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Magnetic and magneto-transport properties of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$

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Abstract

We have investigated the magnetic and the magneto-transport properties of non-superconducting $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (Ru-1212). The Ru sublattice shows a magnetic ordering at $T_c = 148$ K. An antiferromagnetic ordering of the Gd sublattice is clearly observed at 2.8 K. The ρ - T behaviour is semiconducting with a kink in the vicinity of the T_c due to the reduction of spin scattering. Negative magnetoresistance due to a suppression of spin-flip scattering is relatively large, $\sim 4\%$ at $H = 4$ T, even in the highly two-dimensional system.

1. Introduction

The importance of dimensionality in determining the electronic and magnetic properties of perovskite-type transition metal oxides has long been recognized [1–3]. Since the discovery of superconductivity in the K_2NiF_4 -type Sr_2RuO_4 [4], the Ruddlesden–Popper-type compound series $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$, Sr_2RuO_4 ($n = 1$), $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n = 2$) [5–7] and SrRuO_3 ($n = \infty$) [8–11], has received a resurgence of interest. $\text{Sr}_3\text{Ru}_2\text{O}_7$ and SrRuO_3 are ferromagnetic metals with a $4d^4$ (Ru^{4+}) low-spin configuration ($S = 1$). On the other hand, Sr_2RuO_4 with a reduced dimensionality of the Ru–O network is a paramagnetic metal and shows superconductivity below 1 K. Structural dimensionality is therefore one of the crucial factors that determine the electronic and magnetic properties of these compounds.

Recently, Bauernfeind *et al* have reported a layered ruthenate cuprate in which the intermediate layer between the square pyramidal Cu–O blocks consists of vertex sharing RuO_6 octahedra, $\text{RuSr}_2\text{LnCu}_2\text{O}_8$ (Ru-1212), where Ln represents Sm, Eu and Gd [12]. Two-dimensional Ru–O layers are separated by double layers of square-pyramidal cuprate in the Ru-1212 compound, indicating that it has a further reduced dimensionality compared with the limit of the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ type compounds. The Ru-1212 compound contains Ru^{5+} with a $4d^3$ configuration instead of the $4d^4$ of the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ compounds [13]. Well oxidized samples display coexisting ferromagnetism and superconductivity [12–21]. In this

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study, we have investigated the magnetic and the magneto-transport properties of the non-superconducting Ru-1212 compounds with its characteristic low-dimensional structure and electronic configuration.

2. Experimental methods

Samples were prepared by conventional solid state reactions. The starting materials of oxides and carbonates were mixed thoroughly in the appropriate ratio and heated at 1000 °C for 24 h in air and 24 h in a flow of O₂ with intermediate grindings. Powder x-ray diffraction (XRD) data at room temperature were collected on a Rigaku diffractometer with Cu K α radiation in the range of 4° \leq 2 θ \leq 60° at an increment of 0.02° (2 θ) in order to examine sample purity and cell parameters. Silicon was employed as an internal standard. The temperature and field dependence of resistivity was measured using a standard four-probe method at a constant dc current. The dc magnetization was measured with a superconducting quantum interference device (SQUID) magnetometer (MPMS₂: Quantum Design) in the temperature range of 1.8–350 K. The oxygen content was determined using a melt-reduction method (Horiba EMGA-2800). The pulverized sample was melted in a carbon crucible with a nickel and tin flux to reduce oxygen to carbon monoxide, which was detected by infrared absorption.

3. Results and discussion

All the diffraction peaks of the Ru-1212 compound can be indexed on the basis of a tetragonal lattice with $a = 3.840$ Å and $c = 11.56$ Å, which are in good agreement with those reported previously [12, 13, 15]. The a -axis and c -axis lattice parameters are smaller than those of the isostructural NbSr₂GdCu₂O₈ phase by 0.039 Å and 0.06 Å, respectively. Judging from the ionic radii [22] of sixfold coordinated Nb⁵⁺ (0.64 Å), Ru⁴⁺ (0.62 Å) and Ru⁵⁺ (0.57 Å), the charge of Ru in the Ru-1212 compound is believed to be 5+ instead of 4+. This is supported by quantitative analysis of oxygen. The oxygen content determined using a melt reduction method is 18.43 wt%, which is comparable to the calculated value of 18.58 wt% assuming the RuSr₂GdCu₂O₈ oxygen stoichiometry. The Ru-1212 compound, therefore, contains Ru ions with 5+ formal charge.

