RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 13 1 NOVEMBER 1987

Neutron scattering study of magnetic excitations in intercalated $CoCl_2$

H. Zabel
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801

S. M. Shapiro
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973
(Received 22 June 1987)

We have studied by inelastic neutron scattering the magnetic excitations of $CoCl_2$ layers intercalated in graphite. At 4.5 K the stage-2 compound exhibits ferromagnetic xy-type interactions within the Co^{2+} sheets, which are weakly antiferromagnetically coupled along the hexagonal c axis. The magnon dispersion curve was measured for spin waves propagating within the basal planes up to the first powder-average Brillouin zone. At small wave vectors, a splitting of the branch occurs, indicative of weak interplanar coupling. A fit to the measured excitation energies yields exchange and anisotropy parameters which are in good agreement with susceptibility data.

Pristine cobalt dichloride, $CoCl_2$, exhibits a layer-type magnetic structure which approximates a two-dimensional (2D) xy spin system at low temperatures with weak antiferromagnetic coupling between the Co^{2+} sheets.[1] Complete trilayer units of Cl^--Co^{2+}-Cl^- can also be inserted between graphite basal planes with essentially no structural alteration of the ionic bond lengths.[2] This intercalation process effectively reduces the ratio of the inter- to the intraplanar interaction from 10^{-1} in pristine $CoCl_2$ to about 10^{-3} in stage 2 (=two graphite basal planes between any consecutive $CoCl_2$ trilayers) intercalation compounds.[3] There has been much recent interest in the study of these $CoCl_2$-graphite intercalation compounds ($CoCl_2$-GIC's) since it was suggested that a Kosterlitz-Thouless-type phase may exist at low temperatures.[4,5] We are reporting here the first study of spin excitations in any of the transition-metal dichloride intercalation compounds.

The stage-2 $CoCl_2$-GIC has been particularly well characterized by previous susceptibility and elastic neutron scattering experiments.[3,6,7] The main results shall be briefly summarized here to the extent that they pertain to the present experiment. The structure of the compound is schematically shown in the inset of Fig. 1. The triangular $CoCl_2$ sublattice is translationally incommensurate with respect to the graphite basal planes, but locked into a 30° orientation relative to the graphite [100] axis. Unlike pristine $CoCl_2$, intercalated $CoCl_2$ forms coherent islands between the graphite planes of roughly 800-Å diameter. Careful Hendricks-Teller analysis[7] of the (00l) nuclear Bragg reflections indicated that the nominal stage-2 sample used in this experiment is actually composed of a number of stage fractions with fractional weights of 5.5%, 70%, 14%, 8%, and 2.5% for the stages 1, 2, 3, 4, and 5, respectively.

Susceptibility as well as magnetic neutron scattering confirmed that the magnetic ordering process proceeds in two steps.[6,7] At $T_u = 9.5$ K in-plane ferromagnetic ordering of the Co^{2+} ions occurs with the spins oriented parallel to the planes, and at $T_L = 8.5$ K the adjacent Co^{2+} planes couple weakly antiferromagnetically. A recent line-shape analysis[8] of the ferromagnetic neutron scattering could not provide evidence for the existence of a Kosterlitz-Thouless vortex state in the intermediate temperature range between T_u and T_L. Nevertheless, the magnetic excitations might be expected to resemble those of a 2D xy spin system to a better extent than in pristine $CoCl_2$.

The present system can be described by the effective spin-$\frac{1}{2}$ Hamiltonian:[9]

$$H = -J \sum_{i>j} (S_i^x S_j^x + S_i^y S_j^y) - J(1 - J_A/J) \sum_{i>j} S_i^z S_j^z + 2J' \sum_{im} \mathbf{S}_i \cdot \mathbf{S}_m \,. \quad (1)$$

