PHYSICAL REVIEW B **78**, 180403(R) (2008)

Field-induced spin-state transition in the perovskite cobalt oxide $Sr_{1-x}Y_xCoO_{3-\delta}$

S. Kimura,[1] Y. Maeda,[1] T. Kashiwagi,[1] H. Yamaguchi,[1] M. Hagiwara,[1] S. Yoshida,[2] I. Terasaki,[3] and K. Kindo[4]
[1]*KYOKUGEN, Osaka University, Machikaneyama 1-3, Toyanaka 560-8531, Japan*
[2]*Department of Applied Physics, Waseda University, Tokyo 169-88555, Japan*
[3]*Department of Applied Physics, Waseda University, Tokyo 169-88555, Japan and CREST, Japan Science and Technology Agency, Tokyo 108-0075, Japan*
[4]*Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8531, Japan*

(Received 5 June 2008; revised manuscript received 17 September 2008; published 11 November 2008)

High field magnetization and high-frequency electron spin resonance measurements on the perovskite Co oxide $Sr_{1-x}Y_xCoO_{3-\delta}$ ($x=0.22$ and 0.25) have been performed in magnetic fields up to 53 T. We have observed the spin-state transition, induced by the external magnetic fields, for the sample with $x=0.25$. A distinctive feature of this field-induced spin-state transition is that it is assisted by an internal field, originating from ferromagnetic exchange interaction between Co^{3+} ions.

DOI: 10.1103/PhysRevB.78.180403 PACS number(s): 75.30.Kz, 75.30.Wx, 75.50.Dd

Perovskite Co oxides have attracted much attention because of their peculiar behavior. One of the key aspects to bring rich natures to the perovskite Co oxides is a characteristic electronic property of the Co^{3+} ion, in which different spin states lie close in energy. This property makes the compounds susceptible to external perturbations, and often causes spin-state transitions. For instance, thermal activation of the Co^{3+} ions from the nonmagnetic low-spin (LS, $S=0$) state, which is stable under the ligand field potential, to the entropy-favored high-spin (HS, $S=2$) or intermediate-spin (IS, $S=1$) state is responsible for unusual temperature dependence of magnetic and transport properties in $LaCoO_3$.[1,2]

$Sr_{1-x}Y_xCoO_{3-\delta}$ ($\delta \simeq 0.3$) is a ferromagnet with the highest Curie temperature $T_C \simeq 335$ K among the perovskite Co oxides.[3] In $Sr_{1-x}Y_xCoO_{3-\delta}$, an alternate stack of the CoO_6 octahedral layer and the $CoO_{4.25}$ tetrahedral one forms a brownmilleritelike layered structure.[4–6] This compound shows two successive structural phase transitions from the tetragonal to the high-temperature monoclinic phase, then to the low-temperature monoclinic one with decreasing temperature.[4] The spontaneous ferromagnetic moment appears at the lower-temperature phase transition, which is of first order.[4] A notable feature of the ferromagnetism in $Sr_{1-x}Y_xCoO_{3-\delta}$ is that it strongly depends on the chemical composition of the sample.[3,7] In fact, large spontaneous magnetization appears in the sample for only a narrow compositional range $0.2 \leq x \leq 0.25$. Furthermore, the sample without oxygen vacancy shows much lower T_C compared to the samples with $\delta \simeq 0.3$. It was reported that $Sr_{1-x}Y_xCoO_{3-\delta}$ ($\delta \simeq 0.3$) with $0.2 \leq x \leq 0.25$ is insulating in the low-temperature monoclinic phase, and Co ions in these samples are essentially trivalent in the $3d^6$ electron configuration. Figure 1 displays temperature (T) dependence of the magnetization (M), observed in the samples with $x=0.22$ and 0.25, showing that a small compositional difference considerably affects the low-temperature magnetic behavior. Below T_C, the magnetization of the sample with $x=0.22$ shows a maximum around $T \simeq 170$ K and then takes an almost constant value with decreasing temperature. On the other hand, that of the sample with $x=0.25$ shows a large decrease below $T_m \simeq 260$ K. As will be discussed later, we attribute this decrease in the magnetization to the spin-state transition of the Co^{3+} ions; a large portion of the Co^{3+} ions in the sample with $x=0.25$ turns into the nonmagnetic LS state with decreasing temperature as well as $LaCoO_3$.