Magnetic susceptibility was measured as a function of temperature and field. The susceptibility χ –temperature T plot measured in a zero-field-cooled (ZFC) sequence is shown in figure 1(a). There is a magnetic ordering at $T_c = 148$ K, where a steep increase in χ is observed. In the magnetization M –applied field H curve shown in figure 1(b), a slight hysteresis cycle is observed, even at 100 K, as definite as at 5 K. The magnetization at 5 K is not saturated at 5 T, which is similar to SrRuO₃ [9] but contrasts with Sr₃Ru₂O₇, which has a saturation field at as low as 0.2 T [7]. These behaviours typical for the superconducting Ru-1212 compounds [12–21] are also observed here.

As the ferromagnetic transition temperature is in the vicinity of that for SrRuO₃, it should be clear that this transition is not due to a SrRuO₃ type impurity phase but to an intrinsic property of the Ru-1212 phase. We have prepared a multi-phase sample from a starting composition of off-stoichiometric Ru_{1.2}Sr₂GdCu₂O _{x} , in which an SrRuO₃ type impurity is included together with the Ru-1212 phase. The content of the impurity phase is estimated at about 10 vol% from x-ray diffraction. In the χ – T curve of this sample, the magnetic ordering at 148 K becomes broader and the magnetic moment at 5 K is smaller than for pure Ru-1212. For phase pure SrRuO₃, prepared by a solid state reaction of a stoichiometric mixture of SrCO₃ and RuO₂, the ferromagnetic transition is observed at around 160 K as

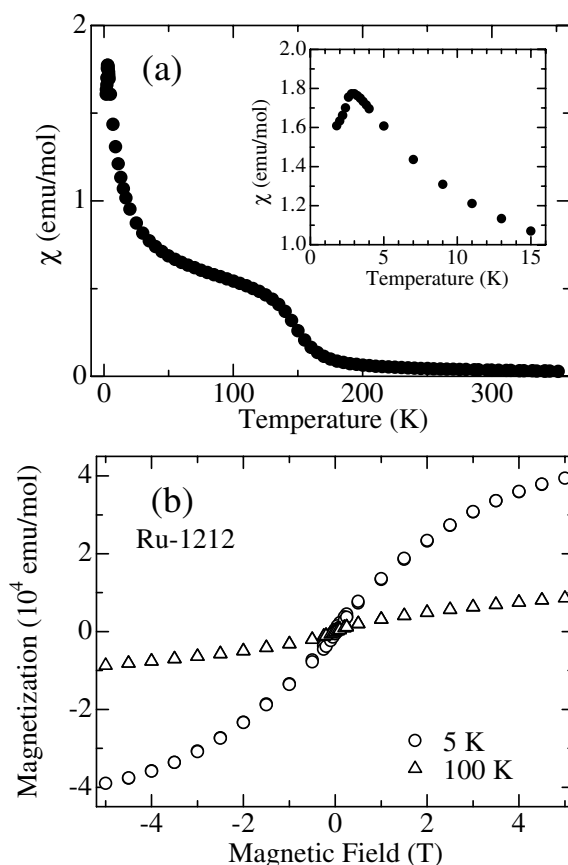


Figure 1. (a) Magnetic susceptibility–temperature plot for Ru-1212 measured in a field of 0.3 T and (b) magnetization–applied field curves for Ru-1212 at 5 K and 100 K.

reported previously [8, 9]. The magnetic moment at 5 K is of the same order as for the Ru-1212 compound, 1.5–1.8 emu mol⁻¹. In the x-ray diffraction pattern, the Ru-1212 compound shows no impurity phase, suggesting that impurity content, if any, is less than 2–3 vol%. Therefore, the ferromagnetic moment is too large to attribute to the SrRuO₃ type impurity. These results indicate that the magnetic behaviour is indeed intrinsic to the Ru-1212 phase.

