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On the Origin of the Metallic and Anisotropic Magnetic Properties of Na_xCoO_2 ($x \approx 0.75$)

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Nonstoichiometric Na_xCoO_2 ($0.5 < x < 1$) consists of CoO_2 layers made up of edge-sharing CoO_6 octahedra and exhibits strongly anisotropic magnetic susceptibilities as well as metallic properties. A modified Curie–Weiss law was proposed for systems containing anisotropic magnetic ions to analyze the magnetic susceptibilities of Na_xCoO_2 ($x \approx 0.75$), and implications of this analysis were explored. Our study shows that the low-spin Co^{4+} ($S = 1/2$) ions of Na_xCoO_2 generated by the Na vacancies cause the anisotropic magnetic properties of Na_xCoO_2 and suggests that the six nearest-neighbor Co^{3+} ions of each Co^{4+} ion adopt the intermediate-spin electron configuration, thereby behaving magnetically like low-spin Co^{4+} ions. The Weiss temperature of Na_xCoO_2 is more negative along the direction of the lower g factor (i.e., $\theta_{\parallel} < \theta_{\perp} < 0$ and $g_{\parallel} < g_{\perp}$). The occurrence of intermediate-spin Co^{3+} ions surrounding each Co^{4+} ion accounts for the apparently puzzling magnetic properties of Na_xCoO_2 ($x \approx 0.75$), i.e., the large negative Weiss temperature, the three-dimensional antiferromagnetic ordering below ∼22 K, and the metallic properties. The picture of the magnetic structure derived from neutron scattering studies below ∼22 K is in apparent conflict with that deduced from magnetic susceptibility measurements between ∼50 and 300 K. These conflicting pictures are resolved by noting that the spin exchange between Co^{3+} ions is more strongly antiferromagnetic than that between Co^{4+} and Co^{3+} ions.

1. Introduction

The crystal structure of $NaCoO_2$ consists of CoO_2 layers made up of edge-sharing CoO_6 octahedra with Na atoms intercalated between the CoO_2 layers.[1−3] Stoichiometric $NaCoO_2$ is semiconducting, while nonstoichiometric Na_xCoO_2 ($0 < x < 1$) is metallic.[4] Since the discovery of superconductivity below ∼4.5 K in $Na_{0.3}CoO_2 \cdot 1.4H_2O$,[5] the unhydrated compound Na_xCoO_2 ($0 < x < 1$) has received much attention.[6−11] To understand charge and spin ordering in the Na-deficient compound Na_xCoO_2, it is crucial to know how the Na atoms are arranged in Na_xCoO_2.[8,11] The magnetic properties of Na_xCoO_2 ($0.5 < x < \sim 0.75$) show a Curie−Weiss behavior with a large negative Weiss temperature.[6,9,10] In particular, the magnetic susceptibilities measured for single-crystal samples of Na_xCoO_2 show a strong anisotropy;[7,9,10] the magnetic susceptibility $\chi_{\parallel}$ parallel to the c direction (i.e., the $c_{\parallel}$ direction, which is perpendicular to the CoO_2 plane) is smaller than the magnetic susceptibility $\chi_{\perp}$ perpendicular to the c direction (i.e., the $c_{\perp}$ direction, which

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(1) Fouassier, C.; Matejka, G.; Reau, J.-M.; Hagenmuller, P. *J. Solid State Chem.* **1973**, *6*, 532.
(2) Jansen, M.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1974**, *408*, 104.
(3) Takahashi, Y.; Gotoh, Y.; Akimoto, J. *J. Solid State Chem.* **2003**, *172*, 22.
(4) Delmas, C.; Braconnier, J. J.; Fouassier, C.; Hagenmuller, P. *Solid State Ionics* **1981**, *3/4*, 165.
(5) Takada, K.; Sakurai, H.; Takayama-Muromachi, E.; Izumi, F.; Dilanian, R.; Sasaki, T. *Nature (London)* **2003**, *422*, 53.
(6) Gavilano, J. L.; Rau, D.; Pedrini, B.; Hinderer, J.; Ott, H. R.; Kazakov, S. M.; Karpinski, J. *Phys. Rev. B* **2004**, *69*, 100404.
(7) Bayrakci, S. P.; Bernhard, C.; Chen, D. P.; Keimer, B.; Kremer, R. K.; Lemmens, P.; Lin, C. T.; Niedermayer, C.; Strempfer, J. *Phys. Rev. B* **2004**, *69*, 100410(R).
(8) Zandbergen, H. W.; Foo, M.; Xu, Q.; Kumar, V.; Cava, R. J. *Phys. Rev. B* **2004**, *70*, 024101.
(9) Chou, F. C.; Cho, J. H.; Lee, Y. S. *Phys. Rev. B* **2004**, *70*, 144526.
(10) Sales, B. C.; Jin, R.; Affholter, K. A.; Khalifah, P.; Veith, G. M.; Mandrus, D. *Phys. Rev. B* **2004**, *70*, 174419.
(11) Bayrakci, S. P.; Mirebeau, I.; Bourges, P.; Sidis, Y.; Enderle, M.; Mesot, J.; Chen, D. P.; Lin, C. T.; Keimer, B. *Phys. Rev. Lett.* **2005**, *64*, 157205.