In this study, we have performed high-frequency electron spin resonance (ESR) and high-field magnetization measurements on $Sr_{1-x}Y_xCoO_{3-\delta}$ with $x=0.22$ and 0.25. We show that the spin-state transition can be induced by external magnetic fields for $Sr_{1-x}Y_xCoO_{3-\delta}$ with $x=0.25$. The magnetization of this sample recovers in the magnetic fields, owing to the field-induced transition to the HS state. Detailed knowledge of the spin-state transition has been provided from intensive studies for the transition-metal complex with organic ligands, called the spin crossover complex, so far.[8] This phenomenon is usually accompanied by variations in spin or vibrational entropy, magnetic moment, and lattice volume, and can, therefore, be induced not only by change in temperature but also by applying magnetic fields or pressure.[8–10] However, there is an important difference between the spin crossover complex and perovskite Co oxides. While the former is a weakly coupled assembly of molecular units, which consist of the magnetic ion and organic ligands, Co^{3+} ions in the latter are embedded in closely connected Co-O networks. This causes not only an elastic interaction—which is believed to mediate between the magnetic ions, leading to

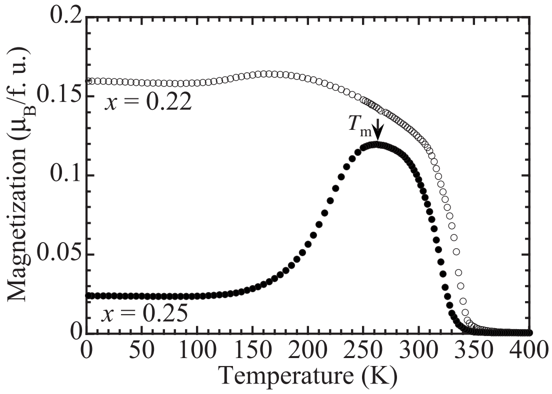

FIG. 1. Temperature dependence of the magnetization in $Sr_{1-x}Y_xCoO_{3-\delta}$ with $x=0.22$ and 0.25, observed in the magnetic field of 0.1 T.

the cooperative transition in the spin crossover complex—but also significant electron-electron interactions for the perovskite Co oxides. Actually, our analysis in this study shows a large contribution of the exchange interaction between the Co^{3+} ions in the HS state for the field-induced spin-state transition. It turned out that the transition is accompanied by ordering of the magnetic moments. We suggest that the subtle balance between the ligand field potential and the ferromagnetic interaction between Co^{3+} ions determines the magnetic properties of $Sr_{1-x}Y_xCoO_{3-\delta}$ at temperature below T_C.

The high-frequency ESR measurements on powder samples of $Sr_{1-x}Y_xCoO_{3-\delta}$ ($\delta=0.3$) with $x=0.22$ and 0.25 were conducted at 4.2 K. The ESR spectra at the frequency from 584.8 to 847.0 GHz were measured by utilizing a far-infrared laser and a pulse magnet. The spectrum at 449.7 GHz was measured by utilizing a vector network analyzer and a superconducting magnet. The magnetization curves were measured by means of a standard pick-up coil method in pulsed magnetic fields up to 53 T. The temperature dependence of the magnetization in static fields was measured with a magnetic property measurement system (MPMS) superconducting interference device magnetometer (Quantum Design). The method for synthesizing the powder samples of $Sr_{1-x}Y_xCoO_{3-\delta}$ is mentioned in Refs. 3 and 4. Laboratory x-ray analyses showed that the samples are in a single phase.

