Ferromagnetism and large negative magnetoresistance in Pb doped Bi-Sr-Co-O misfit-layer compound

I. Tsukada*, T. Yamamoto, M. Takagi, T. Tsubone, S. Konno, and K. Uchinokura†
Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN
(November 20, 2018)

Ferromagnetism and accompanying large negative magnetoresistance in Pb-substituted Bi-Sr-Co-O misfit-layer compound are investigated in detail. Recent structural analysis of (Bi,Pb)₂Sr₃Co₂O₉, which has been believed to be a Co analogue of Bi₂Sr₂CaCu₂O₈₊δ, revealed that it has a more complex structure including a CoO₂ hexagonal layer [T. Yamamoto et al., Jpn. J. Appl. Phys. 39 (2000) L747]. Pb substitution for Bi not only introduces holes into the conducting CoO₂ layers but also creates a certain amount of localized spins. Ferromagnetic transition appears at T = 3.2 K with small spontaneous magnetization along the c axis, and around the transition temperature large and anisotropic negative magnetoresistance was observed. This compound is the first example which shows ferromagnetic long-range order in a two-dimensional metallic hexagonal CoO₂ layer.

I. INTRODUCTION

The discovery of high-temperature (high-Τc) superconductors has stimulated a considerable amount of researches on new conducting metal oxides. Crystal structures of high-Τc cuprates can be regarded as an alternating stack of conducting CuO₂ layers and insulating blocking layers. Many efforts to look for a new blocking layer have been still paid for a discovery of new cuprate superconductors. On the other hand, to find a new conducting layer other than the CuO₂ layer is also an exciting challenge toward an exotic superconductor, and Sr₂RuO₄ is one of the good examples. Bi-M-Co-O (M = Ca, Sr, Ba) system was first investigated by Tarascon et al., according to such an idea. The chemical composition of this system was reported as Bi₂M₃Co₂O₉, and the structure was believed to be as a Bi₂Sr₂CaCu₂O₈₊δ (Bi2212) type one. The system becomes metallic by changing M site from Ca to Ba. The chemical composition of Bi : Sr : Co : O = 2 : 3 : 2 : 9 gives a valence of Co ions as δ₊, and the magnetic susceptibility suggests that most of the Coδ⁺ ions are in a low-spin state (S = 0) with fully occupied t₂g levels and empty e_g levels. Since the energy gap between these levels makes Bi₂M₃Co₂O₉ a band insulator as LaCoO₃, the metallic conductivity induced by different alkaline-earth ions with the same valence cannot be accounted for straightforwardly. Another approach to introduce carriers by Pb substitution for Bi has been accomplished for both bulk and thin-film samples of Bi-Sr-Co-O system. However, the amount of the doped carriers did not correspond quantitatively to the amount of doped Pb, so that the mechanism of carrier doping has remained unclear for a long time.

Recently we found that the structure of so-called (Bi,Pb)₂Sr₃Co₂O₉ phase is completely different from that of Bi-2212 superconductor. The detailed structural analysis has been done by x-ray and electron diffractions on (Bi,Pb)₂Sr₃Co₂O₉ single crystals with various Pb concentration, and this system was found to have misfit layer structure. Our results are very similar to those reported by Leligny et al. for Pb-free sample, in which they stated that the chemical composition is approximately written as [Bi₀.₄₇Sr₂O₂][CoO₂]₁.₈₂. Though the complete structure analysis on what we have called Bi₂Sr₃Co₂O₉ is not yet done, it is very probable that it has basically the same structure as that of [Bi₀.₄₇Sr₂O₂][CoO₂]₁.₈₂ where Pb is partially substituted for Bi. Now, all the experimental results should be reconsidered upon this structure. The most important modification from the old premise is that the Co ions in the conducting CoO₂ layer form a triangular lattice instead of a rectangular lattice. In that sense, recently discovered large thermoelectric material NaCoO₂ [1], which has a hexagonal CoO₂ layers, becomes a good reference to consider the transport and magnetic properties of (Bi,Pb)-Sr-Co-O system.

