Low-temperature interactions of magnetic excitons in $LaCoO_3$

S. R. Giblin*
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom

I. Terry
Department of Physics, University of Durham, Durham DH1 3LE, United Kingdom

D. Prabhakaran and A. T. Boothroyd
Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom

C. Leighton
Department of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Avenue SE, Minneapolis, Minnesota 55455, USA

(Received 13 November 2008; revised manuscript received 7 March 2009; published 8 May 2009)

The low-temperature magnetic behavior of $LaCoO_3$, containing oxygen vacancies, is reported. Magnetic-susceptibility measurements made in the temperature range of 0.5–35 K on a single crystal and a polycrystalline sample provide strong evidence for the existence of magnetic excitons as fundamental entities within the bulk of the material system. Specifically, two distinct types of excitons form, isolated and interacting excitons, both of which are associated with oxygen vacancies. Isolated magnetic excitons act as high-spin paramagnetic particles while the interacting excitons appear to be coupled antiferromagnetically. It is proposed that the interaction arises from the overlap of magnetic excitons as a consequence of the statistical clustering of oxygen vacancies. The striking similarity of these results with those of the lightly doped $La_{0.97}Sr_{0.03}CoO_3$ suggests that the observed excitons are a precursor to magneto-electronic phase separation and supports the idea that phase separation is initiated by disorder in the material system.

DOI: 10.1103/PhysRevB.79.174410 PACS number(s): 75.30.Hx, 75.30.Cr, 75.47.−m

$LaCoO_3$ has provided a wealth of opportunity for researchers since the material was first investigated over 50 years ago.[1,2] Specifically, interest has been focused on an observed thermally induced spin-state transition occurring at ~90 K and another magnetic transition coincident with an insulator to metal transition at temperatures over 600 K. The exact nature of the spin transitions is still a matter of some contention; the lower temperature transition has been interpreted as a low spin (LS), $S=0$ state, $t_{2g}^6e_g^0$ to an intermediate spin (IS), $S=1$ state, $t_{2g}^5e_g^1$ (Refs. 3–7); or a LS to high spin (HS), $S=2$ state, $t_{2g}^4e_g^2$ transition[8–10] resulting in a LS-HS stable matrix of 1:1 ratio.[11–13] Moreover when hole doped with Sr ions, $La_{1-x}Sr_xCoO_3$, perovskite cobaltite becomes an excellent system in which to study magneto-electronic phase separation,[14–16] a property ubiquitous in complex magnetic oxides, which can lead to exotic behavior such as colossal magnetoresistance.

The general form of the temperature dependence of the magnetic susceptibility is shown in the inset of Fig. 1. The data were taken with an applied field of 5 T and the calculated diamagnetic component was subtracted. The thermally induced spin transition is clearly visible as a hump around 90 K; this general form of the susceptibility has been reproduced by all previous studies of $LaCoO_3$. Of particular interest to this work is the low-temperature ($T<30$ K) Curie tail. Initially this tail was not considered to be a property intrinsic to bulk $LaCoO_3$ with claims that it was a consequence of either surface ferromagnetic defects, namely, Co^{2+} (Refs. 8 and 17) or paramagnetic impurities within the bulk. However a different interpretation of the low-temperature paramagnetic tail was initially proposed by Nagaev *et al.*,[18] who claimed that magnetic polaron-like entities are responsible. Explicitly, in this model, localized holes (electrons) bound to cobalt ions or oxygen interstitial (vacancies) sites induce LS to HS transitions in neighboring Co^{3+} ions leaving the remaining cobalt ions in the LS ground state. The radius of a magnetic polaron will extend over several unit cells, creating large spin clusters which are dilute within the solid. It is more appropriate to label these entities as magnetic "excitons," as opposed to polarons, as the host ions have no mag-

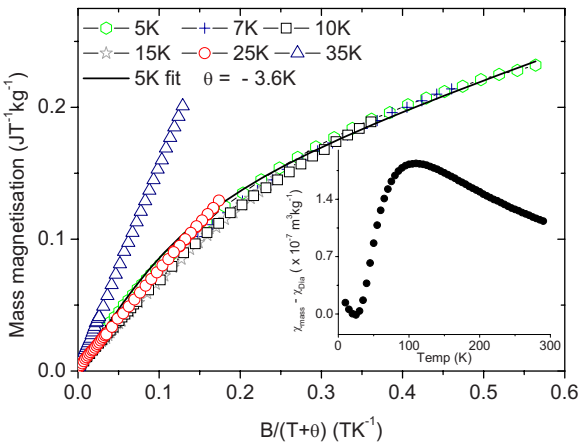

FIG. 1. (Color online) Mass magnetization curves for $LaCoO_{2.98}$ as a function of temperature up to 5 T, demonstrating scaling behavior from 5–25 K. Details of the fit to the 5 K data (solid line) are described in the text. The inset shows the temperature dependence of the susceptibility measured in 5 T.