Before discussion about the field-induced spin-state transition, we describe the results of the high-frequency ESR measurements. The various spin-state degree of freedom in the Co^{3+} ion often causes uncertainties of the spin states for the perovskite Co oxides. In the case of $LaCoO_3$, the precise spin state as a function of temperature is still controversial. Difficulties for determining the precise spin state in $LaCoO_3$ partly come from the fact that thermal activation from the nonmagnetic state is needed for detecting the magnetic spin state in this compound. In contrast to $LaCoO_3$, the finite magnetization survives down to lowest temperature in $Sr_{1-x}Y_xCoO_{3-\delta}$. This fact makes it possible to study the magnetic spin state of $Sr_{1-x}Y_xCoO_{3-\delta}$ in its ground state. To examine the spin state, which brings the low-temperature magnetization of $Sr_{1-x}Y_xCoO_{3-\delta}$, we measured the ESR. As depicted in the inset of Fig. 2, ESR spectra with a broad peak are observed in the samples with both $x=0.22$ and 0.25 at 4.2 K. For powder samples, the resonance absorption lines for the field applied along the magnetic principal axis appear as peaks in the spectra because the magnon density of state along the principal axis is large. Thus, we plot the frequency-field relation of the observed peaks in Fig. 2. The obtained results can be fitted by a classical ferromagnetic resonance mode, which is expressed as $\omega/\gamma=H+2H_A$.[11] Here, γ and H_A are a gyromagnetic ratio and an anisotropy field, respectively. From the fitting, $g=3.6$ and $H_A=3.72$ T are evaluated for both samples. The g value is similar to those obtained for $LaCoO_3$ in the intermediate temperature region by the ESR and neutron scattering measurements.[12,13] It has been known that low-temperature magnetic properties of the $3d^6$ ion in the HS state can be described by a fictitious spin $s=1$ with the effective g value largely different from that of a free electron $g_e=2.0023$.[14] This is because the orbital degeneracy of the $3d^6$ ion is not lifted by the cubic ligand field, and the triplet state with a pseudo-total-momentum $\tilde{J}=1$ becomes the lowest in energy due to the level splitting by spin-orbit coupling. Actually, a recent crystal field calculation showed that the g values and a single ion anisotropy constant D of $LaCoO_3$ can be explained by the lowest triplet, which is extracted from the HS state.[15] Assuming $s=1$ and $H_A=3.72$ T, the single ion anisotropy constant is evaluated to be $D=-6.25$ cm^{-1} from an equation $D=-g\mu_BH_A/(2s-1)$.[16] The absolute value of the evaluated D is also comparable with that of $LaCoO_3$. Therefore, we conclude that the Co^{3+} ion in the HS state gives the finite magnetization of $Sr_{1-x}Y_xCoO_{3-\delta}$ at low temperature.

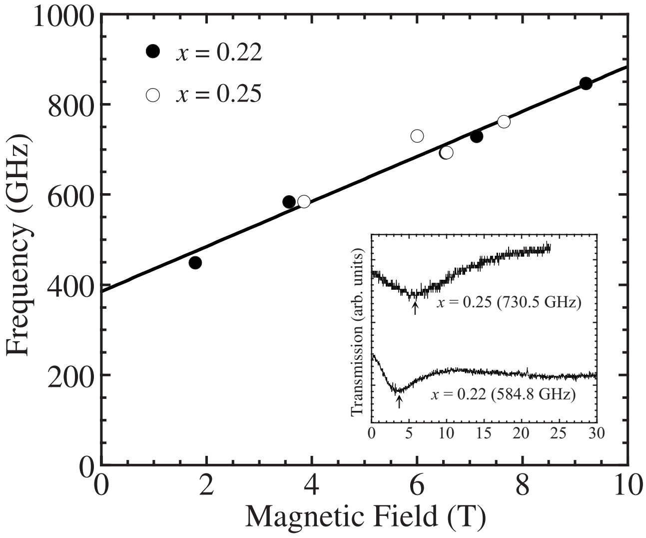

FIG. 2. Frequency-field relation of the ESR resonance points in $Sr_{1-x}Y_xCoO_{3-\delta}$ with $x=0.22$ and 0.25, observed at 4.2 K. A solid line shows theoretical ferromagnetic resonance mode. The inset shows ESR spectra observed at 4.2 K.

Figure 3 shows the magnetization curves of the samples with $x=0.22$ and 0.25 observed at 4.2 K. As reported by the previous study,[3] a large hysteresis around zero magnetic field is observed in both samples. However, the magnetization curves of the samples with $x=0.22$ and 0.25 show consider-

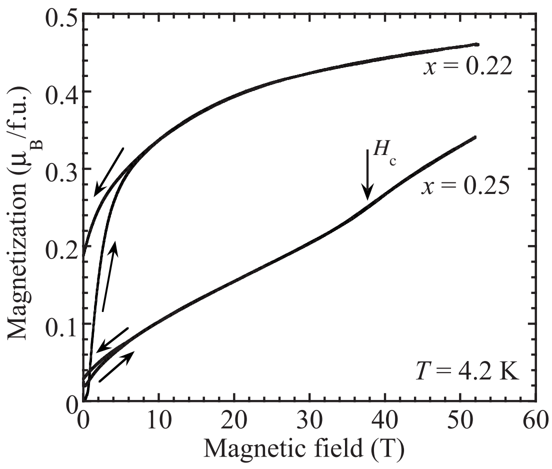

FIG. 3. Magnetization curves of $Sr_{1-x}Y_xCoO_{3-\delta}$ with $x=0.22$ and 0.25, observed at 4.2 K.