In this paper, we report transport and magnetic properties of a heavily Pb-doped single crystal that shows a ferromagnetic long-range order below 3.2 K. One of the characteristics of the ferromagnetic state is high anisotropy. Magnitude of the spontaneous magnetization is not so large as that observed in perovskite (La,Sr)CoO₃. Our results rather suggests that the weak ferromagnetic long-range order is the origin of the spontaneous magnetization, which may be closely related to the direction of each CoO₆ octahedron in the CoO₂ layer.

*Present address: Central Research Institute of Electric Power Industry, 2-11-1 Iwado-kita, Komae-shi, Tokyo 201-8511, JAPAN. E-mail: ichiro@criepi.denken.or.jp
†Also Department of Advanced Materials Science, The University of Tokyo.
II. EXPERIMENTAL RESULTS

A. Sample Preparation

The single-crystal sample was prepared by a floating-zone method using a polycrystalline rod with the nominal composition, Bi : Pb : Sr : Co = 1.2 : 0.8 : 2.0 : 2.0. Pb is easily evaporated during the growth process and the actual composition of the obtained single crystal determined by inductively coupled plasma-atomic emission spectroscopy is Bi : Pb : Sr : Co = 1.52 : 0.47 : 2.13 : 2.00. The ratio of (Bi+Pb) : Sr : Co = 1.99 : 2.13 : 2.00 shows an excellent agreement with the reported chemical composition for Pb-free sample as Bi : Sr : Co = 1.91 : 2.19 : 2.00. The crystal symmetry can be the same as that reported for the crystal with similar chemical composition. C-centered monoclinic with \( a = 4.92 \) Å, \( b_{RS} = 5.23 \) Å, \( b_H = 2.8 \) Å, \( c = 15.05 \) Å, and \( \beta = 93.55^\circ \), where the subscripts \( RS \) and \( H \) denote (Bi\(_1-x\)Pb\(_x\)Sr)O\(_3\) rock-salt layer and CoO\(_2\) hexagonal layer, respectively. Transport and magnetic properties were measured by commercial physical properties measurement system (PPMS, Quantum Design) and SQUID magnetometer (\( \chi \)-MAG, Conductus).

B. Resistivity

The resistivity measurements were carried out along both the in-plane and the out-of-plane directions as shown in Fig. 1. The metallic conductivity was observed along the in-plane (\( \rho_{ab} \)) direction. The resistivity at room temperature was around 10 m\( \Omega \)cm, and \( d\rho/dT > 0 \) behavior was observed down to 25 K. The magnitude of the resistivity is quite high in comparison with a clean conventional metal, which was also observed in the thin-film samples. The preliminary heat-capacity measurement gives a large electronic specific-heat coefficient as \( \gamma = 98.2 \) mJ/Co-mol K\(^2\), which indicates that the effective mass of carriers are strongly enhanced implying the presence of strong electron correlation in this compound. The detailed results will be reported elsewhere.

The out-of-plane resistivity (\( \rho_c \)) shows rather complex behavior (Fig. 1). At room temperature, \( \rho_c \) is larger than \( \rho_{ab} \) by four orders of magnitude. There is a broad peak around 200 K and then decreases down to 30 K. Such a broad-peak feature is similar to that observed in Sr\(_2\)RuO\(_4\) and NaCo\(_2\)O\(_4\) but is different from that observed in Bi-2212 high-\( T_c \) superconductor. In-plane metallic and out-of-plane insulating behaviors, which is believed to be strong indication of charge confinement characteristic to many high-\( T_c \) cuprates, were not found, and thus the system is better described as a highly anisotropic 3D metal. The broad peak of \( \rho_c \) may be determined by the competition between the mean-free-path along the c-axis electron transport and the separation of the neighboring conducting CoO\(_2\) planes. There is an upward turn below 20 K in both \( \rho_{ab} \) and \( \rho_c \). The inset of Fig. 1 shows a closer look at the low-temperature resistivity. A smooth increase in \( \rho_{ab} \) toward 2 K shows a good contrast to the cusp in \( \rho_c \) at 3.2 K. This temperature corresponds to the ferromagnetic transition as will be clarified by the magnetization measurement.