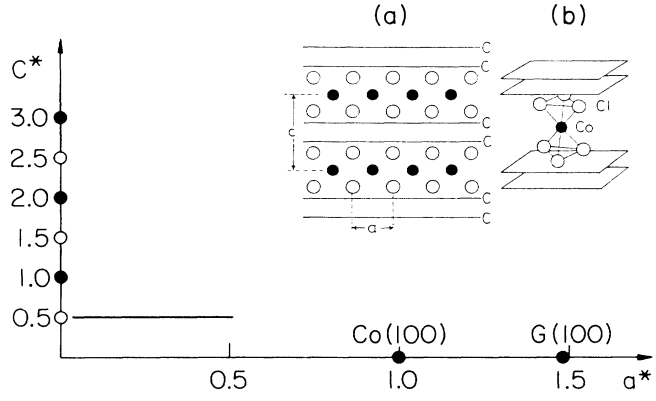

FIG. 1. Partial plane of the reciprocal lattice of $CoCl_2$-GIC. Full dots indicate nuclear reciprocal-lattice points, open circles antiferromagnetic reciprocal-lattice points. a^* refers to the $CoCl_2$ in-plane reciprocal-lattice vector and c^* to the reciprocal-lattice direction normal to the graphite and intercalate planes. The Co(100) and G(100) reciprocal-lattice points of the $CoCl_2$ and graphite lattice, respectively, are in fact reciprocal-lattice rods due to the lack of correlation along the c axis. The heavy line indicates the direction along which the magnetic excitations have been measured. The inset shows the crystal structure of the stage-2 $CoCl_2$-graphite intercalation compound. (a) Edge-on view of the layers: The metal Co^{2+} ions are indicated by closed circles, Cl^- by open circles, and graphite layers by solid lines. Arrows indicate the a and c axis. (b) The structure in a perspective view.

Here J is the in-plane ferromagnetic exchange coupling, J' is the interplanar antiferromagnetic coupling, and J_A is the anisotropy exchange interaction. The first two sums extend over nearest neighbors within the same Co^{2+} plane, and the last sum is over nearest neighbors in adjacent layers. Values for the exchange constants as determined by magnetization measurements[3] are listed in Table I.

The sample preparation has been described in detail elsewhere.[7] It should only be noted here that about 40–50 intercalated single-crystal Kish graphite crystallites were assembled to give a crystal texture similar to pyrolytic graphite with a c-axis mosaic spread of about 10° and random orientation of the a and b axis.

The inelastic neutron scattering measurements were carried out on the triple-axis spectrometers H7 of the Brookhaven National Laboratory High-Flux Reactor. Pyrolytic graphite was used as monochrometer and analyzer and the collimation was either 40′-20′-20′-40′ or 40′-20′-40′-40′. Most data were collected at 4.5 K with final energy fixed at 14.7 and a pyrolytic graphite filter in the scattered beam. Spin excitations at $q < 0.1$ $(4\pi/\sqrt{3}a)$ were measured at the cold neutron source on spectrometer H9 with a fixed final energy of 4.0 meV. In Fig. 1, a partial plane of the reciprocal lattice of stage-2 $CoCl_2$–GIC is shown. The heavy line indicates the direction along which the spin-wave energies have been measured. Figure 2 displays typical scans at (0.36, 0, 0.5) and (0.035,0,0.5) in units of $4\pi/\sqrt{3}a$ and $2\pi/c$, respectively, where $a = 3.55$ Å is the $CoCl_2$ in-plane lattice parameter and $c = 12.65$ Å is the c-axis repeat distance of the stage-2 $CoCl_2$–GIC. In Fig. 2(a) is also shown a high-temperature scan at 20 K, which clearly demonstrates that the excitations seen at 4.5 K are of magnetic nature. The complete dispersion is shown in Fig. 3. Other measurements along $q \| c$ showed that the frequency of the excitations was independent of c, which is consistent with the two-dimensional nature of the system. It should be noted that because of the in-plane powder average the Brillouin zone indicated at $q = 0.5$ $(4\pi/\sqrt{3}a)$ is not very well defined. At small q values a splitting of the dispersion is observed indicating the presence of interplanar coupling. Because of the rather large mosaic of the sample, it was not possible to follow the dispersion for $q < 0.05$. The full line in Fig. 3 represents a fit to the measured spin excitations which is described below. For comparison, in Fig. 3 is also reproduced the spin dispersion of pristine $CoCl_2$ according to the work of Hutchings.[1]