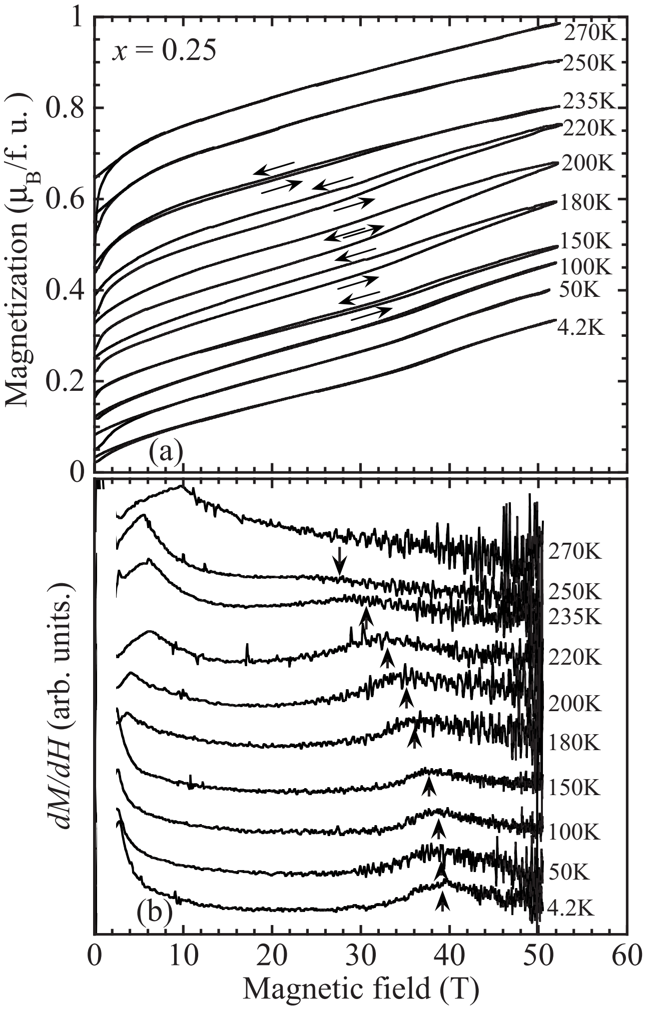

FIG. 4. (a) Temperature dependence of the magnetization curves of $Sr_{1-x}Y_xCoO_{3-\delta}$ with $x=0.25$. Each magnetization curve shifts up by $0.05\mu_B$ with increasing temperature from 4.2 K. (b) Temperature dependence of the derivative of the magnetization (dM/dH) curve of $Sr_{1-x}Y_xCoO_{3-\delta}$ with $x=0.25$ in the field-ascending process.

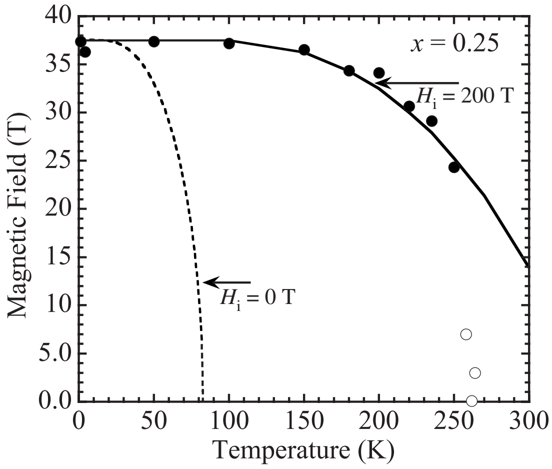

FIG. 5. (a) Temperature dependence of the H_c, observed in $Sr_{1-x}Y_xCoO_{3-\delta}$ with $x=0.25$. Closed circles show the H_c. Open circles show the peak temperature T_m of the $M-T$ curves, measured at $H=0.1$, 3, and 7 T. Solid curve shows a theoretical curve, calculated with the parameter, $g=3.6$, $\Delta=575$ K, and $H_i=200$ T. Dashed curve is that with the parameter, $g=3.6$, $\Delta=91$ K, and no internal field.

