Ferrimagnetic ordering and spin entropy of field-dependent intermediate spins in Na$_{0.82}$CoO$_2$

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The peculiar field-dependent magnetism of Na$_{0.82}$CoO$_2$ has been investigated through an analysis of its DC and AC spin susceptibilities. To account for the easily activated narrow $b_{2g}$-$a_{1g}$ gap of the crystal field for Co in the cobalt oxide layer, the spin-state transition of Co$^{3+}$ (3d$^5$) between the low spin (LS) state $b_{2g}^3a_{1g}^0$ of S=0 and the intermediate spin (IS) state $b_{2g}^0a_{1g}^1$ of S=1 is thus seen as thermally activated and exhibits a Boltzmann distribution. The IS state of Co$^{3+}$ within each $\sqrt{3}a$ hexagonal superlattice formed by the S=1/2 state of the Co$^{3+}$ ions appears randomly within each supercell and shows significant temperature and field dependence. The magnetic field is found to assist in pinning down the thermally activated state of Co$^{3+}$ and swings the Boltzmann distribution weight toward a higher fraction of the IS state. The field dependence of the in-plane magnetic moment from the added number of S=1 spins is used to explain the origin of A-type antiferromagnetic (AF) ordering, particularly that the ferromagnetic (FM)-like behavior below $T_N$ at low field is actually a ferrimagnetic IS spin ordering of Co$^{3+}$.

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**FIG. 1.** (color online) (a) Conventional view of the CoO$_2$ plane of Na$_x$CoO$_2$ as a layer of edge-sharing CoO$_6$ octahedra have been revised into weakly coupled edge-sharing CoO$_2$ chains. (b) The correct crystal field for Co has a square-planar shape with two apical oxygens that belong to the neighboring CoO$_2$ chains of weaker effective charge, see Ref. 15 for details. (c) The electronic configuration of Co$^{3+}$ with d$^6$ sitting in the proposed CEF has a narrow $b_{2g}$-$a_{1g}$ gap with an LS state of S=0 and an IS state of S=1.

Na$_2$CoO$_2$ has been shown to have an intriguing and rich electronic phase diagram as a function of Na ions that are sandwiched between CoO$_2$ layers, including a superconducting state for $x \sim 1/3$ after hydration, a metal-to-insulator transition for $x \sim 1/2$, and a Curie-Weiss metal phase with A-type antiferromagnetic ordering below $T_N \sim 22K$ for $x \sim 0.82-0.86$. In addition, several large hexagonal superlattices were identified for $x \sim 0.71 (\sqrt{2}a)$ and 0.82-0.86 ($\sqrt{3}a$) due to Na vacancy/ion ordering, which has also been shown to have a direct impact on the Fermi surface reconstruction. In addition, Na$_2$CoO$_2$ has also been introduced as a promising thermoelectric material, being used either at low-temperature for its large enhancement of thermopower near 50K for $x$ near 0.85 or at high temperature for its thermoelectric figure-of-merit (ZT) higher than 1. The findings of large enhancement of thermopower and magnetic field suppression have been interpreted as being important evidence that spin entropy may play a key role in the Heikes form of the Seebeck coefficient (the thermopower), i.e., the spin entropy contribution to the Seebeck coefficient of a semiconductor can be suppressed by the magnetic field. Alternative explanations such as strong electron correlations, combined disorder and electronic correlations, and the narrow manifold of $t_{2g}$ bands in this system have also been proposed.