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is parallel to the CoO_2 plane),[9,10] and the $\chi_\perp$ vs $\chi_\parallel$ curves show a very good linear relationship in the temperature region of 50−250 K.[9]

Chou et al.[9] and Sales et al.[10] analyzed the parallel and perpendicular magnetic susceptibilities χ_i ($i = \parallel, \perp$) of $Na_{0.75}CoO_2$ using the modified Curie−Weiss law

$$\chi_i = \chi_i^0 + \frac{C_i}{T - \theta_i} \tag{1}$$

where χ_i^0 represents temperature-independent contributions, which include the van Vleck paramagnetism and the core diamagnetism. The fitting parameters, χ_i^0, C_i, and θ_i, resulting from these analyses are somewhat puzzling. The Curie constant of a magnetic system is related to its effective moment at temperatures sufficiently high that the spin arrangement is random. Thus, one might expect $C_\parallel \approx C_\perp$, but $C_\perp$ is much larger than $C_\parallel$ (e.g., $C_\perp/C_\parallel \approx 2.44$ for $Na_{0.75}CoO_2$).[9] In general, a lower magnetic susceptibility is expected for the direction with a more negative Weiss temperature, but $\theta_\perp < \theta_\parallel < 0$ despite that $\chi_\perp > \chi_\parallel$ at a given temperature.[9,10] This situation arises because $C_\perp \gg C_\parallel$. In general, the temperature-independent contribution χ_i^0 should be small compared with χ_i, but the fitted χ_i^0 is nearly comparable to χ_i in magnitude (e.g., $\chi_\parallel^0/\chi_\parallel \approx 0.41$ at 50 K, and 0.61 at 250 K, in $Na_{0.75}CoO_2$).[9] In addition, χ_i^0 is strongly anisotropic (e.g., $\chi_\perp^0/\chi_\parallel^0 = 0.57$ for $Na_{0.75}CoO_2$).[9] The core diamagnetism cannot be anisotropic, and the van Vleck temperature-independent paramagnetism is often of the same order of magnitude as the diamagnetism but of opposite sign. Thus, there is no compelling reason that χ_i^0 should be so large and strongly anisotropic.

The nature of the magnetic structure of Na_xCoO_2 ($x \approx 0.75$) emerging from the neutron scattering[11−13] studies is in apparent conflict with that deduced from the magnetic susceptibility studies.[9,10] The neutron scattering studies of $Na_{0.82}CoO_2$[11] and $Na_{0.75}CoO_2$[12] carried out below 2 K led to the conclusion that Na_xCoO_2 ($x \approx 0.75$) has a type-A antiferromagnetic (AFM) structure; i.e., the spin exchange within each CoO_2 layer is ferromagnetic (FM) while that between adjacent CoO_2 layers is strongly AFM. Furthermore, FM spin fluctuations within the CoO_2 layers exist up to 200 K.[13] This finding is quite surprising because the Weiss temperatures $\theta_\perp$ and $\theta_\parallel$ are both strongly negative between 50 and 250 K, which indicates strong predominant AFM spin exchange. If the spin exchange between adjacent CoO_2 layers were to occur through the Co−O···O−Co supersuperexchange paths with very long interlayer O···O distances, strong AFM interlayer exchange interactions as the source of a negative Weiss temperature can be ruled out.[14]

In the present work, we address the apparently puzzling observations summarized above. In what follows, we propose a modified Curie−Weiss law, which allows one to describe magnetic systems composed of anisotropic magnetic ions. We then report results of our analysis of the anisotropic magnetic susceptibilities of $Na_{0.78}CoO_2$ measured for a single-crystal sample on the basis of the modified Curie−Weiss law. For the sake of comparison, we also analyze the anisotropic magnetic susceptibilities of $Na_{0.75}CoO_2$ reported by Chou et al.[9] and Sales et al.[10] Then we probe implications of our results concerning the apparently puzzling magnetic properties of Na_xCoO_2 ($x \approx 0.75$).

2. Anisotropic Character of a Low-Spin Co^{4+} (d^5) Ion at an Octahedral Site

The Co^{3+} (d^6) ions of $NaCoO_2$ have the low-spin (LS) configuration $(t_{2g})^6$ and, hence, are diamagnetic and semiconducting.[4] In a nonstoichiometric compound Na_xCoO_2 ($0.5 < x < 1$), the charge neutrality requires the presence of Co^{4+} (d^5) ions in mole fraction $1 - x$. To explain the metallic property of a nonstoichiometric Na_xCoO_2,[4] one might suppose the delocalization of the charges of the Co^{4+} ions, leading to partially empty t_{2g}-block bands. However, this picture does not explain the magnetic properties of Na_xCoO_2. To understand the anisotropic magnetic properties of Na_xCoO_2, it is necessary that the charge of a Co^{4+} ion remains localized (see section 5 for further discussion of the origin of the metallic properties of Na_xCoO_2). In principle, a Co^{4+} (d^5) ion at an octahedral site may adopt the high-spin (HS) configuration $(t_{2g})^3(e_g)^2$ ($S = {}^5/_2$), the intermediate-spin (IS) configuration $(t_{2g})^4(e_g)^1$ ($S = {}^3/_2$), or the LS configuration $(t_{2g})^5$ ($S = {}^1/_2$). A number of studies suggest that the Co^{4+} (d^5) ions of Na_xCoO_2 adopt the LS configuration.[15] The latter has an important consequence. The extensively studied layered magnetic compound $CoCl_2$, which is made up of edge-sharing $CoCl_6$ octahedra containing HS Co^{2+} (d^7) ions, exhibits anisotropic magnetic susceptibilities.[16] The electron configuration $(t_{2g})^5$ of a LS Co^{4+} ion in Na_xCoO_2 is the same as the electron configuration $(t_{2g})^5(e_g)^2$ of a HS Co^{2+} ion in $CoCl_2$, as far as the electron occupation of the t_{2g} levels is concerned. The magnetic anisotropy of $CoCl_2$ arises primarily from the $(t_{2g})^5$ configuration and is related to how the ground electronic state associated with this configuration is modified by the crystal field, spin−orbit interaction, and Zeeman effects.[16,17] As in the case of the $CoCl_6$ octahedra of $CoCl_2$, the CoO_6 octahedra of $NaCoO_2$ are slightly axially flattened (∠O−Co−O = 96.2°).[3] Therefore, the LS Co^{4+} ions of Na_xCoO_2 ($0.5 < x < 1$) should exhibit anisotropic magnetic properties just as do the HS Co^{2+} ions of $CoCl_2$, for which the g factors along the $c_\parallel$ and $c_\perp$ directions were estimated to be $g_\parallel = 3.38$ and $g_\perp = 4.84$.[16] To a first approximation, these g factors should be similar to those of LS Co^{4+} ions in Na_xCoO_2.

