fig. 2 shows that the resistivities of the single-phase sample of $Zn_{0.41}Fe_{2.59}O_4$ is much lower than those of the two-phase system, indicating that the electrical resistivity of the two-phase system is dominated by the insulating α-Fe_2O_3 boundaries. As seen in Fig. 2, the resistivity exhibits a drastic drop at low fields, which just corresponds to a rapid change of the magnetization M shown in the left inset of Fig. 2. The latter stems from the fact that the magnetizations of all the magnetic domains are gradually aligned with increasing the magnetic field. Since the room-temperature MR of the single-phase sample of $Zn_{0.41}Fe_{2.59}O_4$ is very small (about 1.6%) compared with the huge MR observed in the two-phase system, it follows that the huge MR is not due to the bulk phenomenon of $Zn_{0.41}Fe_{2.59}O_4$ grains, but arises from a tunneling type of MR at the grain boundaries. The tunneling of the spin-polarized electrons between the magnetic domains on both sides of the α-Fe_2O_3 boundary is critically affected by the relative angle of their magnetization directions, and may be controlled by an applied magnetic field via a domain-rotation process. The tunneling-type conduction in the two-phase system is further supported by the non-Ohmic character of the resistivity [13], as shown by the I-V curve in Fig. 3, in which there are Ohmic behavior at low fields and deviation from Ohm's law at high fields. In contrast, the Ohmic behavior of the I-V curve remains unchanged in the single-phase sample, as shown in the inset of Fig. 3. Although the present tunneling type of MR has also been observed in some granular systems [2–10], to our knowledge, never before has such a huge tunneling MR been found at room temperature.

Figure 4 shows the temperature dependence of the resistivity for the present sample in the absence of applied magnetic field, the $\ln\rho$ vs T curves given in the inset for the two-phase system and the single-phase $Zn_{0.41}Fe_{2.59}O_4$. As seen from the inset of Fig. 4, the resistivity of single-phase $Zn_{0.41}Fe_{2.59}O_4$ is at least 1 order of magnitude smaller than that of the two-phase system over the whole temperature region. The resistivity of the present sample is dominated by thermally activated tunneling from grain to grain, and the bulk resistivity of the $Zn_{0.41}Fe_{2.59}O_4$ grains may be neglected. It is remarkable that the temperature dependence

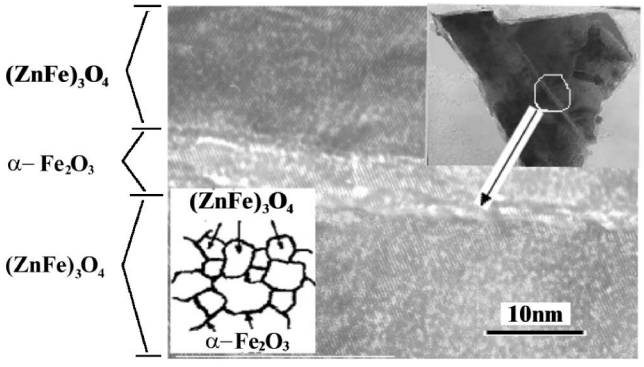

FIG. 1. High-resolution TEM image of the two-phase $(Zn_{0.41}Fe_{2.59}O_4)_{0.89}(\alpha\text{-}Fe_2O_3)_{0.11}$ sample, showing the structure of the $Zn_{0.41}Fe_{2.59}O_4$ grains separated by an α-Fe_2O_3 grain boundary of uniform thickness (about 7 nm). Schematic diagram of its structure is given by the left inset.

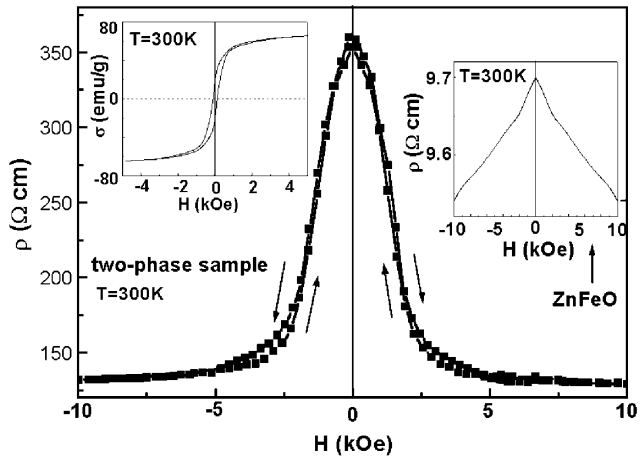

FIG. 2. Resistivity ρ as a function of the applied magnetic field at $T = 300$ K for the two-phase system and the corresponding magnetic hysteresis loops in the left inset. The right inset shows ρ vs H of the single-phase $Zn_{0.41}Fe_{2.59}O_4$ sample at $T = 300$ K.