The inverse magnetic susceptibility $1/\chi$ –temperature T plot for the Ru-1212 compound is shown in figure 2. These data are analysed according to a modified Curie–Weiss law, $\chi = \chi_0 + C/(T - \theta)$, where χ_0 is a sum of temperature-independent terms, C is the Curie constant and θ is the paramagnetic Curie temperature. By fitting the data in the temperature range above 240 K, in which the linear relation is realized, we obtain $\theta = 49.7$ K and $\chi_0 = 1.7 \times 10^{-3}$ emu mol⁻¹. The effective paramagnetic moment μ_{eff} estimated from the Curie constant C is $7.89 \mu_B$ mol⁻¹. This value corresponds to that calculated for the free Gd³⁺ ion ($7.96 \mu_B$) and also to niobium analogous NbSr₂GdCu₂O₈ [23, 24] compound ($7.97 \mu_B$), but is much smaller than that expected for quantum mechanical spins μ_{eff} per mole, $14.2 \mu_B$: $2\mu_B\sqrt{(3/2 \times 5/2)} = 3.9 \mu_B$ from Ru⁵⁺; $2\mu_B\sqrt{(7/2 \times 9/2)} = 7.9 \mu_B$ from Gd³⁺; $2\mu_B\sqrt{(2 \times 1/2 \times 3/2)} = 2.4 \mu_B$ from Cu²⁺. In the case of 3d transition ions, the effective paramagnetic moment is consistent with that calculated by the spin-only formula.

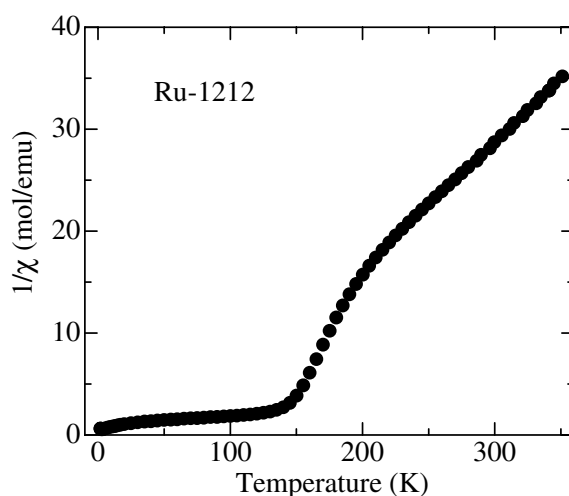


Figure 2. Inverse susceptibility–temperature plots for Ru-1212 measured in a field of 0.3 T.

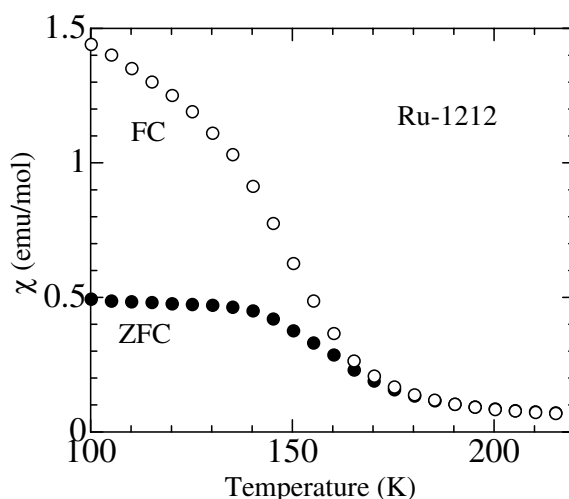


Figure 3. Magnetic susceptibility–temperature plot for Ru-1212 measured in a field of 2 mT.

On the other hand, spin–orbit coupling would normally reduce the observed μ_{eff} value to below that predicted for free ions from the 4d and 5d transition series. The contribution of Cu^{2+} ions to the μ_{eff} value can be inferred from the findings of a previous report. A small effective paramagnetic moment of $0.728 \mu_B$ has been reported for $\text{NbSr}_2\text{YCu}_2\text{O}_{7+\delta}$ [25]. As the Y^{3+} , Sr^{2+} and Nb^{5+} are nonmagnetic in nature, the whole μ_{eff} is presumed to be occupied by the Cu ions, and is smaller than that calculated for the free Cu^{2+} ion. These two effects in the Ru^{5+} and Cu^{2+} ions are thought to cause the small $\mu_{eff} = 7.89 \mu_B \text{ mol}^{-1}$ value for the Ru-1212 compound.