C. Magnetization

The temperature dependence of susceptibility is shown in Fig. 2 with that of Pb-free samples. The magnetic field is applied perpendicular to the \( ab \) plane. Because of the small sample mass, the data above 100 K becomes noisy even under relatively high-field, \( H = 3 \) T. There is no trace of magnetic long-range order in this temperature region. The inset of Fig. 2 shows the inverse susceptibility, \( 1/\chi \) roughly shows \( T \)-linear behavior above 20 K. It is easily seen that the Pb substitution increases the magnitude of effective Bohr magneton. We fit the data by a sum of the Curie-Weiss term and the temperature-independent constant term (solid lines). The effective number of Bohr magneton per Co ion was estimated as \( P_{eff} = \sqrt{4S(S+1)} = 1.28 \) which leads to a small spin number consistent with that most of the Co ions are in a low-spin state. The extrapolation from the high-temperature \( T \)-linear part to \( T = 0 \) K meets the horizontal axis approximately at \( T = 4 \) K, suggesting the ferromagnetic order around this temperature, which is different from the Pb-free sample.
Under low magnetic field, the spontaneous magnetization actually appears along the $c$ axis below 3.2 K, where we observed the cusp in $\rho_c$. Figure 3 shows the magnetization along the three principal axes measured with three different fields. In Fig. 3(a), the evolution of the spontaneous magnetization is observed along the $c$ axis. For $H \parallel a$ and $H \parallel b$, magnetizations are saturated below $T_c$. Saturated value is far smaller than that along the $c$ axis. Similar anisotropy remains even at 1000 Oe, but disappears at 1 T. At 1 T, magnetization becomes almost isotropic along the three principal axes. The slight difference between the magnetizations along the in-plane and the out-of-plane directions is probably due to the difference in $g$ factors.

![Figure 2](image2.png)

**FIG. 2.** Temperature dependence of the susceptibility with $H = 3$ T along the $c$ axis. The solid line is the Curie-Weiss fit with constant term to the data. The dashed line shows the data of the Pb-free sample taken from Ref. 7). The inset shows the temperature dependence of the inverse susceptibility.

**D. Magnetoresistance**

The presence of a cusp in $\rho_c$ at $T_c$ indicates a strong coupling between the conduction carriers and the background magnetic moment. We measured the in-plane and the out-of-plane resistivities under several magnetic fields applied along the $c$ axis as shown in Fig. 4, in which large negative magnetoresistance was observed. At 8 T, $\rho_{ab}$ decreases to 71% of the value at 0 T. The change is as large as that observed in ferromagnetic (La,Sr)CoO$_3$. However, $\rho_{ab}$ does not show a distinct change in its slope at $T_c$, and the reduction of the resistivity below $T_c$ seems to be a parallel shift. This is qualitatively different from that of (La,Sr)CoO$_3$ or the colossal magnetoresistance (CMR) manganites.

![Figure 3](image3.png)

**FIG. 3.** Temperature dependence of the magnetization along the three principal axes at (a) 100 Oe, (b) 1000 Oe, and (c) 1 T. At 100 Oe and 1000 Oe, the magnetization is highly anisotropic, while at 1 T, it becomes almost isotropic.
The negative magnetoresistance along the out-of-plane direction is similar to that of CMR materials. As shown in Fig. 4(b), $\rho_c$ shows more drastic change with the magnetic field. Initial resistivity suppression up to 2 T is remarkable (Fig. 4(b)), and $\rho_c$ becomes less than 80% of the initial value at $T = 2$ K. Above 2 T, the reduction of the resistivity becomes more gradual, and at 8 T $\rho_c$ is suppressed to less than 72% of the initial value. This anisotropy is probably related to the anisotropic magnetization. One of the remarkable features is that the steep increase of the $c$-axis magnetization does not induce large negative magnetoresistance in both $\rho_{ab}$ and $\rho_c$. For example, $\rho_c$ remains almost unchanged with the magnetic field up to 120 Oe as shown in Fig. 4(c), except for a narrow region near $T_c$. After the field exceeds 120 Oe, the resistivity begins to decrease significantly with increasing magnetic field.