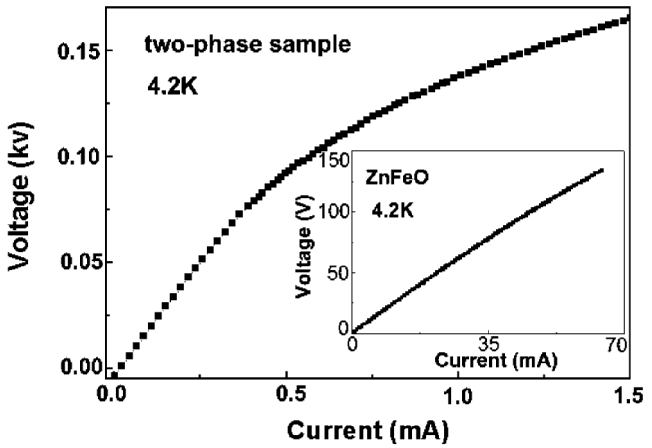

FIG. 3. Current vs voltage for the two-phase system, showing severe deviations from the Ohm's law at high fields. The inset shows current vs voltage for a single-phase $Zn_{0.41}Fe_{2.59}O_4$ sample, where the Ohm's law is obeyed.

of ρ in the form of $\ln\rho$ vs $1/T$, [$\rho \propto \exp(E_c/2k_BT)$], was observed between 4.2 and 110 K for the present two-phase system, as shown in the inset of Fig. 4. We can estimate E_c from the linear part of the plot of $\ln\rho$ vs $1/T$: $E_c = 8.3$ meV, corresponding to the thermal energy of k_BT with $T \simeq 110$ K. Such a simple hopping-type temperature dependence for the conductivity can be attributed to nearly uniform thickness of the insulating α-Fe_2O_3 boundary as well as large size of the $Zn_{0.41}Fe_{2.59}O_4$ grains (>100 nm). This is different from the well-known temperature dependence of $\ln\rho$ vs $1/\sqrt{T}$ for metal-insulator granular materials [14]. The tunneling-type electrical conductivity in granular materials is generally given by

$$\sigma(T) \propto \exp(-2\kappa s - E_c/2k_BT), \qquad (1)$$

where s is the tunnel-barrier thickness, κ is a barrier parameter increasing with barrier height, and E_c is the charging energy [13,14] plus a magnetic energy [15,16]. On the assumption that the granules on each conduction path are equal in size d and separated by barrier thickness s, keeping the ratio s/d (or equivalently sE_c) constant for a given composition, the temperature dependence of $\ln\sigma \propto 1/\sqrt{T}$ can be obtained [14]. In the present case of nearly uniform barrier thickness, Eq. (1) should yield a simple hopping-type temperature dependence for the conductivity: $\sigma(T) \propto \exp(-E_c/2k_BT)$ [13]. Such a temperature dependence of $\ln\sigma \propto 1/T$ has also been observed recently in CoO-coated monodispersive Co cluster assemblies between 7 and 80 K [17].

The temperature dependence of MR for the two-phase system is shown in Fig. 5. The absolute value of MR increases slightly with decreasing temperature in the range of $100 < T < 318$ K, while it increases rapidly below 100 K: from 200% at 100 K to 1280% at 4.2 K. The sudden drop in MR at $T_c = 318$ K is due to the rapid decrement in magnetization there. From the huge room-temperature MR, we discuss the spin polarization of the $Zn_{0.41}Fe_{2.59}O_4$ grains and possible correlations between them. It is well known that there are two definitions for the MR: $\Delta\rho/\rho_H$ used in this work and $\Delta\rho/\rho_0 = [\rho_0 - \rho_H]/\rho_0$, then satisfying the relation of $[1 - \Delta\rho/\rho_0][1 + \Delta\rho/\rho_H] = 1$. In the absence of spin-flip tunneling, the tunneling-type MR ratio is given by [1,16]

$$\Delta\rho/\rho_0 = (1 - b)P^2/(1 + P^2). \qquad (2)$$

Here $b = \langle\cos\theta\rangle$ with θ the angle between the magnetizations on both sides of the tunneling barrier at $H = 0$ and the average $\langle\cos\theta\rangle$ taken over all pairs of grains. We note that $\Delta\rho/\rho_0 = 2P^2/(1 + P^2)$ for FM/I/FM junctions with strong antiferromagnetic (AF) coupling ($\theta = \pi$ and $b = -1$) [1], while $\Delta\rho/\rho_0 = P^2/(1 + P^2)$ for common magnetic granular materials where θs are random between 0 and π so that $b = 0$ [16]. The room-temperature