Conventionally, the magnetic properties of Na$_2$CoO$_2$ have often been discussed starting from the spins of mixed valence Co$^{3+}$/Co$^{4+}$ under the CoO$_6$ octahedral crystal field, where the low-spin (LS) state of d$^5$ for Co$^{4+}$ has S=1/2, and the LS state of d$^6$ for Co$^{3+}$ is nonmagnetic. However, ab initio LDA calculations have yielded a reversed $t_{2g}$ splitting of $a_{1g}$-$e'_{g}$ relative to the classical crystal electric field theory (CEF) prediction, in addition, the predicted $e'_g$ hole pockets along $\Gamma - K$ at $k_z = 0$ have never been observed by the ARPES experiments. We have resolved this issue by revising the view of CEF that the narrow d-orbital splitting should be assigned to be $b_{2g}$-$a_{1g}$ rigorously following the
CEF theory, instead of the previously assumed $e'_g\cdot a_{1g}$, as summarized in Fig. 1. It was proposed and verified that the small gap of $b_{2g}\cdot a_{1g} \sim 17$ meV at H=1 Tesla could be subjected to easy thermal activation above ~100 K, and the fraction of the thermally activated excited intermediate spin (IS) state of S=1/2 ($b_{2g}\cdot a_{1g}^0$) versus the ground state (LS) of S=0 ($b_{2g}\cdot a_{1g}^0$) for Co$^{3+}$ spins was shown to follow the Boltzmann distribution statistically. In this study, we explore the field dependence of the IS state of Co$^{3+}$ and use it to interpret the intriguing spin dynamics of Na$_{0.82}$CoO$_2$, including how and why the narrow $b_{2g}\cdot a_{1g}$ gap size is tuned sensitively by the magnetic field, and why FM-like behavior is observed at low field but an A-type antiferromagnetic (AF) ordering is confirmed at high field.

Based on the narrow $b_{2g}\cdot a_{1g}$ gap from the CEF-lifted 3d degeneracy for Co$^{3+}$ (Fig. 1b), the temperature-dependent Curie constant ($C = N\mu^2_{eff}/3k_B$) for Na$_{0.82}$CoO$_2$ has been revealed from the Curie-Weiss law ($\chi = \chi_c + \chi'$) analysis by using the homogeneous susceptibility $\chi(T)$=$M/T$ data from different temperature sections above ~5 $T_N$. The Curie constants were found to be persistently higher than the value expected from the spin-only S=1/2. In particular, the Curie constant could be interpreted to arise from three contributions, including the localized spins of Co$^{3+}$ in the LS state ($b_{2g}\cdot a_{1g}^0$) of S=1/2, Co$^{3+}$ in the LS state ($b_{2g}\cdot a_{1g}^0$) of S=0, and Co$^{3+}$ in the IS state ($b_{1g}\cdot a_{1g}^0$) of S=1. The thermally activated IS state of Co$^{3+}$ for a system with a narrow $b_{2g}\cdot a_{1g}$ gap of ~17 meV (at H=1 Tesla) appears convincingly responsible for the intriguing magnetic properties.

Measurement results obtained by the same data analysis method previously applied to Na$_{x}$CoO$_2$, including the DC homogeneous susceptibilities ($\chi=M/H$) measured under various fields and a zero-field measurement using AC susceptibility measurement with H$^4$C=5 Oe/10 Hz, are shown in Fig. 2. These high-field and low-field measurement results are consistent with those reported in the literature, although the low-field FM-like behavior is drastically different from that of the A-AF ordering when measured at high field. Using the common temperature range from 5$T_N$-300K that guarantees $k_BT > J_{nn}$ for a meaningful Curie-Weiss law fitting, we determined the Curie constant to be a superposition of $C = C_{Co^{3+}}^S + C_{Co^{3+}}^L + C_{Co^{3+}}^F$ from three types of localized spins, including the S=1/2 ($\mu_{eff} = 1.732\mu_B$) state of Co$^{3+}$, S=0 for Co$^{3+}$ in the ground LS state, and S=1 ($\mu_{eff} = 2.828\mu_B$) for Co$^{3+}$ in the excited IS state. The fraction of Co$^{3+}$ activated to the IS state under various fields, $\alpha$(H), can thus be estimated from the relationship $\mu_{eff}^2 = (1-x) \times 1.732^2 + \alpha(x) \times 2.828^2 + (1-\alpha) \times 0^2$ for x=0.82. The Curie constant and the fraction of Co$^{3+}$ in the IS state ($\alpha$(H)) as a function of field are shown in Fig. 3. The Curie constant grows with the applied field and approaches saturation at ~7 Tesla. When the extracted $\alpha$(H) is plotted against 1/H, as shown in the inset of Fig. 3, it is intriguing to note that an activation behavior with a gap of ~2.6 meV is implied. It is clear that $\alpha$ is not only temperature-dependent, as noted previously, but displays field-dependence when the same temperature range is chosen in the paramagnetic regime.