The field-direction dependence provides us the details of the anisotropic nature. We measure the in-plane resistance under the magnetic field both parallel ($H \parallel ab$, $I \perp H$) and perpendicular ($H \perp ab$, $I \perp H$) to the plane direction. In Fig. 5, the magnetization and the in-plane resistance ($R_{ab}$) are plotted as functions of a magnetic field both parallel and perpendicular to the plane. In Fig. 5(a) the $c$-axis magnetization initially shows a steep increase to 0.06 $\mu_B$/Co site, and then turns to show a gradual increase. In contrast to it, $R_{ab}$ does not change drastically with the initial evolution of the magnetization, and it significantly decreases with the following moderate increase of the $c$-axis magnetization. Figures 5(c) and 5(d) show a closer look at the magnetization and $R_{ab}$ at $H \parallel c$ below 1 kOe. $R_{ab}$ roughly keeps its initial value during the steep increase of magnetization, and then it begins to decrease after the magnetization changes its field dependence above 120 Oe (indicated by a dotted line).

Similar plateau in $R_{ab}$ is also observed when we apply the field along the in-plane direction (Figs. 5(e) and 5(f)). For $H \parallel plane$, we did not observe negative magnetoresistance near $H = 0$ T. On the contrary, small positive magnetoresistance was observed below 2 kOe. The corresponding magnetization evolution with $H \parallel plane$ is rather smooth, and it is difficult to assign where the magnetization shows a kink. However, the initial evolution of the magnetization seems to be proportional to the applied field (indicated by a dashed line in Fig. 5(e)), and starts to deviate from the linear relation roughly above 3 kOe. At the same field, $R_{ab}$ begins to show large negative magnetoresistance, and we think that the low-field and high-field behaviors are qualitatively different as was observed in $H \perp$ plane configuration.

To summarize our observation, 1) the low-field steep increase of magnetization does not induce negative magnetoresistance, and 2) the additional magnetization following the low-field one induces negative magnetoresistance. This result implies that two dominant contributions to the magnetization should be considered.
III. DISCUSSION

A. Pb substitution

First we discuss the origin of magnetic moment induced by Pb substitution for Bi. For this purpose, we assume [Bi$_{0.87}$Sr$_{0.12}$]$_2$(CoO$_2$)$_{1.82}$ as the chemical composition of the parent compound. Since Bi$^{3+}$ and Sr$^{2+}$ ions are nonmagnetic, most of the magnetic properties are attributed to Co ions. The reported chemical composition gives average valence of Co ion as +3.33. Two scenarios then become possible to account for this non-integer valence: 1) one of three Co ions takes localized 4+ state while the others take localized 3+ state, or 2) one mobile hole is doped per three Co$^{3+}$ sites. In the previous magnetization measurement by Tarascon et al., it was suggested that most of the Co ions are in the 3+ state and takes low-spin state with $S = 0$. Even though their treatment of the chemical composition is possibly incorrect, absence of the large magnetic moment is still an experimental fact. Thus the former case does not seem to be the current case. The latter is more probable, and we can imagine that holes have been already doped in a Pb-free sample. Note that metallic conductivity was observed even in the Pb-free samples, which suggests the presence of holes even in the parent compound. Recent photoemission experiment also supports the same conclusion.

It is interesting to see that the magnetic susceptibility of NaCo$_2$O$_4$, which has a similar CoO$_2$ hexagonal layer, is quite similar to our data. The nominal composition of NaCo$_2$O$_4$ gives averaged Co valence as 3.5+. If we adopt localized-moment picture, half of the Co ions should be in the 4+ state that will have $S = 1/2$ or $S = 5/2$ for low-spin or high-spin configurations, respectively. However, the magnetic susceptibility is far smaller than that expected for such localized picture. Recent local density approximation (LDA) calculation for NaCo$_2$O$_4$ implies that Co $t_{2g}$ band is located at the Fermi level ($E_F$), and dominates all the magnetic properties of NaCo$_2$O$_4$. If we apply this expectation also to (Bi,Pb)-Sr-Co-O because of the similarity of the crystal structure of hexagonal CoO$_2$ plane, the doped holes are located at Co $t_{2g}$ band, and we do not have to take the contribution of other bands into account.