netic moment in the absence of the localized electron; uniquely the $S=0$ ground state of the remaining Co^{3+} in the material enables the direct study of these excitons. Further theoretical work has also predicted ferromagnetically coupled Co_2O_{11} clusters,[19] again induced by oxygen vacancies.

The signature of exciton type behavior was first observed by Yamaguchi *et al.*,[20] who deduced a spin state of $S \simeq 16$ obtained from fitting the Curie tail directly. Further work observed the formation of the magnetic excitons in the bulk of the sample at $T \simeq 50$ K.[21] This temperature was taken to be the point at which the excitons induced from oxygen vacancies become magnetically dominant as the majority of the Co^{3+} ions involved in the thermally induced spin transition are in a $S=0$ state. Indeed further work has found evidence of interactions between excitons and the thermally excited Co^{3+} ions,[22] which were determined to be locally antiferromagnetic (AF) and of order $\theta=-220$ K (from high-temperature susceptibility measurements).

The purpose of this work is to investigate the properties of magnetic excitons in $LaCoO_{3-\delta}$ for $T<35$ K. At these low temperatures the number of Co^{3+} ions in a thermally induced $S \neq 0$ state is falling rapidly with T.[6] In essence the majority of the Co^{3+} ions can be viewed to be in the $S=0$ ground state and an electron trapped at an oxygen vacancy can induce those Co^{3+} ions lying within its localization radius to be in their high-spin state[18] creating an exciton. Low-field and low-temperature magnetic measurements demonstrate that the excitons are noninteracting paramagnetic entities unless they are close enough to be exchange coupled, in which case a measurable θ value of around -3.5 K is obtained. Furthermore it will be demonstrated that the behavior shown in the *n*-type oxygen deficient $LaCoO_3$ is the precursor for magneto-electronic phase separation observed in the *p*-type hole-doped $La_{1-x}Sr_xCoO_3$ suggesting the observed magneto-electronic phase separation is initiated by the presence of disorder, regardless of the nature of the localized carrier.

Single crystals of $LaCoO_{2.98\pm0.02}$ were grown via the floating zone method, the oxygen stoichiometry for each sample was obtained from titration experiments.[23] Polycrystalline samples of $LaCoO_{2.96\pm0.02}$ and $La_{0.97}Sr_{0.03}CoO_3$ were grown via the solid-state reaction method, all samples were shown to be single phase via x-ray diffraction. Initial magnetic measurements were made from 2 to 300 K in fields up to 5 T using a commercial quantum design magnetic property measurement system (MPMS) XL superconducting quantum interference device (SQUID) magnetometer. Bulk magnetic measurements were also carried out upon an Oxford instruments (OI) Helium 3 system modified to include a quantum design dc SQUID with a first-order gradiometer pickup coil configuration, which enabled moment changes of 1×10^{-12} J T^{-1} to be detected.[24] This setup allowed dc susceptibility measurements to be made in the temperature range 0.350–6 K in a field of 10 μT with a magnetic field of up to 0.01 T being applied upon cooling.

The temperature dependence of the magnetic susceptibility is shown in the inset of Fig. 1. For $T>150$ K these data can be described by a Curie-Weiss law with $\theta=-220$ K, a fact confirmed by observation that the high-temperature isothermal magnetization curves can be made to fall or "scale" on to a single curve when plotting these data as a function of $B/(T+\theta)$. Below ~90 K any remaining scaling behavior disappears as the proportion of the Co^{3+} ions in the LS state varies exponentially with temperature.[6] At low temperatures the paramagnetic tail becomes dominant, which leads to a minimum in the susceptibility occurring at 25 K. Figure 1 shows the magnetization curves for $LaCoO_{2.98\pm0.02}$ for various different temperatures ≤ 35 K. In this temperature range, where magnetic excitons are believed to dominate, these data appear to scale when plotting $B/(T+\theta)$ but only when a θ value of -3.9 K is used. In fact this magnetic response can be modeled by the combination of two Brillouin functions: one describing a purely paramagnetic component and the other including a θ parameter to describe interactions between some of the magnetic excitons. The magnetization (m) was modeled by