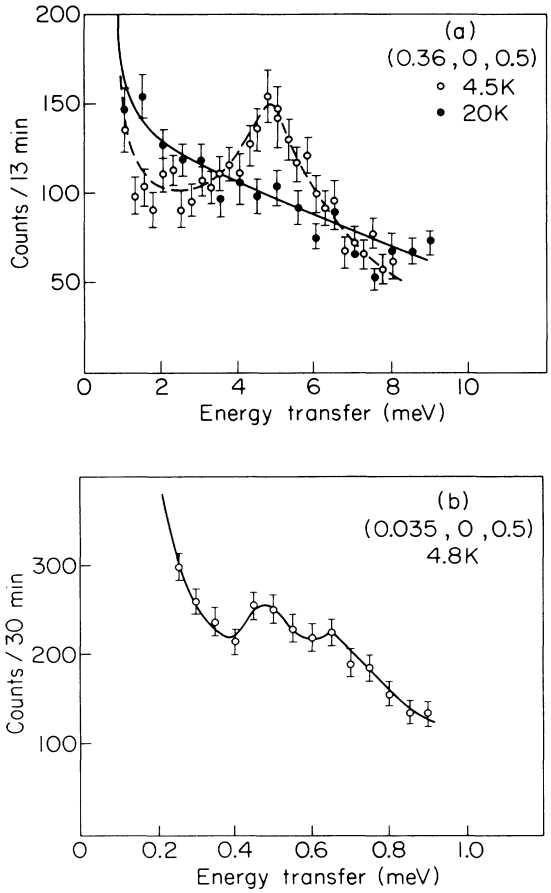

FIG. 2. Spin-wave intensity profiles. (a) Profile at (0.36, 0,0.5) measured at thermal-neutron source (H7) with fixed final energy of 14.7 meV and 40′-20′-20′-40′ collimation. (b) Profile at (0.035,0,0.5) measured at cold neutron source (H9) with fixed final energy of 4.0 meV and 60′-40′-60′-40′-40′ collimation.

TABLE I. Parameters of the spin Hamiltonian for stage $CoCl_2$–GIC's determined from susceptibility (Ref. 3) and from present magnetic excitation measurements. For comparison in the last column the corresponding values for pristine $CoCl_2$ are reproduced from the work of Hutchings (Ref. 1).

	Stage-2 $CoCl_2$–GIC		Pristine $CoCl_2$
	Susceptibility[a]	Spin waves	Spin waves[b]
J	31.0 K	14.6 ± 2 K	28.5 K
J_A/J	0.48	0.50	0.56
J'/J	8.6×10^{-4}	2.5×10^{-2}	7.5×10^{-2}

[a]Reference 3. Notice that due to different definition of the Hamiltonian in Eq. (4) as compared to Eq. (16) in Ref. 3, J is multiplied by factor of 4.
[b]Reference 1.

According to Hutchings,[1] the spin excitations in $CoCl_2$ in zero magnetic field at a point q relative to a magnetic Bragg point $\mathbf{G}_m$ are given by

$$E_{1,2}(q) = \bar{S}[(zJ - J_q \pm z'J' + J'_q) \times (zJ - J_q + z'J' \mp J'_q + zJ_A)]^{1/2} , \quad (2)$$

with

$$J_q = J \sum_{i=1}^{z} e^{i\mathbf{q}\cdot\mathbf{r}_i}, \quad J'_q = J' \sum_{i=1}^{z'} e^{i\mathbf{q}\cdot\mathbf{r}'_i} . \quad (3)$$

Here $\bar{S}(=\frac{1}{2})$ is the effective spin, $z(=6)$ is the number of nearest-neighbor spins in the same layer, and $z'(=2)$ is the number of nearest neighbors in adjacent planes. For

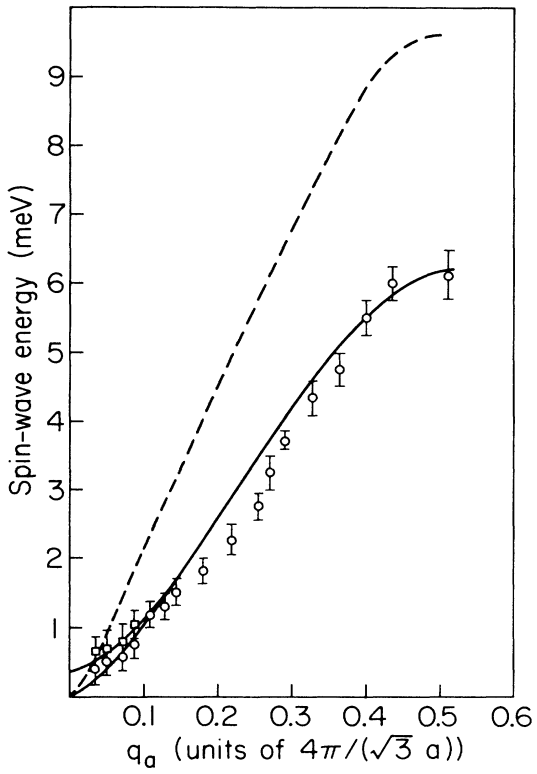

FIG. 3. Spin-wave energy dispersion in $CoCl_2$-GIC at 4.5 K. The solid lines are calculated spin-wave energies according to Eqs. (5) and (6). The dashed line indicates the spin-waves dispersion of pristine $CoCl_2$ as measured by Hutchings (Ref. 1).