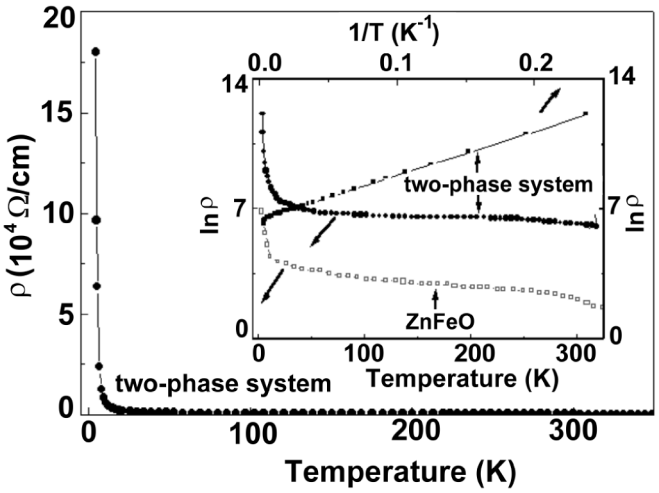

FIG. 4. Temperature dependences of the resistivity ρ at zero-magnetic field for the two-phase system, and $\ln\rho$ vs T in the inset for the single-phase (open squares) and two-phase (solid circles) $Zn_{0.41}Fe_{2.59}O_4$ samples.

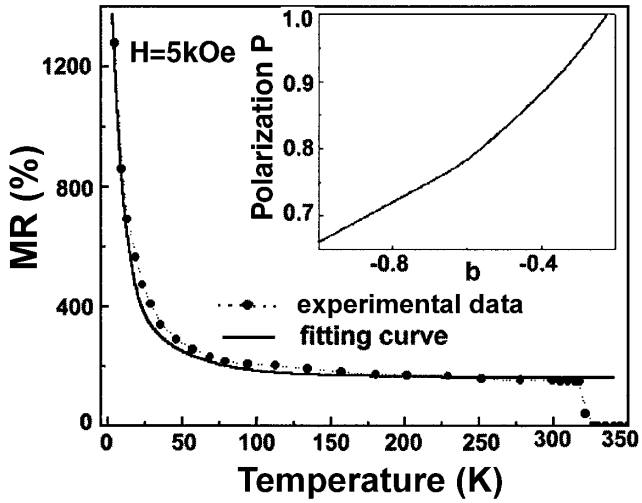

FIG. 5. Temperature dependences of the absolute value of the MR ratio at $H = 5$ kOe for the two-phase $Zn_{0.41}Fe_{2.59}O_4$ sample. The inset shows the spin polarization as a function of b for $\Delta\rho/\rho_0 = 61\%$ at room temperature.

MR shown in Fig. 5 is $\Delta\rho/\rho_H = 158\%$, or equivalently $\Delta\rho/\rho_0 = 61\%$. Substituting this value into Eq. (2) with $b = 0$, one would get an unphysical result of $P > 1$. In order to guarantee $P \leq 1$, from Eq. (2), one gets an inequality of $\Delta\rho/\rho_0 < (1 - b)/2$. Although from Eq. (2) two parameters P and b cannot be solely determined for a given MR, one may estimate their allowed value ranges. For $\Delta\rho/\rho_0 = 61\%$, P as a function of b is shown in the inset of Fig. 5, where P increases from 0.66 to 1 with varying b from -1 to -0.22. As a result, at least two deductions may be drawn for the present two-phase system. From negative values of $-1 \leq b \leq -0.22$, it follows that, unlike in common granular materials where the magnetizations of the granules orientate randomly ($b = 0$), there must be more or less AF correlations between the magnetic domains on both sides of the insulating barrier. The strength of the AF correlations will increase with b varying from -0.22 to -1. This point is further supported by magnetic hysteresis loops of zero-field-cooled and field-cooled samples from the Néel temperature of α-Fe_2O_3 to room temperature, which will be reported elsewhere [18]. Another deduction is the high spin polarization of the $Zn_{0.41}Fe_{2.59}O_4$ grains: $0.66 \leq P \leq 1$. In the present granular system, the AF correlations discussed above are most likely weak (b being close to -0.22), from which it follows that P is close to 1 and $Zn_{0.41}Fe_{2.59}O_4$ may be a half-metallic-type material with high spin polarization even at room temperature. In addition, the lower limit of $P = 0.66$ may be underestimated here due to neglecting the spin-flip tunneling in Eq. (2). In the presence of the spin-flip tunneling process, the MR ratio is given by [19]

$$\frac{\Delta\rho}{\rho_0} = \frac{(1 - b)P^2}{1 + P^2 + 2\gamma/(1 - \gamma)}, \qquad (3)$$

where γ is the ratio between the square matrix elements of spin-flip and spin-conserving tunneling. In this case, it is easy to show that the minimal P will be increased by a factor of $\sqrt{1 + \gamma/(1 - \gamma)}$. As an example, the minimal P would increase from 0.66 to 0.74 if $\gamma = 0.2$ was taken.