Consider the Co$^{3+}$ spin sitting in the energy spectrum, with a narrow $b_{2g}\cdot a_{1g}$ gap; it is reasonable to assume that the magnetic field might pin a larger fraction of spins in the IS state. Because the $b_{2g}\cdot a_{1g}$ gap size of ~17 meV has previously been estimated under an applied field of H= 1 Tesla, the current field-induced activation gap

![FIG. 2. (Color online) (a) Homogeneous spin susceptibilities ($\chi=M/T$) of single-crystal Na$_{0.82}$CoO$_2$ measured at a low applied field of 0.01 Tesla and a high field of 1 Tesla shown in the inset. While the high-field measurement shows the typical A-type antiferromagnetic transition of $T_N$~22K, the low-field measurement suggests a ferromagnetic-like transition with thermal and field hysteresis in both orientations. (b) AC spin susceptibilities measured using an AC field of 5 Oe/10Hz with zero applied field. The insets show the powder-average ($\chi^\| + 2\chi^\bot$) data to extract $\alpha$(T), and the $\alpha$(T) in an Arrhenius plot to suggest a thermal activation gap of ~20 meV.](image-url)
of $\sim 2.6$ meV implies that the actual gap size should be close to $\Delta = 17 + 2.6 \sim 20$ meV when no field is applied. We deduced the $\alpha(H=0)$ value by using the AC susceptibility data shown in the inset of Fig. 2(b); the fitted gap size is $\sim 20$ meV as expected. The field dependence of $b_{2g} - a_{1g}$ gap is summarized in Fig. 3 where the Boltzmann distribution can be interpreted as being revised by the applied field lowering the IS state by approximately 2.6 meV, mostly because of the Zeeman-like magnetic energy gain due to work done on the spin system by the applied field.

The field dependence of the IS/LS fractional change for Co$^{3+}$ can also be interpreted quantitatively via the real space $\sqrt{13a}$ superlattice model for $Na_{0.82}CoO_2$. The $\sqrt{13a}$ hexagonal superlattice has been identified with the help of synchrotron X-ray Laue diffraction and electron diffraction as a result of the Na di-vacancy cluster ordering, and the Co atoms near the Na di-vacancy sites are proposed to be Co$^{4+}$ with $S=1/2$ to form a hexagonal superlattice of $\sqrt{13a}$ size in the CoO$_2$ plane. Because the number and position of Co$^{4+}$ spins ($S=1/2$) are not expected to change with the applied field due to electron-phonon coupling via local distortion, as illustrated in Fig. 3(a), the observed field-dependent Curie constant must arise from the fractional change of the spin state for Co$^{3+}$ between the LS state of $S=0$ and the IS state of $S=1$. It should be noted that the fraction of Co$^{3+}$ spins activated to the IS state for a specific $T,H$ is 0.71 for $H=0$ and 0.82 for $H=1T$, which correspond to the model of $\alpha(H=0)$ value by using the AC susceptibility data shown in the inset of Fig. 2(b); the fitted gap size is $\sim 20$ meV as expected. The field dependence of $b_{2g} - a_{1g}$ gap is summarized in Fig. 3 where the Boltzmann distribution can be interpreted as being revised by the applied field lowering the IS state by approximately 2.6 meV, mostly because of the Zeeman-like magnetic energy gain due to work done on the spin system by the applied field.