able differences. As the sample with $x=0.22$ has a larger spontaneous ferromagnetic moment, magnetization of this sample steeply grows in the beginning of the magnetization process, and then shows a gradual and nonlinear increase with increasing field. On the other hand, that of the sample with $x=0.25$ increases almost linearly above the hysteresis region, and shows an anomaly at $H_c \simeq 38$ T. Above H_c, the magnetization increases with a larger slope. Figures 4(a) and 4(b) show temperature dependence of the magnetization and the field derivative of the magnetization (dM/dH) curves, respectively, observed in the $x=0.25$ sample. In the dM/dH curves, a broad peak is seen at H_c. As the temperature is increased, the spontaneous magnetization around the zero field increases, whereas the peak of the dM/dH shifts toward lower field. The peak broadens with increasing the temperature and then disappears above $T_m=260$ K, at which the M-T curve shows the maximum. In Fig. 5, temperature dependence of the H_c is plotted together with the peak temperature T_m of the M-T curve. We interpret that the anomaly at H_c is due to the field-induced spin-state transition. It is considered that at low temperature, the sample with $x=0.25$ is in a phase-separated state with the HS and LS domains, and the HS domain, which occupies a smaller portion of the sample, gives the small but finite spontaneous magnetization. Then, the external fields convert Co^{3+} ions in the LS domain to the HS state, giving rise to the anomaly at H_c. The temperature dependence of H_c is analyzed by assuming a system similar to that explained the field-induced spin-state transition in the spin crossover complex $[Mn^{III}(taa)]$.[10] A free energy f_{LS} of the nonmagnetic LS state for a Co^{3+} ion is settled to be $f_{LS}=0$. We assume that a free energy f_{HS} of the HS state is expressed as follows:

$$f_{HS} = \Delta - k_B T \log\left\{\frac{\sinh[3g\mu_B(H+H_i)/2k_BT]}{\sinh[g\mu_B(H+H_i)/2k_BT]}\right\}. \qquad (1)$$

The first term Δ is the difference of the internal energy between the HS and LS states, which is assumed to be positive. The second term represents the Zeeman energy of the fictitious spin $s=1$ with $g=3.6$. An important point of this analysis is an introduction of an internal field H_i in the Zeeman term, for taking the ferromagnetic exchange interaction between Co^{3+} ion into account. The spin-state transition occurs when $f_{HS}=f_{LS}=0$ is satisfied. As shown in Fig. 5, the temperature dependence of H_c is reproduced by the theoretical curve, calculated with the parameters $\Delta=575$ K and $H_i=200$ T. The magnetic anisotropy can be neglected in the analysis because it is small enough compared with Δ and H_i. In fact, the calculation without the internal field cannot explain the experimental result; rapid decrease in H_c upon warming is suggested by the calculation whereas the observed H_c is almost constant up to 150 K as shown in Fig. 5. The decrease in H_c upon warming is due to the fact that the HS state is stabilized by a thermal effect. This is because the HS state has a larger entropy compared to the nonmagnetic LS state, owing to the spin degree of freedom. But, the internal field lifts the spin degeneracy and, thus, reduces the entropy in the HS state. Consequently, it suppresses the thermal effect, resulting in the almost constant H_c below 150 K. In the temperature region above 150 K, the magnetization curves show a large hysteresis around H_c. We consider that the relaxation time for the entropy variation is the origin of the observed hysteresis. As we suggested above, the field-induced transition above 150 K is accompanied by a large entropy variation. To provide such an entropy variation, a heat exchange is required. The magnetization measurements in this study are conducted in pulsed magnetic fields with rather short duration of about 7 msec. When the magnetic field is varied rapidly enough, like in this experiment, compared with the time for the heat exchange, the hysteresis appears in the magnetization process.

The finite internal field, suggested from the above analysis, implies that ferromagnetic clusters, in which Co^{3+} ions in the HS state are strongly coupled each other by the exchange interaction, are induced by the external fields. This situation is quite different from the case of the usual spin crossover complex, for which the paramagnetic HS state is induced by the fields.[10] For $LaCoO_3$, an anomaly in the magnetization curve, which was interpreted to be a metamagnetic transition, was reported.[17] However, an analysis for this behavior has not been done yet. It should be mentioned that within the framework of our analysis, a jump of the magnetization, accompanied with the spin-state transition of first order, is expected at H_c. The observed magnetization in $Sr_{1-x}Y_xCoO_{3-\delta}$, however, shows a gradual increase. We consider that this behavior is due to a distribution of the transition field. In the doped compounds such as $Sr_{1-x}Y_xCoO_{3-\delta}$, inhomogeneities inevitably exist in the sample, and therefore, the values of H_i and δ, which are determined by a local structure of the sample, likely distribute in certain extents. This causes the distribution of the transition field, giving rise to the gradual increase in the magnetization around H_c. Further theoretical studies are desired for this issue.