The value of $\theta = 49.7 \text{ K}$ is considerably lower than the $T_c = 148 \text{ K}$, indicative of antiferromagnetic interaction existing in the Ru-1212 compound. We have measured the temperature dependence of susceptibility in ZFC and FC conditions in a field of 2 mT (figure 3). The hysteresis behaviour observed at temperature lower than 170 K implies the

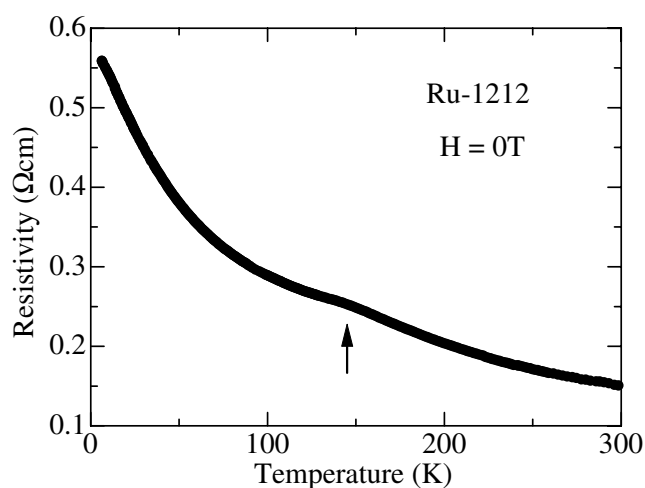


Figure 4. Temperature dependent resistivity for polycrystalline Ru-1212. An arrow represents a kink in resistivity due to a reduction of spin scattering.

coexistence of ferromagnetic and antiferromagnetic interactions. In the Ru-1212 compound, antiferromagnetic ordering is clearly observed at 2.8 K (inset of figure 1(a)), which is in good agreement with that reported previously [26]. We have prepared the isostructural RuSr₂EuCu₂O₈ and confirmed that the antiferromagnetic transition is not observed down to 1.7 K, indicating that the antiferromagnetic ordering at 2.8 K is due to the Gd sublattice. The temperature showing the hysteresis behaviour in the ZFC and FC curves (170 K) is much higher than the ordering temperature of the Gd sublattice. Therefore, the magnetic interactions at 170 K would come from the Ru sublattice, which is in consistent with the results of neutron diffraction experiments [27] and magnetic studies on non-superconducting Ru-1212 [26] previously reported. The antiferromagnetic interactions are thought to be the cause of the reduction of the θ value compared to the magnetic ordering at $T_c = 148$ K.

Figure 4 shows the variation of resistivity as a function of temperature for the Ru-1212 compound. All the compounds in the Sr_{*n*+1}Ru_{*n*}O_{3*n*+1} series, Sr₂RuO₄ ($n = 1$), Sr₃Ru₂O₇ ($n = 2$) and SrRuO₃ ($n = \infty$), show a metallic ρ - T behaviour ($d\rho/dT > 0$), whereas a semiconducting-like transport ($d\rho/dT < 0$) is observed in the Ru-1212 compound as shown in figure 4. We measured thermoelectric power (S) to estimate a hole content (p) on the CuO₂ planes. An obtained S value of $100 \mu\text{V K}^{-1}$ at 300 K corresponds to $p \cong 0.03$ holes per CuO₂ planes [28]. No superconducting transition and a semiconducting ρ - T behaviour are expected for such the underdoped cuprates. Actually, our sample did not show a superconducting transition at $T > 5$ K. On the other hand, a metallic ρ - T behaviour is expected for the two-dimensional RuO₂ network. The metallic conductivity of the Sr_{*n*+1}Ru_{*n*}⁴⁺O_{3*n*+1} compounds is attributed to a threefold-degenerate π^* band formed by covalent interaction of the t_{2g} orbitals of Ru with p_π orbitals of oxygen. This π^* band is two-thirds filled in the Ru⁴⁺ compounds. When the π^* band width is smaller than the intraatomic electron-electron interaction, the π^* band will be split into two new bands by a finite energy gap, where a semiconducting conduction is anticipated. Chen *et al* have reported such band splitting for Na_{0.5}La_{0.5}RuO₃ [29]. The width of the π^* band is influenced by A-site cations in the perovskite and related structure compounds. Na_{0.5}La_{0.5}RuO₃ shows a crossover from metallic transport to a semiconducting-like transport with decreasing temperatures in spite of having the same electronic configuration, $4d^4$, as the

metallic SrRuO₃. Sr is expected to occupy the A site of the ARuO₃ perovskite unit in Ru-1212. The width of the π^* band is therefore thought to be too large to be split into two donor and acceptor bands as in the case of SrRuO₃.