3. Curie−Weiss Law for Anisotropic Magnetic Systems

For our discussion, it is necessary to briefly review the mean-field treatment of Weiss for a magnetic system

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(12) Helme, L. M.: Boothroyd, A. T.; Coldea, R.; Prabhakaran, D.; Tennant, D. A.; Hiess, A.; Kulda, J. *Phys. Rev. Lett.* **2005**, *64*, 157206.

(13) Boothroyd, A. T.; Coldea, R.; Tennant, D. A.; Prabhakaran, D.; Helme, L. M.; Frost, C. D. *Phys. Rev. Lett.* **2004**, *92*, 197201.

(14) For recent reviews, see: (a) Whangbo, M.-H.; Koo, H.-J.; Dai, D. *J. Solid State Chem.* **2003**, *176*, 417. (b) Whangbo, M.-H.; Dai, D.; Koo, H.-J. *Solid State Sci.* **2005**, *7*, 827.

(15) (a) Gašparović, G.; Ott, R. A.; Cho, J.-H.; Chou, F. C.; Chu, Y.; Lynn, J. W.; Lee, Y. S. *Phys. Rev. Lett.* **2006**, *96*, 046403. (b) Choy, T.-P.; Galanakis, D.; Phillips, P., *arXiv: cond-mat/0502164*.

(16) Lines, M. E. *Phys. Rev.* **1963**, *131*, 546.

(17) Dai, D.; Whangbo, M.-H. *Inorg. Chem.* **2005**, *44*, 4407.

composed of isotropic magnetic ions.[18] For a given spin $\hat{S}$ interacting with an external magnetic field $\vec{H}$, the Zeeman energy is described by the Hamiltonian $\hat{H} = g\beta\hat{S}\cdot\vec{H}$, where g is the electron g factor and β is the Bohr magneton. In an extended magnetic system, a given spin also interacts with the magnetic field generated by its neighbor spins. Assuming predominant interaction with nearest-neighbor (NN) spins, the effective Hamiltonian in the mean-field approximation is written as

$$\hat{H} = g\beta\hat{S}\cdot\vec{H} + (zJ\vec{M}/Ng\beta)\cdot\hat{S} \tag{2}$$

where z is the number of NN spin sites interacting with the given spin through the spin-exchange parameter J, $\vec{M}$ is the molar magnetization, and N is Avogadro's number. Equation 2 can be rewritten in terms of the effective magnetic field $\vec{H}^{\text{eff}}$ acting on a given spin as

$$\vec{H}^{\text{eff}} = \vec{H} + zJ\vec{M}/Ng^2\beta^2 \tag{3}$$

When $\vec{H}^{\text{eff}}$ is small, $\vec{M} = \chi\vec{H}^{\text{eff}}$, where χ is the molar magnetic susceptibility. This relation and eq 3 lead to

$$\vec{M} = \frac{\chi\vec{H}}{1 - (zJ/Ng^2\beta^2)\chi} \tag{4}$$

The molar magnetic susceptibility that is actually measured, i.e., $\chi_i^{\text{eff}} = \vec{M}/\vec{H}$, is then expressed as

$$\chi_i^{\text{eff}} = \frac{\chi}{1 - (zJ/Ng^2\beta^2)\chi} \tag{5}$$

By replacement of χ with C/T (the Curie law),

$$\chi_i^{\text{eff}} = \frac{C}{T - (zJ/Ng^2\beta^2)C} = \frac{C}{T - \theta} \tag{6}$$

Given the Curie constant $C = Ng^2\beta^2S(S+1)/3k_B$, the Weiss temperature $\theta = zJS(S+1)/3k_B$ does not depend on the g factor.

For a system composed of anisotropic magnetic ions, it is necessary to modify the above treatment. When the g factors of an anisotropic magnetic ion of a layered compound along the $c_{||}$ and $c_{\perp}$ directions are labeled as $g_{||}$ and $g_{\perp}$, respectively, the magnetic susceptibility χ_i^{eff} measured with the magnetic field H_i ($i = ||, \perp$) can be written as

$$\chi_i^{\text{eff}} = \frac{C_i}{T - (zJ/Ng_i^{\,2}\beta^2)C_i} \tag{7a}$$

$$\chi_i^{\text{eff}} = \frac{C_i}{T - \theta_i} \qquad (i = ||, \perp) \tag{7b}$$

from which we find

$$1/\chi_i^{\text{eff}} = (1/C_i)T - \theta_i/C_i \qquad (i = ||, \perp) \tag{8}$$