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with $T_N\sim 22$K has been repeatedly confirmed by DC homogeneous susceptibility measurement under applied fields greater than $\sim 0.5$ Tesla. However, FM-like behavior with different onsets near 8, 22, and 29 K has also been observed, with strong cooling rate and history dependence. In addition, the staging effect for Na-layers with different stack orderings was found to be consistent with the highly sensitive thermal and field history dependence for $x$ between $\sim 0.71$-$0.86$. We have examined the fitting of Weiss temperature ($\Theta$) from the PM-state spin susceptibility data obtained in fields from zero to 7 Tesla. and the $\Theta$ values were found to be persistently negative and nearly independent of the field. As long as no triangular (or Kagome)-like geometric frustration mechanism occurs in the spin liquid-like systems, a negative $\Theta\sim 2\xi_i J_i$ fitted from the paramagnetic regime implies that an effective AF coupling must lead to a 3D long-range AF ordering at low temperature, and the observed FM-like behavior observed at low field seems to contradict the negative $\Theta$ value.

To examine the puzzling field-dependent spin ordering, we have repeated the DC susceptibility measurements under high and low fields for $Na_{0.82}CoO_2$, including a zero-field AC (5 Oe/10 Hz) susceptibility measurement, as shown in Fig. 2. A spin state transition near $\sim 22$ K is found consistently; however, the typical A-AF behavior appears only at high field, but the low field measurement indicates FM-like behavior at the same onset with significant ZFC/FC hysteresis. Both the magnetization $M(T)$ with thermal hysteresis at low field and the $\chi'(T_N)$ cusp of AC susceptibility at zero field (Fig. 2(b)) suggest that the order parameter is magnetization, as expected for a FM-like transition. In contrast, the negative Weiss temperature $\Theta$ fitted from the high temperature paramagnetic regime implies that the neighboring spins must be antiferromagnetically aligned in the ground state, which leads to the possibility of a 3D long range ferrimagnetic ordering, i.e., coupling in which neighboring spins are AF coupled with incomplete cancellation due to different spin sizes.

Considering the intra-plane inter-Co$^{4+}$ spin distance for $x=0.82$ ($\sqrt{3}a \sim c$) and $x=0.71$ ($\sqrt{2}a \sim c$) of triangular symmetry, and considering the negative $\Theta$ to imply stronger AF coupling for spins in the neighboring planes of inter-plane distance $c/2$, geometric spin frustration is expected for the localized Co$^{4+}$ S=1/2 spins, as illustrated in Fig. 3(a) for $x=0.71$. Indeed, nearly perfect spin frustration has been observed for $x=0.71$, i.e., $x=0.71$ does not show any magnetic ordering down to $\sim 1$ K, as if spin frustration persists like a spin liquid. In contrast, $x=0.82$ shows FM-like behavior at low field and A-AF ordering at high field. In addition to the insignificant superlattice size difference, the main difference between $x=0.82$ and $x=0.71$ is the percentage of IS spin activation for Co$^{3+}$, i.e., $x$ has been found to be zero for $x=0.71$ over the entire temperature and field range, but it is non-zero and field-dependent for $x=0.82$, as shown in Ref. 17 and Fig. 3.

Here, we propose an interpretation of the field-dependent magnetic ordering behavior of $Na_{0.82}CoO_2$, both qualitatively and quantitatively, that especially considers why A-AF ordering occurs at high field, but ordering is FM-like at low field. There are 12 Co$^{3+}$ per $\sqrt{13}a$ superlattice cell (see Fig. 3(a)), and $\alpha=\sqrt{2}\approx 8.3\%$ corresponds to one in twelve Co$^{3+}$ per superlattice cell in the IS state, which naturally leads to a picture in which $\alpha(\Theta=0\approx 4.5\%)$ represents one IS in every two $\sqrt{13}a$ superlattice cells, as illustrated in Fig. 3(b). In particular, the S=1 spins (IS of Co$^{3+}$ exist in every other layer and couple ferromagnetically to the S=1/2 of Co$^{4+}$ with an A-AF ordering below $T_N$, which could be viewed as a superposition of a 3D FM ordering of IS for Co$^{3+}$ and a 3D A-AF ordering for Co$^{4+}$ of S=1/2. The existence of IS for Co$^{3+}$ is clearly responsible for the observed FM-like behavior due to the ferromagnetic coupling between the S=1 of Co$^{3+}$ and the S=1/2 of Co$^{4+}$, which has been described as a Hund's rule coupling by Daghofer et al. based on a spin-orbital-polaron model argument. Such zero field FM behavior has been confirmed using AC susceptibilities, as shown in Fig. 2(b), where $\chi'$ shows a sharp cusp near $T_N$ only due to the large FM magnetization that cannot be flipped in-phase with the small AC field. These results are consistent with the A-AF spin structure proposed and with the zero-field neutron diffraction experiment via spin wave modulation, where the FM contribution from the dilute S=1 (IS) of Co$^{3+}$ in every other layer cannot be resolved from the A-type AF ordering of Co$^{4+}$ along the c-direction anyway.