Finally, we briefly discuss the enhancement of MR at low temperatures. It is found that the experimental data shown by the solid squares in Fig. 5 can be approximately fitted to a simple formula: $\Delta\rho/\rho_H = A + B/T$ with $A = 140\%$ and $B = 40$ K shown by the solid line, where constant term A takes main responsibility for MR at high temperatures, while term B/T describes the anomalous increase of MR at low temperatures. The temperature dependence of $1/T$ for MR was predicted by Helman and Abeles [15] in insulating granular systems by taking into account a magnetic exchange energy E_M which arises when the magnetic moments of the grains are not parallel and electron spin is conserved in tunneling. As pointed out by Inoue and Maekawa [16], however, the consideration of E_M would give rise to a large positive MR at low temperatures. It appears that this theory is irrelative to the present results. Mitani *et al.* [20] proposed that the increase of MR at low temperature is due to the high-order tunneling between large granules through intervening small ones with strong Coulomb blockade, but the predicted temperature dependence of $\Delta\rho/\rho_0 \propto (1 + C/\sqrt{T})$ does not fit the present results. We note that the marked increase in MR below 100 K shown in Fig. 5 is much larger than those observed in conventional metal-insulator granular systems, but very similar to that for the CoO-coated monodispersive Co cluster assemblies [17]. Behavior observed in the latter was ascribed to a prominent cotunneling effect in the Coulomb blockade regime, arising from the uniform Co core size and CoO shell thickness. As a result, even though there has been no definitive theory for giving a quantitative explanation of the $\Delta\rho/\rho_H = A + B/T$ behavior in the present system, the unusual enhancement of the tunneling MR is believed to be associated with the Coulomb blockade effect at low temperatures.

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[1] M. Julliere, Phys. Lett. **54A**, 225 (1975).
[2] C. Kwon *et al.,* Appl. Phys. Lett. **72**, 486 (1998).
[3] J. Z. Sun, D. W. Abraham, K. Roche, and S. S. P. Parkin, Appl. Phys. Lett. **73**, 1008 (1998).
[4] J. O'Donnell *et al.,* Appl. Phys. Lett. **76**, 1914 (2000).
[5] H. Y. Hwang and S. W. Cheong, Science **278**, 1607 (1997).
[6] X. W. Li, A. Gupta, G. Xiao, W. Qian, and V. P. Dravid, Appl. Phys. Lett. **73**, 3282 (1998).
[7] T. Kimura *et al.,* Science **274**, 1698 (1996).
[8] J. M. D. Coey, A. E. Berkowitz, L1. Balcells, and F. F. Putris, Phys. Rev. Lett. **80**, 3815 (1998).
[9] H. Y. Hwang, S. W. Cheong, N. P. Ong, and B. Batlogg, Phys. Rev. Lett. **77**, 2041 (1996).
[10] H. Y. Hwang and S. W. Cheong, Nature (London) **389**, 942 (1997).
[11] K. I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, Nature (London) **395**, 677 (1998).
[12] W. Meyer and H. Neldel, Z. Tech. Phys. **12**, 588 (1937).
[13] C. A. Neugebauer and M. B. Webb, J. Appl. Phys. **33**, 74 (1962).
[14] P. Sheng, B. Abeles, and Y. Arie, Phys. Rev. Lett. **31**, 44 (1973).
[15] J. S. Helman and B. Abeles, Phys. Rev. Lett. **37**, 1429 (1976).
[16] J. Inoue and S. Maekawa, Phys. Rev. B **53**, R11 927 (1996).
[17] D. L. Peng, K. Sumiyama, T. J. Konno, T. Hihara, and S. Yamamuro, Phys. Rev. B **60**, 2093 (1999).
[18] P. Chen *et al.* (unpublished).
[19] R. Y. Gu, D. Y. Xing, and J. Dong, J. Appl. Phys. **80**, 7163 (1996).
[20] S. Mitani *et al.,* Phys. Rev. Lett. **81**, 2799 (1998).