As will be shown in the next section for Na$_x$CoO$_2$ ($x \approx 0.75$), in the temperature region (i.e., 50−300 K) where the $1/\chi_i^{\text{eff}}$ vs T plots are linear, the slope of the $1/\chi_{||}^{\text{eff}}$ vs T plot is nearly the same as that of the $1/\chi_{\perp}^{\text{eff}}$ vs T plot for Na$_x$CoO$_2$ ($x \approx 0.75$). This implies that the Curie constants $C_{||}$ and $C_{\perp}$ are approximately equal. Thus, one may write

$$C_{||} \approx C_{\perp} = Ng_{\text{av}}^{\;2}\beta^2S(S+1)/3k_B \tag{9}$$

where g_{av} is the "average" g factor that reproduces the slopes of the $1/\chi_i^{\text{eff}}$ vs T plots. Then, from eqs 7 and 9, we obtain

$$\theta_i \approx zJ(g_{\text{av}}/g_i)^2S(S+1)/3k_B \qquad (i = ||, \perp) \tag{10}$$

which leads to

$$\frac{\theta_{||}}{\theta_{\perp}} \approx \left(\frac{g_{\perp}}{g_{||}}\right)^2 \tag{11}$$

This expression shows that the Weiss temperature should be larger in magnitude along the direction of the smaller g factor.

To justify the above modification of the Curie−Weiss law, we note the expression of the anisotropic molar susceptibility Lines derived for the Co^{2+} ions of CoCl$_2$[16]

$$\chi_i = \frac{4N\beta^2(A_i + B_ik_BT/\lambda)}{4k_BT + 6J(1 + \sigma_i\alpha)} \qquad (i = ||, \perp) \tag{12}$$

where λ is the effective spin−orbit coupling constant for CoCl$_2$, $\sigma_{\perp} = 0$ and $\sigma_{||} = 1$, and

$$\alpha = 1 - \left(\frac{g_{||}}{g_{\perp}}\right)^2 \tag{13}$$

The parameters A_i and B_i are discussed below. If we set eq 12 equal to the modified Curie−Weiss law (eq 7), we find

$$C_{||} = (N\beta^2/k_B)(A_{||} + B_{||}k_BT/\lambda) \tag{14a}$$

$$C_{\perp} = (N\beta^2/k_B)(A_{\perp} + B_{\perp}k_BT/\lambda) \tag{14b}$$

$$\theta_{||} = (6J/4k_B)(1 + \alpha) \tag{15a}$$

$$\theta_{\perp} = 6J/4k_B \tag{15b}$$

The parameter A_i is proportional to the thermally averaged g_i^2, while B_i is the thermally averaged second-order Zeeman coefficient.[16] Plots of the parameters A_i and B_i as a function of λ/k_BT (Figure 3 of ref 16) indicate that, in the high-temperature region, $B_{||}$ and $B_{\perp}$ are proportional to λ/k_BT. The terms B_ik_BT/λ ($i = ||, \perp$) in the numerator of eq 12 are the slopes of the B_i vs λ/k_BT curves, which reveals that $B_{\perp}k_BT/\lambda$ is greater than $B_{||}k_BT/\lambda$ (i.e., 5.47 vs 4.53). In the high-temperature region, however, $A_{\perp}$ is smaller than $A_{||}$ (1.28 vs 2.21) such that $A_{||} + B_{||}k_BT/\lambda = A_{\perp} + B_{\perp}k_BT/\lambda$ ($\approx$6.75) and, hence, $C_{||} = C_{\perp}$. Furthermore, we obtain from eqs 13 and 15

$$\frac{\theta_{||}}{\theta_{\perp}} = 2 - \left(\frac{g_{||}}{g_{\perp}}\right)^2 \tag{16}$$

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(18) Smart, J. S. *Effective Field Theories of Magnetism*; W. B. Saunders Co.: Philadelphia, 1966.

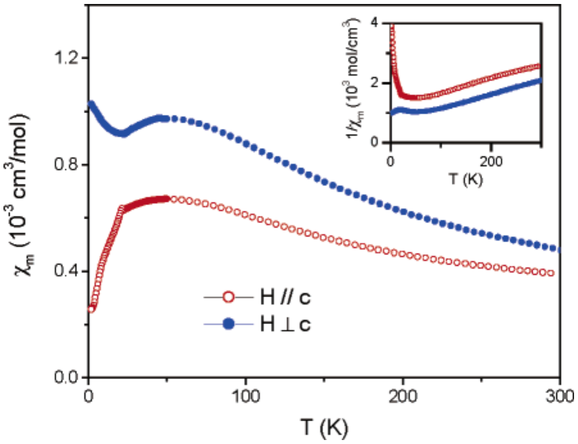

Figure 1. $\chi_{||}$ vs T and $\chi_\perp$ vs T plots measured for $Na_{0.78}CoO_2$. The inset shows the $1/\chi_{||}$ vs T and $1/\chi_\perp$ vs T plots.

This expression is different from eq 11, but similar results are obtained from both expressions (see below).

4. Anisotropic Magnetic Susceptibilities of Na_xCoO_2

Single-crystalline $Na_{0.78}CoO_2$ was grown in an optical floating-zone furnace. Sizable single crystals of approximate dimensions $2 \times 2 \times 0.5$ mm^3 were obtained by cleaving from the ingot. Their chemical composition was analyzed by inductively coupled plasma atomic emission spectroscopy. The c-axis lattice parameter of 10.765 Å, obtained from single-crystal X-ray diffraction measurements along (00l) at room temperature, agrees well with the literature value for samples with comparable Na content.[19] The homogeneity of the magnetic properties was further confirmed by muon spin rotation (μSR) measurements, which provide direct evidence for the occurrence of a bulk long-range magnetic order below 22 K.[20] The purely nonmagnetic signal (except for nuclear contributions) above 22 K also indicates the absence of any significant amount of magnetic impurity phases. The electronic properties of the crystal were further characterized by infrared ellipsometry measurements, which exhibit a strongly temperature-dependent weakly metallic behavior as well as a spin-dependent polaronic behavior in agreement with the report for $Na_{0.82}CoO_2$.[21] The anisotropic magnetic susceptibilities $\chi_{||}$ and $\chi_\perp$ were measured using a MPMS SQUID magnetometer (Quantum Design) in a field of 1 T.