the in-plane interaction a 2D powder average has to be taken:

$$\langle J_q \rangle = J \left\langle \sum_{i=1}^{6} e^{i\mathbf{q}\cdot\mathbf{r}_i} \right\rangle = 6JJ_0(qr_\parallel) \ , \tag{4}$$

where $|\mathbf{r}_i| = r_\parallel$ are the in-plane nearest-neighbor distances, and J_0 is the zero-order Bessel function. Since $\mathbf{q}_\parallel \cdot \mathbf{r}_i' \approx 0$ in the present scattering geometry, the terms containing the out-of-plane interaction reduce to $[z'J' - J_q'] \approx 0$ and $(z'J' + J_q') \approx 4J'$. We then obtain, for the spin-wave energies,

$$E_1(q) = 6J\bar{S}\left[[1 - J_0(qr_\parallel)]^2 + \left(\frac{J_A}{J} + \frac{2}{3}\frac{J'}{J} \right) \times [1 - J_0(qr_\parallel)] + \frac{2}{3}\frac{J'J_A}{J^2} \right]^{1/2} , \tag{5}$$

and

$$E_2(q) = 6J\bar{S}\left[[1 - J_0(qr_\parallel)]^2 + \left(\frac{J_A}{J} + \frac{2}{3}\frac{J'}{J} \right) [1 - J_0(qr_\parallel)] \right]^{1/2} . \tag{6}$$

The last term in $E_1(q)$ is independent of q and describes the gap observed at $q \to 0$, whose size depends on the interplanar interaction and the single-ion anisotropy exchange interaction. A satisfactory fit to the measured spin dispersion has been obtained with the coupling parameters listed in Table I. Those parametrs agree reasonably well with the values obtained from the susceptibility measurements. The exact value for J'/J depends sensitively on the gap size, which could not be experimentally determined with high accuracy. The lower branch shows a linear dispersion for small q's in good agreement with the assumption of an xy spin system. Because of the experimental uncertainty as small q values, it is difficult to state unambiguously whether this branch is gapless at $q = 0$, as would be the case for an ideal xy system, or rather exhibits a small gap reminiscent of a slight in-plane anisotropy. A marked feature of the experimental dispersion curve is the waviness which occurs for $0.15 < q < 0.3$. The origin of this feature is not clear and is not reproduced by the present fit.

In conclusion, we have measured for the first time the spin-wave energies of any magnetic ions intercalated in graphite. In this intercalation compound, the $CoCl_2$ layers are separated on the average by two graphite basal planes. The experimental dispersion, determined at 4.5 K, conforms to a 2D xy ferromagnetic spin system with weak antiferromagnetic interplanar coupling. The interaction parameters obtained from a fit to the dispersion agree reasonably well with those from magnetization measurements, except for J' which is very dependent upon the value of the energy of the lower branch at $q = 0$. It would be of considerable interest to study the temperature variation of the spin dynamics, in particular, close to the upper transition temperature at $T_u = 9.5$ K, where one might expect a central peak from diffusive xy fluctuations. These experiments are currently in progress.

We would like to acknowledge stimulating discussions with R. J. Birgeneau, P. A. Lindgård, and M. Suzuki, and help with the sample preparation by D. G. Wiesler. One of us (H.Z.) wishes to thank the Brookhaven National Laboratory for the generous hospitality during his stay there. The work at Brookhaven was supported by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC02-76CH00016. The work at the University of Illinois at Urbana-Champaign is funded by the National Science Foundation under Contract No. NSF-DMR 86-05565.

[1]M. T. Hutchings, J. Phys. C **6**, 3143 (1973).

[2]For recent short reviews of graphite intercalation compounds and their magnetic properties, see M. S. Dresselhaus, *Festkörperprobleme (Advances in Solid State Physics)*, edited by P. Grosse (Vieweg, Braunschweig, 1985), Vol. 25, p. 21; M. S. Dresselhaus, Phys. Today **37** (No. 3), 60 (1984); H. Zabel and P. C. Chow, Comments Condens. Matter Phys. **12**, 225 (1986).

[3]D. G. Wiesler, M. Suzuki, P. C. Chow, and H. Zabel, Phys. Rev. B **34**, 7951 (1986).

[4]M. Suzuki, H. Ikeda, and Y. Endoh, Synth. Met. **8**, 43 (1983).

[5]M. Elahy, M. Shayegan, K. Y. Szeto, and G. Dresselhaus, Synth. Met. **8**, 35 (1983).

[6]D. G. Wiesler, M. Suzuki, H. Zabel, S. M. Shapiro, and R. M. Nicklow, Physica B **136**, 22 (1986).

[7]D. G. Wiesler, M. Suzuki, and H. Zabel, this issue, Phys. Rev. B **36**, 3695 (1987).

[8]D. G. Wiesler and H. Zabel, this issue, Phys. Rev. B **36**, 7303 (1987).

[9]M. E. Lines, Phys. Rev. **131**, 546 (1963).