The occurrence of Ru⁵⁺ in complex oxides is rare but not without precedent. Ru is pentavalent in Ba₃Ru₂(Mg,Ni)O₉ [30], fluorite-related Ln₃RuO₇ [31] and M₂LnRuO₆ [32, 33], where M = alkaline earth metals and Ln = lanthanides. The M₂LnRuO₆ compounds adopt ordered perovskite-type structures, alternate arrangement of cations on the octahedral B sites, and display antiferromagnetism [33]. It has been reported that the ferromagnetism of SrRuO₃ arises from an itinerant 4d band rather than localized moments [9]. The SrRuO₃ compound has a 4d⁴ low-spin configuration ($S = 1$) and a narrow itinerant π^* band that is two-thirds filled. Although the band filling is different between Ru⁴⁺ and Ru⁵⁺ (half filled π^* band) Ru⁵⁺ d electrons in the M₂LnRuO₆ compounds are regarded as itinerant rather than localized [33]. The temperature-independent part of susceptibility χ_0 is a measure of the density of states near the Fermi surface [7, 11, 34]. The value of $\chi_0 = 1.7 \times 10^{-3}$ emu mol⁻¹ is comparable with that of SrRuO₃ and Sr₃Ru₂O₇, and about two orders of magnitude larger than that of Na_{0.5}La_{0.5}RuO₃. A χ_0 value as large as that of SrRuO₃ and Sr₃Ru₂O₇ is unlikely in the case of π^* -band splitting. Therefore, the RuO₂ layer in the Ru-1212 should be highly conducting. The resistivity of Ru-1212 at room temperature (150 m Ω cm) is actually much lower than that of the isostructural Nb-1212 compound with a 3d⁰ configuration, suggesting that the two-dimensional RuO₂ network is a highly conductive layer.

It is noteworthy that a kink in resistivity is observed in the vicinity of T_c (upward arrow in figure 4). This anomaly is due to a reduction of spin scattering where a conduction electron scatters by exchanging spin with a magnetic moment or spin excitation. Such a kink is also observed in SrRuO₃ single crystals [35] at around the ferromagnetic transition temperature. In these compounds a negative magnetoresistance can be expected because an applied magnetic field decreases the magnitude of spin scattering due to the increase in the energy necessary for spin flip that is commonly observed in ferromagnets.

Figures 5 and 6 show the temperature and field dependences of magnetoresistance for Ru-1212, respectively, where the magnetoresistance is defined as $[\rho(4\text{ T}) - \rho(0\text{ T})]/\rho(0\text{ T})$.

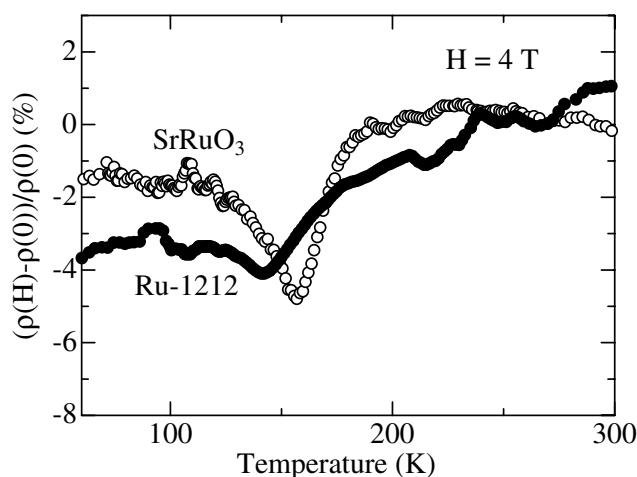


Figure 5. Temperature dependent magnetoresistance $(\rho(H = 4\text{ T}) - \rho(0\text{ T}))/\rho(0\text{ T})$ in a field of 4 T for Ru-1212 (closed circles) and SrRuO₃ (open circles).