To understand the spin dynamics of $x=0.82$ better, it is easier to separate the spins into two classes, the localized S=1/2 of Co$^{4+}$ at the corner of each $\sqrt{13}a$ superlattice and the spins of Co$^{3+}$ under IS/LS fluctuation. The increasing field would introduce additional IS into the layers that initially lacked IS, and as long as no spin flop occurs for $H< H_{sf}$, an evolution from the lowest population of $\alpha(H=0)=\frac{1}{12}\approx 4.2\%$ (i.e., one IS in every other superlattice cell) to the saturated level of $\alpha(H=\infty)\approx 8.3\%$ (i.e., one IS per superlattice cell) would be expected. The two extreme cases are shown in Fig. 3(b) and (d) as a mixed system of (FM IS for Co$^{3+}$)+(A-AF for Co$^{4+}$) for the former and a perfect A-AF for the latter. It is interesting to note that when $\frac{1}{12}\leq \alpha(H)\leq \frac{1}{13}$ in the low field condition, the incomplete AF cancellation of the antiferromagnetically aligned IS between neighboring layers would lead to a ferrimagnetic ordering of IS, as illustrated in Fig. 3(c). Considering the random nature of the IS state of Co$^{3+}$ in space and time, the in-plane FM coupling among Co$^{4+}$ spins could also be viewed as an effective Kondo coupling mediated by the itinerant electrons, although no conventional itinerant electrons are involved here; rather,
randomly selected Co$^{3+}$ electron sites fluctuate between the levels of a narrow gap ($b_{2g}^0 a_{1g}^0 - b_{2g}^0 a_{1g}$) as a result of $t_{2g}$ degeneracies lifted by the crystal field.

In summary, following the modified square-planar crystal field description of Co in the $CoO_2$ plane of $Na_0.52CoO_2$, the narrow $b_{2g}-a_{1g}$ gap for Co$^{3+}$ allows spin excitation from the LS ($S=0$) to the IS ($S=1$) state with sensitive thermal activation under the influence of field. The applied magnetic field was found to be effective in pinning an increased population in the IS state and shifting the weight of Boltzmann distribution. The ferromagnetically coupled spins of field-dependent IS for Co$^{3+}$ and the $S=1/2$ for Co$^{4+}$ order at low temperature into an A-type AF ordering at high field but a ferrimagnetic ordering at low field. In particular, depending on the magnetic field, the existence of IS is a necessary condition to induce the required in-plane FM spin coupling among the localized spins of $S=1/2$ for Co$^{4+}$ for the 3D ferrimagnetic or A-AF ordering below $T_N$. Since the A-type AF ordering is proposed and confirmed to exist under high field, but early neutron scattering experiments were performed in zero field without considering the existence of IS, we believe a comparative neutron scattering with and without applied field should help to verify the IS model proposed in this study.