Then how the Pb substitution changes the spin system? One of the important roles of the Pb substitution is to introduce additional holes. Using the measured chemical composition and assuming that the oxygen content is the same as that in the parent compound, we can estimate the average valence of Co ions as 3.52+ for our sample. The number of holes fairly increases and the electronic conduction is enhanced, which has been already observed in our previous studies.

Another significant role of the Pb substitution is to modify the crystal parameters. As was reported, Pb substitution induces a discontinuous decrease in the $b$-axis length of the Bi$_{0.87}$Sr$_{0.12}$O$_2$ layer and expands the $c$-axis length simultaneously. Since we have no data on the structural change in the CoO$_2$ layer, at present it is difficult to discuss the effect of the structural change to the electronic state. As is shown in Fig. 3 and ref. 7, however, the increase of the effective Bohr magneton above $T_c$ by the Pb substitution suggests that the Pb substitution also increases the number of localized spins, and such spins may contribute to the formation of ferromagnetic long-range order.

Before discussing the relation between ferromagnetic long-range order and magnetoresistance in the next section, it is better to mention the possibility of itinerant ferromagnetism in this system. It is well known that ferromagnetic long-range order can also be observed in an itinerant electron system. In our case, the c-axis magnetization seems to be explained also by weak ferromagnetism of itinerant electrons. However, the anisotropic magnetization in the weak-ferromagnetic state is hardly explained by the itinerant ferromagnetism. To our knowledge, there has been no theory of itinerant ferromagnetism with highly anisotropic magnetization. Although this does not exclude the possibility that our highly two-dimensional system exhibits an itinerant ferromagnetism by unknown mechanism, it is better to explain our results based on the localized-spin model.

B. Ferromagnetic long-range order and magnetoresistance

Once we assume that the localized moments are induced by Pb substitution, we can explain the field dependence of the magnetization. The magnitude of the spontaneous magnetization is quite small below $T_c$, and subsequently the field-induced magnetization keeps increasing at least up to 7 T. This field dependence strongly indicates that the system goes into a weak-ferromagnetic state. In a conventional weak ferromagnet a certain antiferromagnetic unit has a finite ferromagnetic moment, and a magnetization process is separated in two parts. In a low-field region, inversion of the direction of the weak ferromagnetic moment gives steep evolution of the magnetization, while at high-field region each spin tends to be aligned along the magnetic field. At the present case, spins are probably confined roughly within the $ab$ plane, and are tilted a little toward the $c$-axis direction. Then a single CoO$_2$ layer can have a weak ferromagnetic moment along the $c$ direction. The absence of net bulk magnetization at $H = 0$ Oe indicates that such weak ferromagnetic layers are stacked randomly or alternatingly along the $c$ axis. When the $c$-axis field reaches 120 Oe, these weak ferromagnetic moments point to the same direction. Above the critical field each spins begins to be aligned along the $c$ axis, which corresponds to an increase in the magnitude of weak-ferromagnetic moment.
FIG. 5. Magnetic field dependence of the magnetization and $R_{ab}$ along both for $H \parallel$ plane and $H \parallel c$. (a) and (b) show the data up to 7 T. (c) and (d) show a closer look around the saturation field under $H \parallel c$ where the magnetization and $R_{ab}$ change their field dependence. (e) and (f) show a closer look around the saturation field under $H \parallel$ plane where $R_{ab}$ changes its field dependence.

The magnetization process along the plane direction is rather moderate as shown in Fig. 5(e). However, a careful look at the magnetization allows us to divide its behavior in two regions. The linear evolution of the magnetization is observed up to 3 kOe, where the in-plane resistance begins to decrease. Above 3 kOe, magnetization deviates from this linear relation (dashed line). This feature is different from that of a typical weak ferromagnet with strong easy-axis anisotropy. The presence of finite linear M/H regions along both directions during the field inversion process suggests a more complicated situation of Pb-doped Bi-Sr-Co-O, and we expect that the hexagonal network of Co ions plays an important role.