The $\chi_{||}$ vs T and $\chi_\perp$ vs T plots of $Na_{0.78}CoO_2$ are presented in Figure 1. These plots were analyzed by using eq 8, without including a temperature-independent contribution as a fitting parameter. As shown in the inset of Figure 1, the curves of $1/\chi_{||}$ vs T and $1/\chi_\perp$ vs T are quite linear in the 50−300 K region. The linear parts of these plots lead to the values of $C_{||}$, $\theta_{||}$, $C_\perp$, and $\theta_\perp$ listed in Table 1, which reveals that $C_{||} \approx C_\perp$. The value of $C_{||} \approx C_\perp \approx 0.21$ for $Na_{0.78}CoO_2$ was calculated under the assumption of 0.22 mol of Co^{4+} ions per formula unit. Thus, for 1 mol of Co^{4+} ions, $C_{||} \approx C_\perp \approx$ 0.95 results. Using these values of the Curie constants and $S = {}^1/_2$ for a LS Co^{4+} ion in eq 9, we find $g_{av} \approx 3.18$. Note that $\theta_{||}/\theta_\perp \approx 245/144 \approx 1.7$, while $(g_\perp/g_{||})^2 \approx (4.84/3.38)^2 \approx 2.0$. Thus, the relationship $\theta_{||}/\theta_\perp \approx (g_\perp/g_{||})^2$ of eq 11 is supported. Moreover, $2 - (g_{||}/g_\perp)^2 \approx 1.5$, so that the relationship $\theta_{||}/\theta_\perp \approx 2 - (g_{||}/g_\perp)^2$ of eq 16 also holds.

Table 1. Fitting Parameters of the Anisotropic Magnetic Susceptibilities $\chi_{||}$ and $\chi_\perp$ of Na_xCoO_2 (x = 0.78 and 0.75) by the Modified Curie−Weiss Law[a]

x	H	$C_{\|\|}$	$\theta_{\|\|}$	$C_\perp$	$\theta_\perp$	$\theta_{\|\|}/\theta_\perp$
0.78[b]	1	0.208	−245	0.214	−144	1.70
0.75[c]	0.1	0.380	−420	0.387	−279	1.51
0.75[c]	5	0.315	−332	0.347	−206	1.61
0.75[d]	1	0.322	−354	0.310	−223	1.59

[a] H is in units of T, $\theta_{||}$ and $\theta_\perp$ are in units of K, and $C_{||}$ and $C_\perp$ are in units of cm^3·K/mol. [b] This work. [c] Reference 10. [d] Reference 9.

For comparison, the $\chi_{||}$ vs T and $\chi_\perp$ vs T data of $Na_{0.75}CoO_2$ reported by Chou et al.[9] and Sales et al.[10] were also analyzed by using eq 8, the results of which are summarized in Table 1. As expected, the values of $C_{||}$ and $C_\perp$ are approximately equal. The Weiss temperature is less negative for the $c_\perp$ direction than for the $c_{||}$ direction (i.e., $\theta_{||} < \theta_\perp < 0$) for both $Na_{0.78}CoO_2$ and $Na_{0.75}CoO_2$, and their $\theta_\perp/\theta_{||}$ ratios lie between $(g_{||}/g_\perp)^2$ and $2 - (g_{||}/g_\perp)^2$. The substantially negative Weiss temperatures $\theta_{||}$ and $\theta_\perp$ of Na_xCoO_2 ($x \approx 0.75$) suggest the presence of strong predominant AFM spin-exchange interactions. Because the interlayer Co−O···O−Co supersuperexchange should be negligible to a first approximation,[14] this means that the intralayer spin exchange should be strongly AFM. As was already mentioned, however, the neutron scattering studies[11,12] show that the intralayer spin exchange is FM while the interlayer spin exchange is strongly AFM. How to resolve these conflicting pictures will be discussed in section 5. In the remainder of this section, we will assume that the occurrence of strongly AFM spin exchange in Na_xCoO_2 ($x \approx 0.75$), deduced from the magnetic susceptibility measurements in the temperature region of ∼50−300 K, arises from the intralayer spin exchange.

The concentration of Co^{4+} ions in Na_xCoO_2 ($x \approx 0.75$) is low, and the susceptibility curves show a broad maximum at ∼50 K (see Figure 1), which is characteristic of low-dimensional short-range magnetic ordering. Therefore, if only the Co^{4+} ions are responsible for the observed AFM behaviors of Na_xCoO_2, it would be necessary for the Co^{4+} ions to form low-dimensional aggregates, e.g., chain fragments or rings with $z = 2$. Then, J refers to the NN spin-exchange interaction in such low-dimensional aggregates. On the basis of eq 10, the value of J for $Na_{0.78}CoO_2$ can be estimated by using $z = 2$, $\theta_{||} = -245$ K, $\theta_\perp = -144$ K, $g_{||} = 3.38$, $g_\perp = 4.84$, $S = {}^1/_2$, and $g_{av} \approx 3.18$. Thus, $J/k_B \approx -550$ K for the $c_{||}$ direction and $J/k_B \approx -670$ K for the $c_\perp$ direction. The value of J for $Na_{0.78}CoO_2$ can also be estimated by using eq 15, which is relevant for $z = 6$. These expressions lead to $J/k_B \approx -330$ K for the $c_{||}$ direction and $J/k_B \approx -290$ K for the $c_\perp$ direction. Thus, the value of J/k_B estimated from eq 10 is greater in magnitude than that found from eq 15 by a factor of about 2. This suggests that the z

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(19) Huang, Q.; Foo, M. L.; Pascal, R. A., Jr.; Lynn, J. W.; Toby, B. H.; He, T.; Zandbergen, H. W.; Cava, R. J. *Phys. Rev. B* **2004**, *70*, 184110.

