Thermodynamic Properties in the Approach to the Quantum Critical Point of the Spin-Ladder Material $Na_2Co_2(C_2O_4)_3(H_2O)_2$

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Magnetic susceptibility and heat capacity measurements as a function of temperature on a single-crystal sample of a spin-ladder material, $Na_2Co_2(C_2O_4)_3(H_2O)_2$, are reported. Principal susceptibilities, parallel and perpendicular to the ladder direction, respectively, show broad maxima around 22 and 17 K. Both susceptibilities decay exponentially down to about 5 K and thereafter they are essentially independent of temperature. These findings amount to a signature of a quantum phase transition from a spin-liquid to Néel ordered state previously predicted theoretically. No anomaly is found in the heat capacity around the transition temperature.

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Quantum phase transitions (QPT) have been extensively mined in a wide variety of systems [1]. Among them, magnetic systems form a very rich seam in which to observe QPT phenomena. Systems include itinerant electron magnets [2,3], heavy fermion compounds [4–10], two-dimensional quantum antiferromagnets [11], field-induced Néel order in a Haldane antiferromagnet [12], and spin glasses [13]. The system of interest here is a spin-ladder material, in which chains of antiferromagnetically coupled ions interact through an interchain coupling [14–21].

The ground state of a two-leg antiferromagnetic spin ladder is a singlet with an energy gap, Δ, to the lowest excited state. In a real material, because of the presence of an interladder exchange interaction, J', a magnetic long-range order, is observed [22,23]. The effects of interladder interaction on the phase transition in a spin $\frac{1}{2}$, two-leg Heisenberg antiferromagnetic ladder have been studied theoretically [24,25]. Troyer *et al.* [25] have shown from the numerical study that a QPT from disordered to Néel states occurs at a critical value of $J'/J \simeq 0.11$, where J is the exchange interaction within a ladder. In this QPT the control parameter J'/J is determined by material properties and it is difficult to change. However, if one can find a compound with J'/J close to 0.11, one could study the quantum critical behavior in a spin ladder. In this Letter, we demonstrate that $Na_2Co_2(C_2O_4)_3(H_2O)_2$ (abbreviated to SCO, hereafter) is a candidate compound.

SCO has a monoclinic crystal structure (space group $P2_1/c$) shown in Fig. 1. The lattice constants are $a = 5.864$ Å, $b = 15.723$ Å, $c = 6.963$ Å, and $\beta = 100.36°$ [26]. As is seen from Fig. 1(a), Co^{2+} ions form a ladder structure along the a axis. Co^{2+} ions are bridged by intervening oxalate molecules along the a axis and normal to it. The exchange interactions along the rung and ladder are denoted by J_1 and J_2, respectively. Ladders are coupled by an exchange interaction, J', in the bc plane as shown in Fig. 1(b). J' is weaker than either J_1 or J_2 because it arises from the exchange path through a hydrogen bond [26]. The temperature dependence of the magnetic susceptibility of a powder sample of SCO exhibits a broad maximum at about 21 K [26]. Price *et al.* analyzed the susceptibility data using several magnetic models and obtained $J_1 = J_2 \sim -4$ to -5 cm^{-1} and $J' \sim 0.2$ cm^{-1} [26].

Single crystals of SCO were synthesized following the procedure described in [26], and crystals with the sizes ~ 1.5 mm $\times$ 0.5 mm $\times$ 0.5 mm were obtained. Magnetic susceptibilities, χ, were measured with a Quantum Design Superconducting Quantum Interference Device magnetometer. An ultralow field option was used to reduce the remanent magnetic field to $\sim 5 \times 10^{-6}$ T at the sample position. The heat capacity was measured with a Quantum Design Physical Property Measurement System.

Figure 2 shows the temperature, T, dependence of χ parallel ($\chi_\parallel$) and perpendicular ($\chi_\perp$) to the ladder direc-

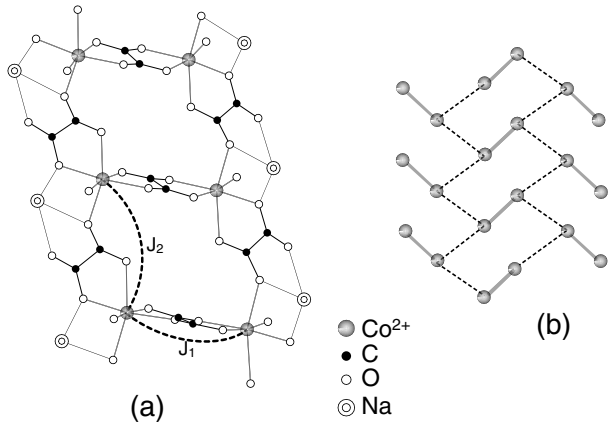

FIG. 1. (a) The crystal structure of $Na_2Co_2(C_2O_4)_3(H_2O)_2$. Hydrogen atoms are omitted for clarity. (b) The arrangement of the ladders in the bc plane normal to the ladder direction. Thick lines show the rungs of the ladders and dotted lines are drawn to show the exchange interaction path between the nearest neighboring Co atoms.