Next we discuss the mechanism of large negative magnetoresistance. One of the characteristics of the magnetoresistive behavior is the resistance plateau below the critical field. The weak ferromagnetic state can explain this plateau. Since the low-field magnetization perpendicular to the $ab$ plane is considered to be an ordering process for the weak ferromagnetic moment of each CoO$_2$ layer. The change in the direction of weak ferromagnetic moment is probably accomplished by the inversion of each spin. This process does not modify the relative angle of spins in the same CoO$_2$ layer, and therefore, the in-plane resistance does not need to be influenced. A similar process has been discussed in a layered perovskite manganite (La,Sr)$_3$Mn$_2$O$_7$. In such a manganite, a ferromagnetic moment is attributed to each layer, and there is a transition at which the long-range order of this moment develops along the $c$ directions. At this transition temperature, the in-plane resistivity does not change much while the out-of-plane resistivity drastically changes. Once the field exceeds the critical value, each spin begins to rotate toward the same direction, and as a result, in-plane resistance can decrease under a strong coupling between the itinerant holes and the localized moments. When the field is applied parallel to the plane, large magnetoresistance begins to appear above 3 kOe. This indicates that spins do not drastically change their relative angle below 3 kOe. As we mentioned before, the in-plane magnetization process is not simple, but again the hexagonal lattice may play a key role. We need further investigations of this system to reveal the magnetic structure with various experimental techniques, such as NMR, ESR, and neutron scattering.

The origin of the weak ferromagnetism is still an open question. In a conventional weak ferromagnetic state, spin-spin interaction is basically antiferromagnetic, and
the secondary interaction tend to cant spins toward a certain direction. Two kinds of the origin of such spin canting have been known: antisymmetric exchange interaction and single-ion anisotropy. The former was first discussed by Dzyaloshinskii and later microscopically formulated by Moriya. However, this type of antisymmetric interaction can exist only when the crystal symmetry of two neighboring magnetic ions is sufficiently low. Since we do not consider that all the Co ions have localized magnetic moments, it is difficult to imagine that the antisymmetric interaction plays an important role between such diluted magnetic moments. The latter single-ion anisotropy is also inapplicable if the induced moment is attributed to a low-spin Co$^{4+}$ ion. The orbital angular momentum of the low-spin Co$^{4+}$ state is probably quenched, and thus the single-ion anisotropy cannot exist. Only when Co$^{4+}$ ion is in a high-spin state, this scenario is possible. Preliminary photoemission spectroscopy suggests that the Co$^{4+}$ ion induced by Pb-substitution is in the low-spin state and thus we cannot simply apply this mechanism.

IV. CONCLUSION

To summarize we have investigated the transport and the magnetic properties of single-crystal (Bi$_{1.52}$Pb$_{0.47}$)Sr$_{2.13}$Co$_{2.00}$O$_y$. The large anisotropy is found in the electronic conduction parallel and perpendicular to the plane, which reaches to $10^4$. The ferromagnetic transition takes place at very low temperature with small spontaneous magnetization. The large negative magnetoresistance is observed around the transition temperature, which strongly depends on the direction of magnetic field. Recently several layered compounds including hexagonal CoO$_2$ layers have been investigated from the viewpoint of electric and magnetic properties: such as Na$_2$Co$_2$O$_4$ (ref. 11), and Ca$_3$Co$_4$O$_9$ misfit layer compound. The similarity between Ca$_3$Co$_4$O$_9$ and our system is interesting, and from these compounds the common physics that is characteristic to the hexagonal metallic CoO$_2$ layer will be deduced.

ACKNOWLEDGMENT

We thank I. Terasaki, Y. Tokura, T. Mizokawa and J. M. Tranquada for enlightening discussions. This work was supported in part by the Grant-in-Aid for Scientific Research on Priority Area “Mott transition,” Grant-in-Aid for COE Research “SCP coupled system,” Grant-in-Aid for Encouragement of Young Scientists (I. T.) from the Ministry of Education, Science, Sports and Culture.