$$m = N_1 g_J \mu_B J_1 B_J(y_1) + N_2 g_J \mu_B J_2 B_J(y_2), \tag{1}$$

where N_i is the number of atoms per unit volume for the ($i=1$) noninteracting and ($i=2$) interacting species, g_J is the Landé factor, μ_B is a Bohr magneton, J_i is the total angular-momentum quantum number, and B_{Ji} is the Brillouin function. y_i can be described by

$$y_i = \frac{g_J \mu_B J_i B}{k_B(T+\theta)}, \tag{2}$$

where k_B is the Boltzmann constant, B is the magnetic-flux density, and T is the temperature. For the noninteracting species $i=1$ and $\theta=0$. Good fits to the data (e.g. that of the 5 K data is shown in Fig. 1) were obtained by assuming a spin-only contribution to the total angular momentum with $J=S=13$ for both the noninteracting and interacting excitons. The number of atoms per unit volume for the interacting and noninteracting species was $N_2=0.4\times10^{20}$ cm^{-3} and $N_1=10.6\times10^{20}$ cm^{-3}, respectively; $\theta=-3.6$ K for the interacting component. It is noted that previous investigations have suggested that Co^{3+} ions may have a magnetic moment with a significant orbital contribution[12] which could affect the susceptibility; for simplicity Fig. 1 is fitted using a spin-only model to show that there are interacting excitons. The data of Fig. 1 suggest that the magnetic response of the exciton is dominated by the spin of the HS Co^{3+} ions, in agreement with the observations of Yamaguchi *et al.*[20]

The modeled data provide two significant results: the observed total moment is consistent with the number of oxygen vacancies, suggesting that excitons are indeed a property of the bulk material, and for both Brillouin functions an S value of 13 is required to ensure accurate fitting. This is in agreement with Yamaguchi *et al.*[20] who simply fitted the low-temperature magnetic susceptibility to Curie's law. However the data shown in Fig. 1 clearly require a magnetic species with an AF interacting component superimposed. This result may be a consequence of some magnetic excitons being in close enough proximity to interact, possibly forming a magnetic biexciton. The close proximity of the interacting excitons is presumed to be a consequence of the statistical clustering of the oxygen vacancies to which the magnetic excitons are bound. This behavior is in a direct analogy with

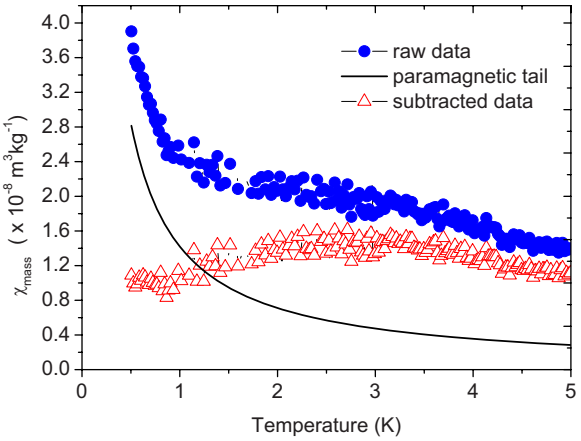

FIG. 2. (Color online) Temperature dependence of magnetic susceptibility of $LaCoO_{2.98\pm0.02}$ cooled and measured in a residual field of 10 μT. The raw data along with the subtraction of the paramagnetic fit are shown.

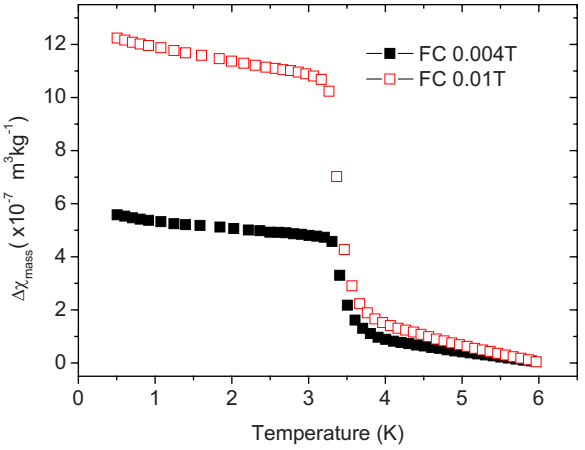

FIG. 3. (Color online) Temperature dependence of magnetic susceptibility of $LaCoO_{2.98\pm0.02}$ cooled in a field of 4 and 10 mT and measured in a residual field of 10 μT.