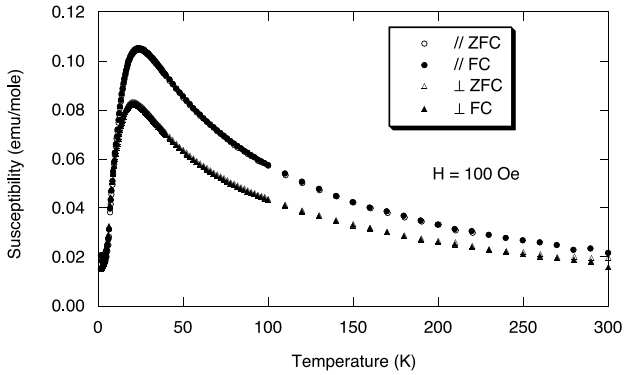

FIG. 2. The temperature dependence of the magnetic susceptibility parallel ($\|$) and perpendicular ($\perp$) to the ladder direction of a single-crystal sample of $Na_2Co_2(C_2O_4)_3(H_2O)_2$. ZFC means the measurement performed with warming after the sample had been cooled in zero field to 1.8 K and a magnetic field of 100 Oe had been applied there. While FC susceptibility was measured with cooling from 300 K in the same magnetic field.

tion. Both of $\chi_\|$ and $\chi_\perp$ increase with decreasing T and exhibit broad maxima, also observed on a powder sample [26]. This indicates that the ground state is a singlet. There is pronounced spatial anisotropy in the susceptibility: (1) $\chi_\|$ is larger than $\chi_\perp$ at temperatures above about 10 K and (2) the temperature at which χ is maximum is higher for $\chi_\|$ than $\chi_\perp$. We note, however, that $\chi_\|$ and $\chi_\perp$ are almost identical below about 10 K (see Fig. 3 for details). No appreciable anisotropy in $\chi_\perp$ in the plane normal to the a axis is observed. We measured both of the zero-field-cooling (ZFC) and field-cooling (FC) runs. A small difference between the FC and ZFC susceptibilities is seen at low temperatures (see Fig. 3 for details). We fitted the measured susceptibility, $\chi_{\rm meas}$, at high temperatures ($100\ {\rm K} < T < 300\ {\rm K}$) to the formula, $\chi_{\rm meas} = \chi_0 + C/(T - \Theta)$. Here, the first term represents a temperature-independent susceptibility, such as the diamagnetic susceptibility due the constituent atoms, and the second term is the Curie-Weiss susceptibility. We obtain $\chi_0 \simeq -8 \times 10^{-3}$ emu/mole, and this value is larger than the diamagnetic susceptibility (-1.39×10^{-4} emu/mole) of this sample estimated in Ref. [26].

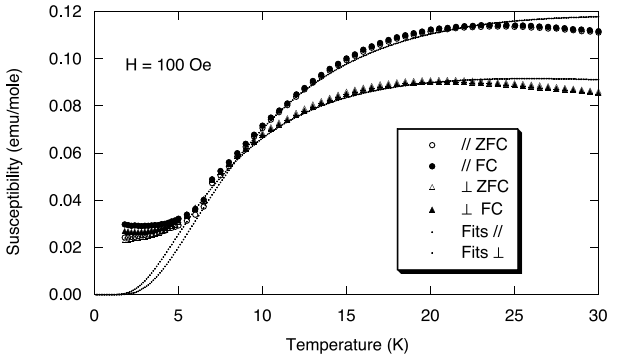

FIG. 3. The low temperature part of the magnetic susceptibility of a single-crystal sample of $Na_2Co_2(C_2O_4)_3(H_2O)_2$ parallel ($\|$) and perpendicular ($\perp$) to the ladder direction. The dotted lines are theoretical ones discussed in the text.

In Fig. 3 we display the low temperature part of the T dependence of $\chi_\|$ and $\chi_\perp$. The data are well represented by the formula for a spin, $S = \frac{1}{2}$ two-leg Heisenberg ladder [21],

$$\chi = ae^{-\Delta/T}/\sqrt{T}, \tag{1}$$

where a is a constant. In Fig. 3 we see that Eq. (1) is good for temperatures between 20 (17 K for $\chi_\perp$) and 7 K. From the fitting, $a_\| = 1.1$, $\Delta_\|/k_{\rm B} = 16$ K, and $a_\perp = 0.77$, $\Delta_\perp/k_{\rm B} = 13$ K, where $k_{\rm B}$ is the Boltzmann's constant. A noteworthy feature of the susceptibilities is that below about 5 K they deviate from the prediction of Eq. (1) and become less temperature dependent.