(20) Bernhard, C.; et al., in preparation.

(21) Bernhard, C.; Boris, A. V.; Kovaleva, N. N.; Khaliullin, G.; Pimenov, A. V.; Yu, L.; Chen, D. P.; Lin, C. T.; Keimer, B. *Phys. Rev. Lett.* **2004**, *93*, 167003.

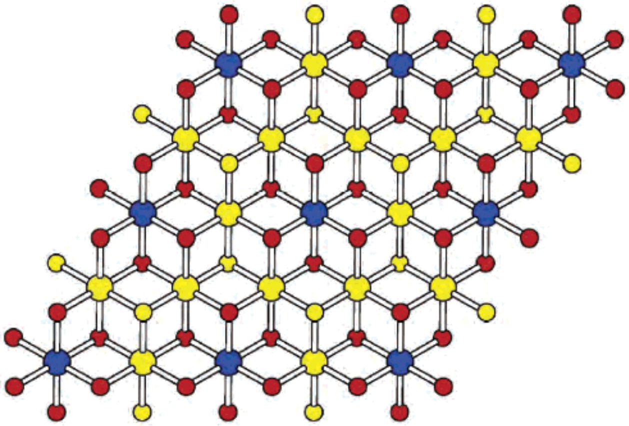

Figure 2. Ordered arrangement of the Co^{4+} ions in an isolated CoO_2 layer of $Na_{0.75}CoO_2$. The large blue circles represent the Co^{4+} ions, the large yellow circles the NN Co^{3+} ions, and the small red circles the O atoms attached to the Co^{4+} ions. To emphasize the site symmetry of the NN Co^{3+} ions, the O atoms linked only to the NN Co^{3+} ions are represented by small yellow circles.

value should be greater than 2. In any case, what is clear is that the intralayer spin exchange is quite strong in $Na_{0.78}CoO_2$. Though not shown, the same is found for $Na_{0.75}CoO_2$ using the values of $\theta_{\|}$ and $\theta_{\perp}$ listed in Table 1.

5. Discussion

So far, we have not considered the possibility that the CoO_6 octahedra of the Co^{3+} (d^6) ions of Na_xCoO_2 surrounding the Co^{4+} ions might undergo a slight change in geometry and that their preferred spin state may deviate from the diamagnetic state resulting from the electron configuration $(t_{2g})^6$ expected for the undistorted environment. Consider the six Co^{3+} ions in the immediate vicinity of a given Co^{4+} ion in Na_xCoO_2 (Figure 2). In a CoO_6 octahedron, a Co^{4+} ion requires shorter Co−O bonds than does a Co^{3+} ion. A given Co^{4+} ion can satisfy this requirement by shortening its six Co−O bonds. This will, in turn, lengthen those Co−O bonds of every Co^{3+} ion that are connected to the O atoms surrounding each Co^{4+} ion. For simplicity of our discussion, the six Co^{3+} ions surrounding a Co^{4+} ion will be referred to as the NN Co^{3+} ions. This Co−O bond lengthening will reduce the extent of the Co−O antibonding in, and, hence, lowers the energy of, the e_g levels of the NN Co^{3+} ions. Then, it becomes possible that the NN Co^{3+} ions may adopt the IS electron configuration $(t_{2g})^5(e_g)^1$ with $S = 1$, as has been proposed in the literature.[21,22] Each CoO_6 octahedron containing a NN Co^{3+} ion will lose the 3-fold rotational axis due to the unsymmetrical distortion associated with the Co−O bond lengthening (Figure 2). Therefore, its t_{2g} and e_g levels will each split. For convenience, the orbital designations t_{2g} and e_g will be used for the distorted CoO_6 octahedra containing NN Co^{3+} ions because the extent of the distortion would be small. The t_{2g} level occupation of an IS Co^{3+} ion, i.e., $(t_{2g})^5$, is the same as that of a LS Co^{4+} ion or a HS Co^{2+} ion. Therefore, the NN Co^{3+} ions are expected to provide anisotropic magnetic properties.

The above discussion implies that the actual mole fraction of the anisotropic spin sites in Na_xCoO_2 can be considerably larger than $1 - x$ because of the presence of NN Co^{3+} ions. If the Co^{4+} ions are similar to their NN Co^{3+} ions in their magnetic properties, they will form patches of geometrically frustrated spin arrangement [23] in which a given spin site may have as many as six neighbor sites (i.e., up to $z = 6$). This reduces the magnitude of the spin-exchange J/k_B value by a factor of up to 3 (i.e., down to approximately −200 K from eq 10, which is more consistent with about −300 K from eq 15).