Finally, we discuss the difference of the magnetic behavior between the samples with $x=0.22$ and 0.25. We suggest an important role of a competition between the ferromagnetic exchange interaction and the ligand field potential. Since the ferromagnetic interaction between the Co^{3+} ions stabilizes the HS state, it competes with the ligand field potential, which favors the LS state. The competition is considered to be affected by a substitution of Sr^{2+} with Y^{3+} ion. The substitution reduces the lattice volume of $Sr_{1-x}Y_xCoO_{3-\delta}$ because of a smaller ionic radius of Y^{3+} compared with that of Sr^{2+}.[3] Hence, it likely causes an enhancement of the ligand field potential. Thus, the stronger ligand field potential is expected for the sample with $x=0.25$. We consider that the ferromagnetic interaction overcomes the ligand field potential and, thus, maintains the large spontaneous magnetization down to low temperature for the sample with $x=0.22$, whereas the large portion of the Co^{3+} ions turns into the nonmagnetic LS state upon cooling because of the dominance of the ligand field potential in the sample with $x=0.25$.

This work was partly supported by Grant No. 18740183 from the JSPS and by Grant-in-Aid for Scientific Research (Grant No. 451) from MEXT, Japan. This work was carried out under the Visiting Researcher's Program at KYOKUGEN.

---

[1] P. M. Raccah and J. B. Goodenough, Phys. Rev. **155**, 932 (1967).

[2] M. A. Korotin, S. Yu. Ezhov, I. V. Solovyev, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B **54**, 5309 (1996).

[3] W. Kobayashi, S. Ishiwata, I. Terasaki, M. Takano, I. Grigoraviciute, H. Yamauchi, and M. Karppinen, Phys. Rev. B **72**, 104408 (2005).

[4] S. Ishiwata, W. Kobayashi, I. Terasaki, K. Kato, and M. Takata, Phys. Rev. B **75**, 220406(R) (2007).

[5] S. Ya. Istomin, J. Grins, G. Svensson, O. A. Drozhzhin, V. L. Kozhevnikov, E. V. Antipov, and J. P. Attfield, Chem. Mater. **15**, 4012 (2003).

[6] R. L. Withers, M. James, and D. J. Goossens, J. Solid State Chem. **174**, 198 (2003).

[7] S. Fukushima, T. Sato, D. Akahoshi, and H. Kuwahara, J. Appl. Phys. **103**, 07F705 (2008).

[8] P. Gutlich, A. Hauser, and H. Spiering, Angew. Chem., Int. Ed. Engl. **33**, 2024 (1994).

[9] A. Bousseksou, N. Negre, M. Goiran, L. Salmon, J. P. Tuchagues, M. L. Boillot, K. Bouheddaden, and F. Varret, Eur. Phys. J. B **13**, 451 (2000).

[10] S. Kimura, Y. Narumi, K. Kindo, M. Nakano, and G. E. Matsubayashi, Phys. Rev. B **72**, 064448 (2005).

[11] C. W. Haas and H. B. Callen, in *Ferromagnetic Relaxation and Resonance Line Width*, Magnetism I (Academic, New York, 1963), p. 449.

[12] S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, Phys. Rev. B **66**, 094404 (2002).

[13] A. Podlesnyak, S. Streule, J. Mesot, M. Medarde, E. Pomjakushina, K. Conder, A. Tanaka, M. W. Haverkort, and D. I. Khomskii, Phys. Rev. Lett. **97**, 247208 (2006).

[14] K. Inomata and T. Oguchi, J. Phys. Soc. Jpn. **23**, 765 (1967).

[15] Z. Ropka and R. J. Radwanski, Phys. Rev. B **67**, 172401 (2003).

[16] J. Kanamori and H. Minatono, J. Phys. Soc. Jpn. **17**, 1759 (1962).

[17] K. Sato, M. I. Bartashevich, T. Goto, Y. Kobayashi, M. Suzuki, K. Asai, A. Matsuo, and K. Kindo, J. Phys. Soc. Jpn. **77**, 024601 (2008).