$CoCl_2$-intercalated graphite: A quasi-two-dimensional magnetic system

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Precise measurements of the magnetic susceptibility for stage -2, -4, and -5 graphite-$CoCl_2$ intercalation compounds (GIC's) are reported. Comparison of the experimental results with the theoretical calculations based on a two-dimensional planar model with a sixfold symmetry-breaking field shows two phase transitions. The two transitions at T_{cu} and T_{cl} are respectively identified with a transition of the system from a disordered state to an intermediate Kosterlitz-Thouless (KT) xy state with short-range order followed by a second transition from this xy state to a long-range-ordered state. The stage dependence of the magnetic susceptibility is investigated and the nature and the role of the interplanar magnetic coupling in modifying the magnetic behavior of the system is discussed. The behavior of the system in the presence of a large range of external magnetic fields is studied and the validity of the Kadanoff scaling hypothesis is checked. Finally the magnetic behaviors of $CoCl_2$-GIC and K_2CuF_4, another interesting two-dimensional system, are compared and their similar behavior over a finite region of the phase diagram is discussed.

I. INTRODUCTION

Recent theoretical and experimental activity in the study of two-dimensional magnetism has focused on the role of dimensionality on the functional form of the magnetic behavior near phase transitions. It was first pointed out by Peierls[1,2] that long-range order cannot appear in one- and two-dimensional magnetic solids. It has also been rigorously shown by Mermin and Wagner[3] and by Mermin[4] that in a rotationally invariant two-dimensional system, spontaneous magnetization cannot occur. Yet phase transitions at finite temperatures can occur in two-dimensional systems.[5,6] In recent years, research on two-dimensional magnetism has focused on understanding the nature of these phase transitions using various theoretical models or in observations on actual experimental systems.

Intercalation of magnetic species in graphite provides a very useful system for the study of two-dimensional magnetism, and the investigation of dimensionality in magnetic[7] and structural[8] behavior generally. In these systems the interplanar interaction or magnetic moments can be systematically and continuously reduced by inserting a controlled number n of diamagnetic graphite layers between each adjacent pair of magnetic intercalate layers. The number n is called the stage of the graphite intercalation compound (GIC). In the case of the transition-metal chloride intercalation compounds, the distance between the neighboring magnetic layers can be varied from ~ 9 Å (stage 1) to more than 30 Å (stage 7).

Many of the transition-metal chloride intercalation compounds have been the subject of magnetic investigations[9–16] and in almost all cases, the existence of magnetic phase transitions have been reported. However, in most cases the nature of the phase transition is not well established. Recent susceptibility measurements on $FeCl_3$-GIC, $CoCl_2$-GIC, and $NiCl_2$-GIC have shown similarities in both the temperature and the magnetic field dependence of the magnetic behavior of these intercalation compounds.[17] In the present work we have chosen the $CoCl_2$-GIC system for a more critical investigation because of our better understanding of the magnetic properties of pristine $CoCl_2$, which already has a very weak interplanar interaction.[18] In addition, the $CoCl_2$-GIC is available in a number of different well-staged compounds and the magnetic transition temperature is in an easily accessible temperature range.

Magnetic properties of $CoCl_2$ in its pristine form have been extensively studied.[18–27] The lattice structure of $CoCl_2$ is the same as that of $CrCl_2$ with a trigonal space group $R\bar{3}m$, consisting of hexagonal layers of Co^{+2} separated from each other by two hexagonal layers of Cl^-. The Co sites form a planar triangular lattice. Although the primitive cell is rhombohedral with one molecule per unit cell ($a_0=6.16$ Å, $\alpha=33°\,26'$, $u=0.25$) it is often convenient to use of a larger hexagonal unit cell ($a_0=3.553$ Å, $c_0=17.359$ Å) which contains three $CoCl_2$ molecules. In this hexagonal cell, the metal ions are located at (0,0,0), $\pm(\frac{1}{3},\frac{2}{3},\frac{2}{3})$ and the six chlorine ions are displaced by $(0,0,\pm u)$ from each Co^{+2} ion.[18] Pristine $CoCl_2$ undergoes an antiferromagnetic phase transition at the Néel temperature $T_N=24.71\pm0.05$ K.[18] For temperatures below T_N, the spins lie in the layer plane and align in two-dimensional ferromagnetic sheets which are stacked antiferromagnetically. From neutron scattering experiments[26] the magnetic interactions have been established by determination of the intraplanar and interplanar interaction constants, $J=28.5\pm0.3$ K and $J'=2.16\pm0.16$