The existence of a large number of active magnetic spin sites in Na_xCoO_2, much higher than expected from the charge neutrality requirement, and the presence of different spin sites (e.g., the LS Co^{4+} and IS Co^{3+} sites) are consistent with the μSR experiments on $Na_{0.82}CoO_2$[7] and $Na_{0.78}CoO_2$.[20] It also explains why Na_xCoO_2 ($x \approx 0.75$) can undergo a three-dimensional (3D) AFM ordering below ~22 K because the Co^{4+} ions and their NN Co^{3+} ions may become connected and cover the whole trigonal lattice of each CoO_2 layer. As an illustration, an ordered arrangement of the Co^{4+} ions in an isolated CoO_2 layer of $Na_{0.75}CoO_2$ is depicted in Figure 2. The possible presence of a large number of the IS Co^{3+} ions in Na_xCoO_2 ($0.5 < x < 1$) also allows one to understand why these nonstoichiometric compounds are highly magnetic as well as weakly metallic.[4,7] As was already discussed, the anisotropic magnetic properties of Na_xCoO_2 are explained by considering the $(t_{2g})^5$ electron configuration of the Co^{4+} site and their NN Co^{3+} sites. Each IS Co^{3+} site has one electron in the e_g level. The e_g levels of all CoO_6 octahedra, regardless of whether they contain Co^{4+} or Co^{3+} ions, overlap well to form wide e_g-block bands, which become partially filled because of the IS Co^{3+} ions. This then explains the observed metallic properties of nonstoichiometric Na_xCoO_2 ($0.5 < x < 1$).

It is of interest to note the dependence of the Curie constants and Weiss temperatures on the probing magnetic field. Sales et al.[10] reported magnetic susceptibility measurements of $Na_{0.75}CoO_2$ at $H = 0.1$ and 5 T. Our analysis of their susceptibility data shows that the Curie constants and Weiss temperatures decrease slightly in magnitude as the probing magnetic field increases (Table 1). This is a puzzling observation, but one might speculate whether it is caused by a very small amount of FM impurities in single-crystal samples. To prove this point, it would be necessary to carry out systematic magnetic susceptibility measurements as a function of the probing magnetic field. In any event, it should be emphasized that the main conclusions of our work are not affected by the above observation.

Finally, we discuss why the magnetic susceptibility and neutron scattering measurements of Na_xCoO_2 ($x \approx 0.75$) present conflicting magnetic pictures. It is important to recall that the Weiss temperatures of Na_xCoO_2 are determined from the linear part of the $1/\chi_i$ vs T plots ($i = \perp, \|$) well above the 3D magnetic ordering temperature of ~22 K (i.e.,

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(22) Khaliullin, G., *arXiv: cond-mat/0510025*.

(23) (a) Greedan, J. E. *J. Mater. Chem.* **2001**, *11*, 37. (b) Dai, D.; Whangbo, M.-H. *J. Chem. Phys.* **2004**, *121*, 672.

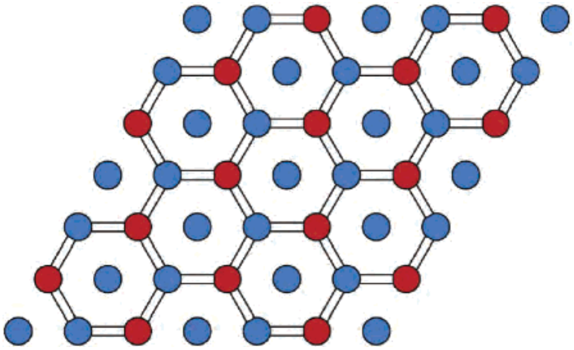

Figure 3. Model for the FM CoO_2 planes of $Na_{0.75}CoO_2$ below ~22 K. The honeycomb lattice of IS Co^{3+} spins has an AFM coupling between adjacent ions, while the LS Co^{4+} spins located at the hexagon centers are ferromagnetically ordered. The blue and red circles represent up-spin and down-spin sites, respectively.

between 50 and 300 K), whereas the neutron scattering experiments are performed well below that temperature (i.e., below ~2 K). For $x \approx 0.75$, almost the whole trigonal lattice of each CoO_2 layer is covered by the Co^{4+} and NN Co^{3+} ions. The most probable arrangement is close to the ordered arrangement shown for $x = 0.75$ in Figure 2; namely, the NN Co^{3+} ions form a honeycomb lattice in which the Co^{4+} ions occupy the hexagon centers. (The arrangement of the Co^{4+} and Co^{3+} ions should be intimately related to that of the Na^+ ions. To minimize electrostatic repulsion, Na^+ ions should be located closer to the Co^{3+} ions than to the Co^{4+} ions.) In the remainder of this work, we will assume that patches of such an arrangement of Co^{4+} and NN Co^{3+} ions cover each trigonal lattice of CoO_2 in Na_xCoO_2 when $x \approx 0.75$. To explain the metallic property of Na_xCoO_2, the e_g electron of each IS Co^{3+} ion should be slightly delocalized. This implies that the average spin $\langle S \rangle$ of each IS Co^{3+} would be lower than that of an isolated IS Co^{3+} ion, but should be considerably greater than that of each LS Co^{4+} ion. If we assume that the NN spin-exchange parameter J between adjacent LS Co^{4+} and IS Co^{3+} ions is the same as that between adjacent IS Co^{3+} ions, the NN spin-exchange energy $-J\hat{S}_i \cdot \hat{S}_j$ between two spin sites i and j should favor an AFM coupling between adjacent IS Co^{3+} ions over that between LS Co^{4+} and IS Co^{3+} ions. This will weaken the geometric spin frustration expected when magnetic ions cover a trigonal lattice and lead the honeycomb lattice of IS Co^{4+} ions to have an AFM coupling between all adjacent ions. As a consequence, the spin-exchange interaction of each LS Co^{4+} ion with its six nearest neighbors will be effectively zero (i.e., three AFM plus three FM interactions; Figure 3). The elastic neutron scattering measurements[11] of Na_xCoO_2 show the Bragg reflections below ~22 K that arise from ferromagnetically ordered CoO_2 planes with an average net moment of 0.13 μ_B per Co. The latter observation can be explained in terms of the FM ordering of the LS Co^{4+} ions, because the IS Co^{3+} ions of the honeycomb lattice will not contribute to these peaks because of their AFM coupling. Then the average effective moment expected from the elastic neutron scattering experiment is 0.25 μ_B per Co for $Na_{0.75}CoO_2$,[11] which is reasonable given the experimentally observed value of 0.13 μ_B per Co. It is also consistent with the heat capacity study of Na_xCoO_2,[7] which shows that a small fraction (i.e., ~10%) of the total available spins are involved in the long-range AFM ordering below ~22 K and the remainder is removed in short-range ordering above ~22 K.