certain dilute magnetic semiconductors that show magnetic ion clustering, demonstrating spin-glass behavior below the nearest-neighbor percolation limit.[25]

The data of Fig. 1 therefore suggest that two independent magnetic species are responsible for the Curie tail observed in the magnetic susceptibility of $LaCoO_{2.98\pm0.02}$, namely, noninteracting and interacting (AF exchange-coupled) magnetic excitons. Further insight into the magnetic nature of these entities was obtained from temperature-dependent magnetic-susceptibility measurements of $LaCoO_{2.98\pm0.02}$ in the range 0.5–5 K as shown in Fig. 2. Superimposed upon the measurement is the Curie fit for a residual field of 10 μT calculated from the magnetic response as in Fig. 1. When this Curie-type behavior is removed there is an apparent change in slope of the susceptibility occurring at about 3 K which is very close to the θ value (−3.6 K) obtained from fitting the data of Fig. 1. Field-cooled (FC) experiments were performed to isolate this component of magnetization that appears to show a degree of magnetic ordering. In this experimental configuration the field applied during cooling was increased from 10 μT up to 4 or 10 mT and, importantly, the resulting measurements were made upon warming in a measuring field of 10 μT, ensuring that the remnant component of magnetization dominated. Figure 3 shows the change in the temperature dependence of the magnetic susceptibility induced by the FC. It is clear that, at $T \approx 3.5$ K, increasing the cooling field significantly increases the relative change in the magnetization suggesting an alignment of magnetic species with a high degree of magnetic remnance. It was not possible to fit these data with either a Brillouin function or critical exponents.

Hysteretic behavior observed in $LaCoO_{2.98\pm0.02}$ at low temperatures ($T \leq 5$ K) has previously been ascribed to a surface component of magnetization. Specifically, a fivefold-coordinated Co^{3+} ion on a ideal surface has a lower crystal-field splitting than a bulk octahedral-coordinated Co^{3+} ion[26,27] inducing a moment. However, this work did not account for oxygen-vacancy-induced magnetism[18] and cannot account for the muon spin-rotation investigations which suggest bulk magnetic exciton behavior.[21,22] In order to determine the effect of an increased surface area a polycrystalline sample with a known oxygen vacancy was investigated ($LaCoO_{2.96\pm0.02}$). Initial high-field susceptibility measurements produced a graph similar to that shown in the inset of Fig. 1, although the data did not scale with $B/(T+\theta)$, most likely due to the increased surface area and consequent impurities. Above 90 K the data overlap, although the paramagnetic tail of the polycrystal is more significant. There are two possibilities for such an increase, either an exciton or surface contribution. To illuminate the nature of the polycrystalline sample, low-field and -temperature measurements were performed. The sample was FC in 10 mT and the sample measured in the remnant field of 10 μT. The temperature dependence of the susceptibility is shown in Fig. 4, at high temperatures the form of the susceptibility is the same as the single-crystal data with a transition apparent around 3.3 K. This is not surprising given the similar oxygen nonstoichiometry of the two samples. However as the temperature is

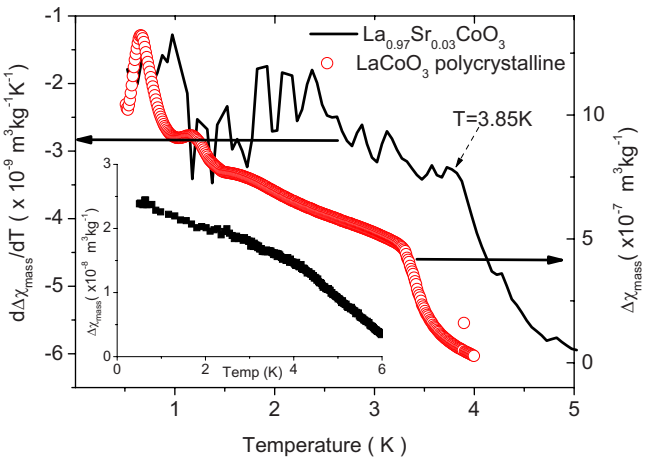

FIG. 4. (Color online) Temperature dependence of magnetic susceptibility of the polycrystalline $LaCoO_{2.96\pm0.02}$ (circles) and the derivative of the susceptibility of $La_{0.97}Sr_{0.03}CoO_3$ (line). Both samples were cooled in a field of 10 mT and measured in a residual field of 10 μT. The inset shows the temperature dependence of the susceptibility for $La_{0.97}Sr_{0.03}CoO_3$.

lowered there are two further distinct magnetic transitions, these observations clearly contradict the single-crystal data. As the samples have similar levels of paramagnetic impurities and oxygen vacancies it is reasonable to conclude that the difference is a consequence of the increased surface area, either from a higher concentration of Co^{3+} ions that possess fivefold coordination or possibly the presence of high-spin Co^{2+} ions. The apparent low-ordering temperatures suggested by the data of Fig. 4 suggest such entities are weakly interacting.