K, respectively, and the corresponding c-axis anisotropy constants $J_A = 16.0 \pm 1.3$ K and $J'_A = 3.3$ K. The in-plane anisotropy field is estimated to be 10×10^{-2} T (Ref. 27) from the spin-flop field $H_{SF} = 0.2$ T (Ref. 18) and the saturation field $H_S = 3.3$ (Ref. 23).

The structure of the intercalation-compound graphite-$CoCl_2$ consists of a three-layer sandwich of Cl-Co-Cl layers, with essentially the same sandwich structure and lattice constants as in the pristine compound. This similarity in lattice constants suggests an approximate equality in the corresponding magnetic exchange interactions. With regard to c-axis magnetic couplings, the intercalate sandwich is structurally incommensurate with respect to the graphite layers adjacent to each sandwich. Thus the interlayer magnetic couplings in the intercalation compounds are expected to be very weak because of the increased magnetic interlayer distances compared to pristine $CoCl_2$ and the probable absence of long-range interlayer positional correlations.

In the magnetic measurements on graphite-$CoCl_2$ intercalation compounds reported by Karimov,[11,14,16] the differential magnetic susceptibility was found to exhibit a sharp anomaly at 8.1 K.[11] On the basis of the field dependence of the magnetization[14] and the onset of spontaneous magnetization in the absence of an externally applied field,[14] Karimov determined that $CoCl_2$-GIC undergoes two phase transitions at 9.05 and 8.1 K.[16] The upper transition at T_{cu} was identified with a transition from the paramagnetic state to a planar-model state, and then the lower transition at T_{cl} would be from this planar-type state to a state with net magnetization at the lowest temperatures.[28] The anomalous but similar field dependences of the susceptibility of GIC-$CoCl_2$, GIC-$NiCl_2$, and GIC-$FeCl_3$ of different stages, reported by Elahy *et al.*[17] also support the existence of two phase transitions closely spaced in temperature.

In this work we report accurate experimental susceptibility data which can be used to establish the functional form of the in-plane susceptibility of graphite-$CoCl_2$ intercalation compounds (stages 2, 4, and 5) and to test this functional form against predictions by the xy model. We will also discuss the relevance of the experimental results on these systems to the planar model with six-fold symmetry-breaking fields[29] and compare our results with the theoretical predictions for the model of José, Kirkpatrick, Kadanoff, and Nelson (JKKN).[29] The c-axis correlation of the magnetic plane modifies the two-dimensional behavior of the system. The effect of interplane interaction is studied in conjunction with the stage dependence of the measured magnetic susceptibility. Finally the behavior of the system over large ranges of magnetic field will be considered and the implications of the scaling hypothesis will be discussed. Similarities and differences of $CoCl_2$-GIC and some other interesting two-dimensional systems will also be pointed out.

II. EXPERIMENTAL DETAILS

Samples of graphite-$CoCl_2$ were prepared by the standard two-zone vapor transport method for graphite intercalation compounds.[7,30–32] Prior to heat treatment, the pristine $CoCl_2$ and the host highly oriented pyrolytic graphite (HOPG) sample were separated at a distance of a few cm inside a Pyrex tube. Before sealing the ampoule, an atmosphere of Cl_2 (at ~ 350 Torr pressure)[33] was introduced and some $AlCl_3$ ($\sim 5\%$ of $CoCl_2$ by weight) was added to the ampoule to act as a complexing halide.[34,35] A two-zone furnace was used to heat the $CoCl_2$ to ~ 500 K and the HOPG to a few degrees higher temperature. A larger temperature difference between the graphite and the $CoCl_2$ compound results in a higher stage of the intercalation compound. The temperature differences used for the stage-2, -4, and -5 samples were ~ 2, ~ 4, and ~ 6 K, respectively. Typically the samples were kept inside the furnace for between 4 and 7 days. The intercalated samples were characterized for stage index by (00l) x-ray diffractograms. Cooling the samples to below liquid-helium temperature did not have any effect on the staging of the samples, as verified by the x-ray diffractograms. A more detailed description of the interesting structural properties of $CoCl_2$-GIC has been recently reported.[36]