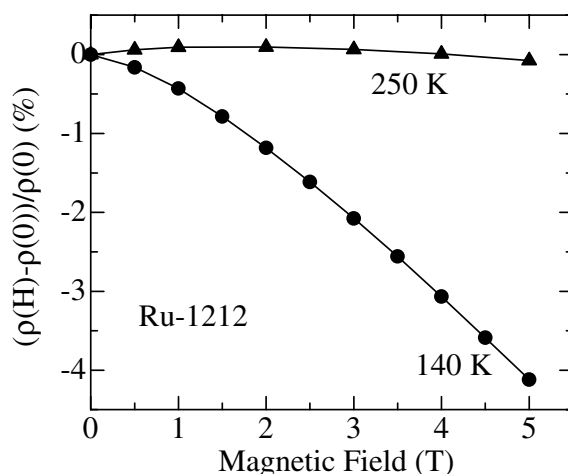


Figure 6. Magnetic field dependent magnetoresistance $(\rho(H = 4 \text{ T}) - \rho(0 \text{ T}))/\rho(0 \text{ T})$ at 140 and 250 K for Ru-1212.

A negative magnetoresistance peak (4–5%) is observed for both compounds near each T_c . For the magnetoresistance measurements, the direction of dc current is perpendicular to the applied magnetic field. Although this geometry realizes an orbital magnetoresistance due to the Lorentz force, it usually gives a positive magnetoresistance and its amplitude has been estimated to be less than 1% for SrRuO₃ [10]. The observed negative magnetoresistance is therefore attributed to the suppression of spin flip scattering. The fairly large magnetoresistance of 4% for Ru-1212 is comparable with that for SrRuO₃. This implies that the increase in energy needed for spin flip in a magnetic field is similar for these compounds.

Hole-doped manganese oxides with perovskite structure are well known to be ferromagnetic conductors. The ferromagnetism is believed to arise from the transfer of e_g electrons, which are strongly Hund coupled with the localized t_{2g} spins (double-exchange interaction). In the series of $(\text{La, Sr})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ compounds, $(\text{La, Sr})\text{MnO}_3$ ($n = \infty$) and $(\text{La, Sr})_3\text{Mn}_2\text{O}_3$ ($n = 2$) exhibit a large negative magnetoresistance effect around the ferromagnetic transition temperature [36]. On the other hand, $(\text{La, Sr})_2\text{MnO}_4$ ($n = 1$) with the most reduced dimensionality does not show the magnetoresistance effect, in contrast to Ru-1212, in which the ferromagnetism and magnetoresistance come from the two-dimensional Ru–O layer. The character of itinerant electrons could explain this difference. In $(\text{La, Sr})_2\text{MnO}_4$, carriers may have a large out-of-plane component of the $d_{3z^2-r^2}$ orbital, resulting in a decrease of itineracy and weakening of the double-exchange interaction. On the other hand, itinerant electrons in the π^* band of Ru-1212 have an in-plane component of the d_{xy} orbital, so that the itineracy is not highly sensitive to the dimensionality of the Ru–O network. It has been reported that the electrons are highly itinerant in two-dimensional Sr₂RuO₄ [34], although it is not a ferromagnetic but a paramagnetic metal.

4. Conclusions

In conclusion, we have synthesized a non-superconducting Ru-1212 compound by a solid state reaction method. Analysis of oxygen content and the tetragonal lattice parameters indicate that the valence state of Ru is pentavalent in Ru-1212. A magnetic ordering of the Ru sublattice and antiferromagnetic ordering of the Gd sublattice are individually observed at

148 K and 2.8 K, respectively. In the semiconducting ρ - T behaviour, a kink is observed in the vicinity of the magnetic ordering temperature due to the reduction of spin scattering. Negative magnetoresistance is relatively large, $\sim 4\%$ at $H = 4$ T, suggesting a suppression of spin-flip scattering by the applied magnetic field.