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[1] K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature 422, 53 (2003).
[2] F. C. Chou, M.-W. Chu, G. J. Shu, F.-T. Huang, W. W. Pai, H.-S. Sheu, and P. A. Lee, Phys. Rev. Lett. 101, 127404 (2008).
[3] G. J. Shu, F.-T. Huang, M.-W. Chu, J.-Y. Lin, P. A. Lee, and F. C. Chou, Phys. Rev. B 80, 014117 (2009).
[4] L. Balicas, Y.-J. Jo, G. J. Shu, F. C. Chou, and P. A. Lee, Phys. Rev. Lett. 100, 126405 (2008).
[5] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B 56, 12885(R) (1997).
[6] M. Lee, L. Viciu, L. Li, Y. Wang, M. L. Foo, S. Watauchi, R. A. Pascal Jr., R. J. Cava, and N. P. Ong, Nature Materials 5, 537-540 (2006).
[7] K. Fujita, T. Mochida, and K. Nakamura, Jpn. J. Appl. Phys. 40, 4644647 (2001).
[8] Y. Wang, N. S. Rogado, R. J. Cava, and N. P. Ong, Nature 423, 42528 (2003).
[9] J. O. Haerter, M. R. Peterson, and B. S. Shastry, Phys. Rev. Lett. 97, 226402 (2006).
[10] P. Wissgott, A. Toschi, G. Sangiovanni, and K. Held, Phys. Rev. B 84, 085129 (2011).
[11] H. J. Xiang and D. J. Singh, Phys. Rev. B 76, 195111 (2007).
[12] G.G. Amatucci, J.M. Tarascon, and L.C. Klein, Journal of the Electrochemical Society 143, 1114 (1996).
[13] D. J. Singh, Phys. Rev. B 61, 13397 (2000).
[14] M. D. Johannes, I. I. Mazin, and D. J. Singh, Phys. Rev. B 71, 214410 (2005).
[15] S. Landron and M.-B. Lepetit, Phys. Rev. B 77, 125106 (2008).
[16] H.-B. Yang, Z.-H. Pan, A. K. P. Sekharan, T. Sato, S. Souma, T. Takahashi, R. Jin, B. C. Sales, D. Mandrus, A. V. Fedorov, Z. Wang, and H. Ding, Phys. Rev. Lett. 95, 146401 (2005).
[17] G. J. Shu and F. C. Chou, Phys. Rev. B 88, 155130 (2013).
[18] S. P. Bayrakci, C. Bernhard, D. P. Chen, B. Keimer, R. K. Kremer, P. Lemmens, C. T. Lin, C. Niedermayer, and J. Stempfier, Phys. Rev. B 69, 100410(R) (2004).
[19] J. L. Luo, N. L. Wang, G. T. Liu, D. Wu, X. N. Jing, F. Hu, and T. Xiang, Phys. Rev. Lett. 93, 187203 (2004).
[20] T. F. Schulze, P. S. Hafliger, Ch. Niedermayer, K. Mattenberger, S. Bubenkofer, and B. Batlogg, Phys. Rev. Lett. 100, 026407 (2008).
[21] F.-T. Huang, M.-W. Chu, G. J. Shu, H. S. Sheu, C. H. Chen, L.-K. Liu, P. A. Lee, and F. C. Chou, Phys. Rev. B 79, 014413 (2009).
[22] M. Roger, D. J. P. Morris, D. A. Tennant, M. J. Gutmann, J. P. Coff, J. U. Hoffmann, R. Feyherm, E. Dudzik, D. Prabhakaran, and A. T. Boothroyd, Nature 445, 631 (2007).
[23] H. Alloul, I. R. Mukhamedshin, A. V. Dooglov, Ya. V. Dmitriev, V.-C. Ciomaga, L. Pinsard-Gaudart, and G. Collin, Phys. Rev. B 85, 134433 (2012).
[24] J.-S. Rhyee, J. B. Peng, C. T. Lin, and S. M. Lee, Phys. Rev. B 77, 205108 (2008).
[25] M. Daghofer, P. Horsch, and G. Kahlilullin, Phys. Rev. Lett. 96, 216404 (2006).
[26] L. Balents, Nature 464, 199 (2010).
[27] R. M White, Quantum Theory of Magnetism, 3rd Ed., Springer.
[28] S. P. Bayrakci, I. Mirebeau, P. Bourges, Y. Sidis, M. Enderle, J. Mesot, D. P. Chen, C. T. Lin, and B. Keimer, Phys. Rev. Lett. 94, 157205 (2005).