The neutron scattering experiments[11,12] show that the intralayer spin exchange ($J_\perp$) and the interlayer spin exchange ($J_\parallel$) are quite substantial, and the interlayer spin exchange is stronger, in magnitude (i.e., $J_\perp = 3.3$ meV and $J_\parallel = -4.5$ meV in ref 11; $J_\perp = 6.0$ meV and $J_\parallel = -12.2$ meV in ref 12). Because the Co^{4+} ions are well separated from each other within and between CoO_2 layers, these strong interactions are difficult to understand in terms of the usual spin-exchange interactions resulting from localized spins, i.e., superexchange interactions involving Co−O−Co paths and supersuperexchange interactions involving Co−O···O−Co paths.[14] The spin wave dispersion of Na_xCoO_2 ($x \approx 0.75$) observed from the neutron scattering studies[11,12] are well reproduced by first-principles electronic band structure calculations.[24] It is most likely that the strong spin-exchange interactions of Na_xCoO_2 are mediated by the delocalized electrons of the e_g-block bands. The intralayer FM coupling can be explained if the e_g-block bands of each CoO_2 layer have a half-metallic character, because a FM coupling between the spins of the LS Co^{4+} ions with those of the conduction electrons leads effectively to a FM coupling between the spins of the LS Co^{4+} ions. This is quite likely because the electronic band structure calculations[24] for the FM state show a half-metallic character. (In other words, the intralayer FM coupling is mediated by a RKKY mechanism.[25] One might consider double-exchange[26] interactions between adjacent LS Co^{4+} and IS Co^{3+} ions as a cause for the intralayer FM coupling. However, this double-exchange mechanism cannot explain the strong predominant AFM spin exchange seen by the magnetic susceptibility measurements nor the very small effective magnetic moment on Co seen by the neutron scattering experiments.) In addition, an interlayer AFM coupling would be energetically more favorable than an interlayer FM coupling because the wave function of the AFM state has nodes between the CoO_2 layers, thereby preventing the CoO_2 layers from transferring some valence electron density from the CoO_2 layers into the region between them.[27]

6. Concluding Remarks

For a magnetic system made up of anisotropic magnetic ions, the Curie−Weiss law is modified as in section 3. The anisotropic magnetic susceptibilities of Na_xCoO_2 ($x \approx 0.75$) are well described by the modified Curie−Weiss law without including the temperature-independent contribution. Our analysis shows that $C_\parallel \approx C_\perp$, and the Weiss temperature is more negative along the direction of the lower g factor (i.e.,

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(24) Johannes, M. D.; Mazin, I. I.; Singh, D. J. *Phys. Rev. B* **2005**, *71*, 214410.

(25) (a) Rudemann, M. A.; Kittel, C. *Phys. Rev.* **1954**, *96*, 99. (b) Kasuya, T. *Prog. Theor. Phys.* **1956**, *16*, 45. (c) Yoshida, K. *Phys. Rev.* **1957**, *106*, 893.

(26) Zener, C. *Phys. Rev.* **1951**, *82*, 403.

(27) Villesuzanne, A.; Whangbo, M.-H. *Inorg. Chem.* **2005**, *44*, 6339.

$\theta_{\parallel} < \theta_{\perp} < 0$ and $g_{\parallel} < g_{\perp}$). The LS Co^{4+} ($S = {}^1/_2$) ions of Na_xCoO_2 generated by the Na vacancies lead to anisotropic magnetic properties, as do the HS Co^{2+} ($S = {}^3/_2$) ions of $CoCl_2$. The metallic and anisotropic magnetic properties of Na_xCoO_2 are accounted for if it is assumed that the six Co^{3+} ions surrounding each Co^{4+} ion adopt the IS electron configuration $(t_{2g})^5(e_g)^1$. Our analysis suggests that the magnetic properties of Na_xCoO_2 ($x \approx 0.75$) deduced from the magnetic susceptibilities in the temperature region of ∼50−300 K should arise from the intralayer spin-exchange interactions associated with the IS Co^{3+} and LS Co^{4+} ions. The magnetic susceptibility and neutron scattering studies of Na_xCoO_2 present apparently contradicting pictures of the magnetic structure. This conflict is resolved by noting that the AFM spin exchange between adjacent IS Co^{3+} ions is stronger than that between adjacent IS Co^{3+} and LS Co^{4+} ions, so an AFM coupling takes place between all adjacent IS Co^{3+} ions of the honeycomb lattice when the temperature is lowered toward ∼22 K. The spin wave dispersion seen from the inelastic neutron scattering studies below ∼2 K as well as the Bragg reflections of ferromagnetically ordered CoO_2 planes below ∼22 K should be related to the intralayer FM and interlayer AFM coupling between the LS Co^{4+} ions mediated by the delocalized conduction electrons of the partially filled e_g bands.

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