The differential magnetic susceptibility measurements were made using a standard ac bridge[37,38] operating at a frequency of 300 Hz and a maximum ac field h_{max} of 0.6 Oe. The two secondary coils each consisted of ~ 5000 turns of No. 46 (0.013-mm-diam) copper wire and were balanced inductively to within 0.01%. The samples were mounted at the end of a thin phenolic rod ($\chi < 5 \times 10^{-5}$ emu/cm^3) that could be moved in and out of the center of a secondary coil along the common axis of the coils. The center of the secondary coil was determined by slowly moving the sample inside the coil and maximizing the output signal of the inductance bridge. A pair of spacers on the sample-holder rod assured that in each measurement the sample moved to exactly the same positions inside and outside the coil. The accuracy of positioning the sample and the reproducibility of the output signal were measured to be better than 0.2% and 0.1%, respectively. The differential susceptibility of the sample was found by subtracting the bridge signal with the sample outside of the coil from the signal with the sample at the center of the coil. Both χ_a and χ_c were measured by orientation of the sample with the ac field in-plane along the a axis and along the c axis, respectively. Upon intercalation, the mosaic spread of the c axis increases to $\sim 2°$. The mosaic spread is sufficiently small, so that negligible error is introduced into the separation of χ_a and χ_c.

The signal was calibrated by comparison of the sample signal with the signal from a ferromagnetic nickel sphere. The volume susceptibility of a spherical ferromagnet is $3/4\pi$ emu/cm^3 in CGS units. The absolute volume susceptibility of the sample in CGS units was determined by the following relation:

$$\chi = \frac{3}{4\pi}(S_S/S_{Ni}) \tag{1}$$

in which S_S and S_{Ni} are the sample and Ni sphere signals, each corrected for background.

The above formula assumes a spherical sample while the samples reported in this paper were rectangular parallelpipeds. The sample shape introduces an error in our calibration calculation which is estimated to be only a few

percent. This correction is based on the known ratio of the sample volume to the coil volume of about 0.03.

Another source of error associated with the measurement is the demagnetization correction for the sample. For spins lying in the plane of the Co^{+2} layer, the in-plane demagnetization factor is zero for χ_a and 4π for χ_c. In general the intrinsic or actual susceptibility, l_i, and the measured value, l_m, are related by $l_m^{-1}+l_i^{-1}=D$, where D is the demagnetization factor along the measurement axis.[39] An estimate of D for our samples, with typical dimensions of $a=0.6$ cm, $b=0.3$ cm, and $c=0.1$ cm, can be obtained by approximating the demagnetization factor to be the same as for an ellipsoid with the same principal axes of the sample dimensions. Using the tables for the ellipsoids,[39,40] we found $D_a=1.0$, $D_b=2.7$, and $D_c=8.9$ for the demagnetization factors along the length, width, and thickness of the samples, respectively (note $D_a+D_b+D_c=4\pi$).

Our Maxwell mutual inductance bridge allows accurate separation of real and imaginary parts of the susceptibility. All susceptibilities reported in this paper are the real part. The imaginary contribution is 1 order of magnitude smaller and is associated with the loss mechanism, e.g., domain-wall motion.

The bridge used in this experiment was designed for 1% accuracy and a sensitivity of $\pm 10^{-15}$ emu/cm^3 with the maximum ac modulation field of $h_{\max}=0.6$ Oe, but the sensitivity could be increased further by increasing the amplitude of the sinusoidal current feeding the primary coil. Such an increase in sensitivity would be required to measure the susceptibility of the nonmagnetic intercalation compounds.

In order to sweep the temperature of the sample, the primary and the secondary coils were positioned inside two concentric cylindrical cans. The inner can was filled with the exchange gas, while the outer can enclosed a vacuum and was placed in the central chamber of a "supervaritemp" Dewar. The sample chamber of the Dewar could be filled with helium gas at any desired temperature as well as with liquid helium. Temperatures below 4.2 K were achieved by pumping on the liquid-helium bath. A 25-Ω heater, wound around a thick, long, slit copper cylinder covering the inner wall of the inner can, provided temperature control, stability, and uniformity throughout the sample chamber. The temperature inside the sample chamber was measured simultaneously in two ways by using both a calibrated diode and a carbon glass sensor. The temperature dependence of the susceptibility was measured on several cycles going both up and down in temperature. No temperature hysteresis was observed to within 0.1 K.