The data of Figs. 1 and 2 clearly indicate that the excitons, each of $S=13$, occur in two possible states; dilute excitons exist as paramagnetic species that do not interact while neighboring excitons appear to interact antiferromagnetically. Above about 4 K both types of excitons exhibit paramagnetic behavior suggesting the exchange-coupled Co^{3+} HS moments within the exciton respond coherently to magnetic field (i.e., the magnetic exciton is analogous to a superparamagnatic particle). Nagaev *et al.*[18] did not predict the internal interaction of the exciton, concluding that it could be either AF or ferromagnetically coupled but it is clear that the intraexchange energy is much greater than the interexciton exchange energy (i.e., $\gg 3.6$ K). In both cases an S value of 13 would suggest that the exciton extends over several unit cells, though AF intraexchange interactions would result in a exciton with the magnetic moment arising from uncompensated spins at the edge of the entity. From this description of the magnetic exciton the remnant behavior observed in Fig. 3 can be interpreted as arising from a field-dependent AF interaction between two large excitons. The possibility of the remnant behavior being associated with the internal magnetic anisotropy of the exciton appears to be ruled out by the existence of the paramagnetic response attributed to isolated excitons.

At low hole doping the behavior of the excitons should be reminiscent of ferromagnetic clusters in phase-separated materials. $La_{0.97}Sr_{0.03}CoO_3$ has been used as a comparison as it is well below the known percolation limit of hole-induced ferromagnetic clusters ($x=0.18$) and the spin-glass concentration level ($x=0.09$).[28] When hole doped, Co^{4+} ions are expected to induce a moment in surrounding Co^{3+} ions forming "nanodroplets" of ferromagnetism,[14,16] the exact mechanism for interaction between the clusters at low doping levels is not well understood. The high-field high-temperature susceptibility of $La_{0.97}Sr_{0.03}CoO_3$ does not show the spin-state transition of pristine $LaCoO_3$ and no further magnetic transition is obvious. Experiments were performed in the low-temperature low-field magnetometer to allow further investigation. Initial zero field cooled measurements resulted in a temperature-independent magnetic susceptibility measured in 10 μT, however after FC experiments in 10 mT a magnetic transition is observed. This implicitly suggests that the mechanism involved in $La_{0.97}Sr_{0.03}CoO_3$ is a consequence of the Sr hole doping and not simply of oxygen vacancies; no paramagnetic tail was observed in $La_{0.97}Sr_{0.03}CoO_3$ as it is likely the nanodroplets formed have a magnetic anisotropy[14,16] revealing a transition upon FC. The temperature dependence of the raw and differential magnetic susceptibility is shown in Fig. 4 inset and the main figure respectively, this subtle transition occurs at 3.85 K, a similar temperature to that observed in overlapping excitons in the parent material. The field-dependent behavior is different in the doped sample due to different intercluster interactions which may be modified as the valence state of Co ion is changed when hole doping. Previous measurements of the mean valence state of the Co ion suggest that the sample may be n or p type due to compensation of Sr by oxygen vacancies;[29] however, in both compositions it is the overlapping of the clusters (either oxygen-induced excitons or hole-induced nanodroplets) that results in the magnetic transition with approximately the same ordering temperature.

In conclusion this work has investigated the low-temperature behavior of $LaCoO_3$ containing oxygen vacancies; the induced magnetic excitons are a fundamental property of the bulk of the system. Specifically two distinct types of excitons form: isolated and interacting excitons. The isolated particles act as a paramagnetic impurity, while those excitons that overlap undergo AF interactions. The overlapping excitons occur most probably due to the distribution of oxygen vacancies, comparison of the results with hole-doped $La_{0.97}Sr_{0.03}CoO_3$ demonstrates a striking resemblance and suggests that the observed excitons are a precursor to magnetic phase separation. It is possible to observe the excitons in this particular complex magnetic oxide because of the LS ground state of the pristine $LaCoO_3$.

S.R.G. would like to thank EPSRC-GB for funding. Work at UMN was supported primarily by DOE, with additional funding from NSF.