1. J. G. Bednorz and K. A. Müller: Z. Phys. B 64 (1986) 189.
2. Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz and F. Lichtenberg: Nature (London) 372 (1994) 532.
3. J. M. Tarascon, R. Ramesh, P. Barboux, M. S. Hedge, G. W. Hull, L. H. Greene, M. Giroud, Y. LePage, W. R. McKinnon, J. V. Waszczak and L. F. Schneemeyer: Solid State Commun. 71 (1989) 663.
4. Y. Watanabe, D. C. Tsui, J. T. Birmingham, N. P. Ong and J. M. Tarascon: Phys. Rev. B 43 (1991) 3026.
5. I. Terasaki, T. Nakahashi, A. Maeda and K. Uchinokura: Phys. Rev. B 47 (1993) 451.
6. P. M. Raccah and J. B. Goodenough: J. Appl. Phys. 39 (1968) 1209; G. H. Jonker and J. H. Van Santen: Physica 19 (1953) 120; R. R. Heikes, R. C. Miller and R. Mazelsky: Physica 30 (1964) 1600; V. G. Bhide, D. S. Rajoria, G. R. Rao and C. N. R. Rao: Phys. Rev. B 6 (1972) 1021.
7. I. Tsukada, T. Yamamoto, M. Takagi, T. Tsubone and K. Uchinokura: Mat. Res. Soc. Symp. Proc. 494 (1998) 119.
8. T. Yamamoto, I. Tsukada and K. Uchinokura: Jpn. J. Appl. Phys. 38 (1999) 1949.
9. T. Yamamoto, I. Tsukada, K. Uchinokura, M. Takagi, T. Tsubone, M. Ichihara and K. Kobayashi: Jpn. J. Appl. Phys. 39 (2000) L747.
10. H. Leligny, D. Grebholle, O. Pérez, A. C. Masset, M. Hervieu, C. Michel and B. Raveau: C. R. Acad. Sci. Paris, Série IIc, 2 (1999) 409.
11. I. Terasaki, Y. Sasago and K. Uchinokura: Phys. Rev. B 56, (1997) R12685.
12. Exactly saying, the c-axis direction is not perpendicular to the ab plane because of the monoclinic crystal symmetry. However, we use the c-axis direction to denote the direction perpendicular to the ab plane throughout the paper, because it makes comparison with the previous literatures easy.
13. T. Yamamoto, I. Tsukada and K. Uchinokura: in preparation.
14. F. Lichtenberg, A. Catana, J. Mannhart and D. G. Schlom: Appl. Phys. Lett. 60 (1992) 1138.
15. T. Ito, H. Takagi, S. Ishibashi, T. Ido and S. Uchida: Nature (London) 350 (1991) 596.
16. S. Yamaguchi, H. Taniguchi, H. Takagi, T. Arima, and Y. Tokura: J. Phys. Soc. Jpn. 64 (1985) 1885; R. Mahendiran and A. K. Raychaudhuri: Phys. Rev. B 54 (1996) 16044.
17. I. Tsukada, I. Terasaki, T. Hoshi, F. Yura, and K. Uchinokura: J. Appl. Phys. 76 (1994) 1317; I. Tsukada, M. Nose, and K. Uchinokura: J. Appl. Phys. 80 (1996) 5691.
18. T. Mizokawa, P. Steeneken, H. Tjiang, K. Schulze, G. A. Sawatzky, I. Tsukada, T. Yamamoto, and K. Uchinokura: in preparation.
19. T. Tanaka, S. Nakamura, and S. Iida: Jpn. J. Appl. Phys. 33 (1994) L581.
20. D. J. Singh: Phys. Rev. B 61 (2000) 13397. This paper also discuss the possibility of band ferromagnetism in NaCo$_2$O$_4$. We do not deeply step into this issue now, but at least his calculation suggests the presence of ferromagnetic instability in a hexagonal CoO$_2$ layers.
21. T. Kimura, Y. Tomioka, H. Kuwahara, A. Asamitsu, M. Tanimura, and Y. Tokura: Science 274 (1996) 1698.
22 I. E. Dzyaloshinskii: JETP 5 (1957) 1259.
23 T. Moriya: Phys. Rev. 120 (1960) 91.
24 A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, and J. Hejtmanek: Phys. Rev. B 62 (2000) 166.