References

- [1] Mohan Ram R A, Ganapathi L, Ganguly P and Rao C N R 1986 *J. Solid. State Chem.* **63** 139
- [2] Mohan Ram R A, Ganguly P and Rao C N R 1987 *J. Solid. State Chem.* **70** 82
- [3] Cava R J, Takagi H, Zandbergen H W, Hessen B, Krajewski J J and Peck W F Jr 1992 *Phys. Rev. B* **46** 14 101
- [4] Maeno Y, Hashimoto H, Yoshida K, Nishizaki S, Fujita T, Bednorz J G and Lichtenberg F 1994 *Nature* **372** 532
- [5] Williams T, Lichtenberg F, Reller A and Bednorz G 1991 *Mater. Res. Bull.* **26** 763
- [6] Itoh M, Shikano M and Shimura T 1995 *Phys. Rev. B* **51** 16 432
- [7] Gao G, McCall S and Crow J E 1997 *Phys. Rev. B* **55** 672
- [8] Callaghan A, Moeller C W and Ward R 1996 *Inorg. Chem.* **5** 1572
- [9] Longo J M, Raccach P M and Goodenough J B 1968 *J. Appl. Phys.* **39** 1327
- [10] Gausepohl S G, Lee M, Char K, Rao R A and Eom C B 1995 *Phys. Rev. B* **52** 3459
- [11] Gao G, McCall S, Bolivar J, Shepard M, Freibert F, Henning P, Crow J E and Yuen T 1996 *Phys. Rev. B* **54** 15 144
- [12] Bauernfeind L, Widder W and Braun H F 1995 *Physica C* **254** 151
- [13] McLanghlin A C and Attfield J P 1999 *Phys. Rev. B* **60** 14 605
- [14] Bernhard C, Tallon J L, Niedermayer Ch, Blasius Th, Golnik A, Brucher E, Kremer R K, Noakes D R, Stronach C E and Ansaldo E J 1999 *Phys. Rev. B* **59** 14 099
- [15] McLanghlin A C, Zhou W, Attfield J P, Fitch A N and Tallon J L 1999 *Phys. Rev. B* **60** 7512
- [16] Pickett W E, Weht R and Shick A B 1999 *Phys. Rev. Lett.* **83** 3713
- [17] Fainstein A, Winkler E, Butera A and Tallon J 1999 *Phys. Rev. B* **60** 12 597
- [18] Chmaissem O, Jorgensen J D, Shaked H, Dollar P and Tallon J L 2000 *Phys. Rev. B* **61** 6401
- [19] Tallon J L, Loram J W, Williams G V M and Bernhard C 2000 *Phys. Rev. B* **61** 6471
- [20] Bernhard C, Tallon J L, Brucher E and Kremer R K 2000 *Phys. Rev. B* **61** 14 960
- [21] McCrone J E, Cooper J R and Tallon J L 1999 *J. Low Temp. Phys.* **117** 1199
- [22] Shannon R D 1976 *Acta Crystallogr. A* **32** 751
- [23] Vybornov M, Perthold W, Michor H, Holubar T, Hilscher G, Rogl P, Fischer P and Divis M 1995 *Phys. Rev. B* **52** 1389
- [24] Jhans H, Malik S K and Vijayaraghavan R 1993 *Physica C* **215** 181
- [25] Awana V P S, Menon L and Malik S K 1996 *Physica C* **262** 266
- [26] Felner I, Asaf U, Reich S and Tsabba Y 1999 *Physica C* **311** 163
- [27] Lynn J W, Keimer B, Ulrich C, Bernhard C and Tallon J L 2000 *Phys. Rev. B* **61** 14 964
- [28] Obertelli S D, Cooper J R and Tallon J L 1992 *Phys. Rev. B* **46** 14 928.
- [29] Chen X L, Bauernfeind L and Braun H F 1997 *Phys. Rev. B* **55** 6888
- [30] Donohue P C, Katz J L and Ward R 1966 *Inorg. Chem.* **6** 339
- [31] van Berkel F P F and Ijdo D J W 1986 *Mater. Res. Bull.* **21** 1103
- [32] Donohue P C and McCann E L III 1977 *Mater. Res. Bull.* **12** 519
- [33] Battle P D and Jones C W 1989 *J. Solid. State. Chem.* **78** 108
- [34] Cava R J, Batlogg B, Kiyono K, Takagi H, Krajewski J J, Peck W F Jr, Rupp L W Jr and Chen C H 1994 *Phys. Rev. B* **49** 11 890
- [35] Shepard M, Gao G, McCall S, Freibert F and Crow J E 1996 *J. Appl. Phys.* **79** 4821
- [36] Morimoto Y, Asamitsu A, Kuwahara H and Tokura Y 1996 *Nature* **380** 141