Figure 4 shows the T dependence of χ measured at designated magnetic fields applied along the ladder direction. With increasing magnetic field, H, the temperature at which $\chi_\|$ is maximum, shifts down. This behavior of the H dependence of χ is explained as due to a decrease in Δ with H. With the application of H, excited states Zeeman split and the energy of one of the lowest excited state decreases with H resulting in a decrease in the spin gap. We observed a similar behavior in $\chi_\perp$. It is noted that the magnetic susceptibility, defined as M/H where M is the magnetization of the sample, converges to a finite value ($\simeq$0.02 emu/mole in this case) with decreasing temperature.

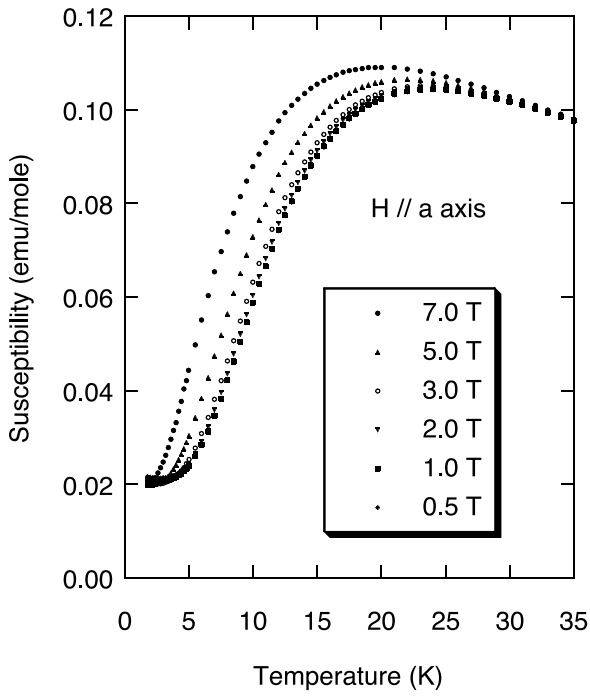

FIG. 4. The temperature dependence of the magnetic susceptibility of a single-crystal sample of $Na_2Co_2(C_2O_4)_3(H_2O)_2$ measured in magnetic fields applied to the ladder direction.

We measured the heat capacity, C, on the same single-crystal of SCO. Figure 5 shows the T dependence of C measured in zero field. A broad peak associated with the formation of the spin gap is observed. We have analyzed the data using the low temperature formula for an $S = \frac{1}{2}$ two-leg Heisenberg ladder [21],

$$C = bT^{-3/2}e^{-\Delta/T}, \quad (2)$$

where b is a constant and we took only the first term in Eq. (39) of Ref. [21] [27]. From the fitting we get $b = 1.5 \times 10^3$ ($\mathrm{JK^{-1}\,mol^{-1}}$) and $\Delta/k_B = 20$ K. Since Eqs. (1) and (2) are approximate, the difference in the values of Δ determined from the susceptibility and heat capacity measurements is not significant.

The ground state of a free Co^{2+} ($3d^7$) is ^4F with total orbital angular momentum, $L = 3$ and total spin, $S = \frac{3}{2}$. In an octahedral crystal field, the orbital degeneracy is partially lifted and the ground state is a triplet with effective orbital momentum, $\tilde{l} = 1$ [28]. In the presence of a spin-orbit coupling between $\tilde{l}$ and S, there are six Kramers doublets. A tetragonal distortion of the crystal field lifts the degeneracy in these Kramers doublets and, in favorable cases, we can take only the lowest Kramers doublet to discuss the magnetism at low temperatures (typically, below $\sim$100 K). In consequence, we may use a fictitious spin $\frac{1}{2}$. For the fictitious spin system the g value and exchange interactions become anisotropic. From the analysis of the heat capacity data, we find that the entropy is about 67% of $R\ln(2)$ at 20 K, where R is the gas constant. This finding justifies the use of only the lowest Kramers doublet and the fictitious spin $\frac{1}{2}$ in our discussion. (If one assumed spin only, $S = \frac{3}{2}$, for Co^{2+} as in Ref. [26], the entropy would be doubled.) To the best of our knowledge, there are no theory on spin ladders with Ising anisotropy. So, henceforth we assume that the results of the existing theories on spin $\frac{1}{2}$ Heisenberg ladders predict qualitatively the same behavior for a spin $\frac{1}{2}$ ladder with an Ising anisotropy.