III. RESULTS

A. Temperature dependence of the zero-field susceptibility

In Fig. 1 we plot the results for the in-plane volume susceptibility, $\chi_\perp$, of the stage-2, -4, and -5 graphite-$CoCl_2$ intercalation compounds as a function of temperature at zero external field. The curve for stage 2 has an asymmetric peak of magnitude 0.12 emu/cm^3 at 7.8 K, with a width at half maximum of 1.9 K. On the high-temperature side of the peak, the magnitude of $\chi_\perp$ drops to 10%, 1%, and 0.1% of its maximum value at 9.7, 14.8, and 31.0 K, respectively. On the low-temperature side, the drop is slower but at 2.5 K the susceptibility is already less than 10% of its maximum value. The large value of the susceptibility at the peak is comparable to the volume susceptibility of a spherical ferromagnet which is $3/4\pi=0.24$ emu/cm^3.

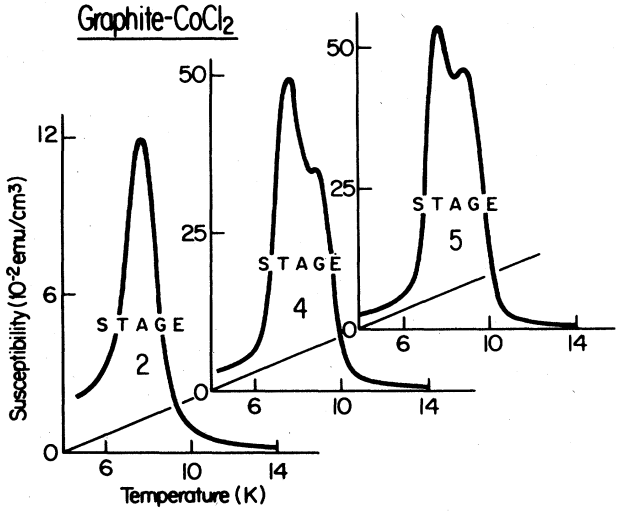

FIG. 1. In-plane magnetic susceptibility of stage-2, -4, and -5 $CoCl_2$-GIC as a function of temperature in the absence of an external magnetic field.

The functional form of the susceptibility for temperatures above the peak can be examined to obtain parameters for the magnetic state. The mean-field theory predicts that above the critical temperature T_c the susceptibility χ is given by

$$\chi=\frac{\partial M}{\partial T}=\frac{C}{T-T_c} \tag{2}$$

with $C=Ng^2\mu_B^2S(S+1)$, where N and S are the number and magnitude of the angular momentum of the spins in the system. A comparison of the experimental data with mean-field theory shows that in a plot of the inverse susceptibility, $1/\chi_\perp$ versus T, no linear dependence on temperature is observed for $T\leq 4T_c$.[6] We also fit our data on the high-temperature side of the susceptibility peak by a least-squares fit to a function of the form

$$\chi=b(T/T_c-1)^{-\gamma}. \tag{3}$$

In the case of the stage-2 compound, we have obtained the results shown in Table I, using $\gamma=1.98$ which yields the best fit for this functional form. Karimov[12] and Suzuki and Ikeda[41] and Suematsu *et al.*[42] have also been successful in fitting their $\chi_\perp$ results for $NiCl_2$-GIC samples to the functional form $(T/T_c-1)^{-2}$ in the high-temperature regime $T\gg T_c$.

However, in the high-temperature range ($T>\sim 150$ K), the magnetization obeys the Curie-Weiss law with a Curie-Weiss temperature, $\Theta\approx 31$ K, as found[43] from ex-

TABLE I. Parameters for $1/\chi$ vs T plot for stage-2 $CoCl_2$-GIC. For the indicated γ values, T_c was optimized to yield minimum Chi^2 for fitting a function of the form $\chi=b(T/T_c-1)^{-\gamma}$ to the experimentally measured susceptibility of stage 2 $CoCl_2$-GIC (see Fig. 1). The value of $Chi^2=4$ was obtained by fitting the experimental points to the KT form of Eq. (6).