*sean.giblin@stfc.ac.uk

[1] W. C. Koehler and E. O. Wollan, J. Phys. Chem. Solids **2**, 100 (1957).

[2] R. R. Heikes, R. C. Miller, and R. Mazelsky, Physica (Amsterdam) **30**, 1600 (1964).

[3] 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).

[4] Y. Kobayashi, N. Fujiwara, S. Murata, K. Asai, and H. Yasuoka, Phys. Rev. B **62**, 410 (2000).

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

[6] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Gruninger, T. Lorenz, P. Reutler, and A. Revcolevschi, Phys. Rev. B **66**, 020402(R) (2002).

[7] R. F. Klie, J. C. Zheng, Y. Zhu, M. Varela, J. Wu, and C. Leighton, Phys. Rev. Lett. **99**, 047203 (2007).

[8] M. A. Senaris-Rodriguez and J. B. Goodenough, J. Solid State Chem. **116**, 224 (1995).

[9] M. Abbate, J. C. Fuggle, A. Fujimori, L. H. Tjeng, C. T. Chen, R. Potze, G. A. Sawatzky, H. Eisaki, and S. Uchida, Phys. Rev. B

47, 16124 (1993).
[10] M. Zhuang, W. Zhang, C. Hu, and N. Ming, Phys. Rev. B **57**, 10710 (1998).
[11] K. Asai, P. Gehring, H. Chou, and G. Shirane, Phys. Rev. B **40**, 10982 (1989).
[12] M. W. Haverkort, Z. Hu, J. C. Cezar, T. Burnus, H. Hartmann, M. Reuther, C. Zobel, T. Lorenz, A. Tanaka, N. B. Brookes, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, Phys. Rev. Lett. **97**, 176405 (2006).
[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] J. Wu, J. W. Lynn, C. J. Glinka, J. Burley, H. Zheng, J. F. Mitchell, and C. Leighton, Phys. Rev. Lett. **94**, 037201 (2005).
[15] D. Phelan, Despina Louca, S. Rosenkranz, S.-H. Lee, Y. Qiu, P. J. Chupas, R. Osborn, H. Zheng, J. F. Mitchell, J. R. D. Copley, J. L. Sarrao, and Y. Moritomo, Phys. Rev. Lett. **96**, 027201 (2006).
[16] D. Phelan, D. Louca, K. Kamazawa, S. H. Lee, S. Rosenkranz, M. F. Hundley, J. F. Mitchell, Y. Motome, S. N. Ancona, and Y. Moritomo, Phys. Rev. Lett. **97**, 235501 (2006).
[17] J. Q. Yan, J. S. Zhou, and J. B. Goodenough, Phys. Rev. B **70**, 014402 (2004).
[18] E. L. Nagaev, A. I. Podelshchikov, J. Phys.: Condens. Matter **8**, 5611 (1996).
[19] K. Tsutsui, J. Inoue, and S. Maekawa, Phys. Rev. B **59**, 4549 (1999).
[20] S. Yamaguchi, Y. Okimoto, H. Taniguchi, and Y. Tokura, Phys. Rev. B **53**, R2926 (1996).
[21] S. R. Giblin, I. Terry, D. Prabhakaran, T. Prokscha, A. T. Boothroyd, J. Wu, and C. Leighton, Europhys. Lett. **70**, 677 (2005).
[22] S. R. Giblin, I. Terry, D. Prabhakaran, A. T. Boothroyd, J. Wu, and C. Leighton, Phys. Rev. B **74**, 104411 (2006).
[23] Inductively coupled plasma mass spectoscopy found a maximum concentration of paramagnetic impurities of 65 ppm.
[24] D. Read, S. R. Giblin and Ian Terry, Rev. Sci. Instrum. **77**, 103906 (2006).
[25] M. A. Novak, O. G. Symko, D. J. Zheng, and S. Oseroff, J. Appl. Phys. **57**, 3418 (1985).
[26] J.-Q. Yan, J.-S. Zhou, and J. B. Goodenough, Phys. Rev. B **70**, 014402 (2004).
[27] J. B. Goodenough, *Magnetism and the Chemical Bond* (Wiley, New York, 1963).
[28] J. Wu and C. Leighton, Phys. Rev. B **67**, 174408 (2003).
[29] A. Mineshige, M. Inaba, T. Yao, Z. Ogumi, K. Kikuchi, and M. Kawase, J. Solid State Chem. **121**, 423 (1996).