One may argue that the almost temperature-independent χ in Fig. 3 might come from the sum of the intrinsic χ, which decays exponentially to zero, and a Curie tail due to magnetic impurities which increases as T^{-1} with $T \to 0$. Since the magnetization of a paramagnet obeys the Brillouin function, it saturates at high fields, $g\mu_B H/k_B T > 1$, where μ_B is the Bohr magneton. Then, the field dependence of $\chi(= M/H)$ in Fig. 4 should decrease with increasing H at a given temperature, in contradiction to the observation. The behavior of χ in Fig. 3 is very similar to the theoretical one reported in Ref. [25]. Theory predicts that the coupled spin ladder is in a spin-liquid state for J' smaller than $0.11J$ and the susceptibility vanishes as $T \to 0$. For $J' > 0.11J$, a QPT takes place from the spin-liquid to Néel state. By comparison with the theory, we estimate $J'/J \sim 0.15$ in SCO, which is close to the critical value $J'/J \simeq 0.11$. Note that the critical value $J'/J = 0.11$ obtained in Ref. [25] is valid only when $J_1 = J_2 = J$ and when no anisotropies are present. In the material at hand, where anisotropies are present, the number 0.11 will only give a rough estimate for the critical coupling. The T dependence of C in Fig. 5 shows no sharp anomaly around 5 K associated with the possible Néel order. This suggests that the anomaly is too small to be detected experimentally. A peculiar behavior of the susceptibility in SCO at low temperatures is the loss of anisotropy, and $\chi_\parallel$ and $\chi_\perp$ are almost identical below $\simeq$ 10 K. When an antiferromagnetic long-range order sets in, χ parallel to the sublattice magnetization, M_s, decreases to zero as $T \to 0$, while χ perpendicular to M_s is almost independent of T. If there is no anisotropy in the system, M_s turns its direction normal to H to gain the magnetic energy even in an infinitesimal H. In this case χ is independent of T in the lowest order. This scenario fits our observation. However, it remains to be answered why the anisotropy vanishes at the low temperatures.

In conclusion, we measured the magnetic susceptibility and heat capacity of a single-crystal sample of a spin-ladder compound SCO. Principal susceptibilities parallel and perpendicular to the ladder direction show broad maxima at about 22 and 17 K, respectively. Both parallel and perpendicular susceptibilities decay exponentially at low temperatures down to about 5 K, below which the susceptibilities are almost independent of temperature. These results are discussed in the context of a quantum phase transition (QPT) which is predicted theoretically. No anomaly is found in the heat capacity associated with the transition. Further experimental study with neutron scattering, nuclear magnetic resonance, or muon spin rotation

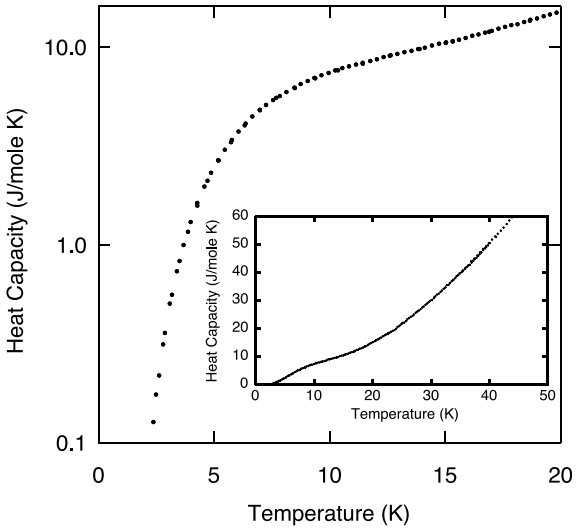

FIG. 5. The temperature dependence of the heat capacity, including the contribution of lattice, of a single-crystal sample of $Na_2Co_2(C_2O_4)_3(H_2O)_2$ measured in zero field plotted in a logarithmic scale. Inset shows the temperature dependence of the heat capacity plotted in a linear scale for a wider temperature range.

techniques will unveil the nature of the phase transition. It would be interesting to try to dope holes or electrons into the sample to find a possible superconductivity [16,29]. There are no theories for a spin ladder with an Ising anisotropy. The introduction of an Ising anisotropy would decrease the critical value J'/J for the emergence of a QPT from 0.11 and the long-range order would set in at a higher temperature than the Heisenberg case. It would also be interesting to calculate how the excitation spectra change with increasing anisotropy. We hope that the present experiment will stimulate theoretical work on a spin ladder with an Ising anisotropy.

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