Temperature range	γ	T_c	Chi^2
9–29 K	1	8.7	116.0
2–29 K	2	7.7	24.0

trapolation of $\chi_\perp^{-1}$. This Θ value is very close to that of the pristine $CoCl_2$, where $\Theta=31.2$ K,[26] thereby implying that the intraplanar ferromagnetic spin interaction remains essentially unchanged by intercalation into graphite. The deviation from Curie-Weiss behavior up to such a high temperature is presumably due to the two dimensionality of the spin interaction. Indeed for pristine $CoCl_2$ which has a much stronger interlayer interaction, the deviation from the Curie-Weiss law occurs below 75 K (the Curie-Weiss relation is based on mean-field theory which is exact[44] only for systems with dimensionality $d>4$).

Near T_c, the shape of the temperature dependence above the susceptibility peak will be shown to fit well to a two-dimensional model of the Kosterlitz-Thouless[45] form. The applicability of such a two-dimensional model to our system could best be understood from the following considerations.

On the basis of our structural studies of graphite-$CoCl_2$, we can assume the following magnetic Hamiltonian for the system in the absence of an external magnetic field:

$$H=-J\sum_{i>j}\vec{S}_i\cdot\vec{S}_j+J_A\sum_{i>j}S_{iz}S_{jz}+J'\sum_{i>k}\vec{S}_i\cdot\vec{S}_k\ , \qquad (4)$$

where the value of the intraplanar coupling constant J, and its associated anisotropy J_A are taken to be essentially the same as in the pristine $CoCl_2$ compound, i.e., $J=28.5$ K and $J_A=16.0$ K, respectively. The introduction of several diamagnetic graphite layers is expected to further decrease the already small value of J' in the pristine compound. In fact, our magnetic field-dependent behavior of the susceptibility indicates that J'/J in a stage-2 compound has an upper bound of 1×10^{-4}. For comparison, the dipole-dipole interaction for two spins separated by the magnetic layer distance in stage-2 $CoCl_2$-GIC gives a lower limit for this ratio of $\sim4\times10^{-5}$ K.

As the critical region of the susceptibility anomaly is approached from above, the correlation length ξ increases with decreasing temperature. Consider a correlated in-plane domain containing $(\xi/a_0)^2$ spins, where a_0 is the lattice constant. The exchange energies of the domains with alignment axes in the xy plane and along the c axis are $(-J/4)(\xi/a_0)^2$ and $(-J/4+J_A/4)(\xi/a_0)^2$, respectively. When the temperature fluctuations in the energy of the domain become comparable with the energy difference between these two configurations, i.e., when

$$(-J/4+J_A/4)(\xi/a_0)^2-(-J/4)(\xi/a_0)^2=(J_A/4)(\xi/a_0)^2\sim kT\ , \qquad (5)$$

then it becomes unfavorable for a spin to rotate in the direction of the c axis and the spins are represented by an xy system.

At much lower temperatures, the coherence length, $\xi\sim a_0(J/J')^{1/2}\sim100a_0$, and the effect of the adjacent magnetic plane is felt. However, for our samples, ξ was limited by the finite size of the intercalate islands. If we assume that, on the average, each island contains less than 10^4 spins, then the system should satisfy the two-dimensional criterion above the critical region. Then the interplanar coupling is of secondary importance in comparison with the finite-size effect. We thus conclude that, in the temperature range of interest, the two-dimensional xy model is appropriate to the graphite-$CoCl_2$ system.

The Kosterlitz-Thouless (KT) theory[45,46] for the two-dimensional xy model has been extended by José *et al.*[29] (JKKN) to include the effect of the sixfold symmetry-breaking anisotropy field. The JKKN analysis shows that there exists a region in temperature with infinite initial susceptibility on both sides of the peaks in χ which diverges as $\exp(b\,|\,t\,|^{1/2})$. At the upper critical temperature the divergence of the susceptibility corresponds to a KT-type vortex binding-unbinding phase transition while at the lower critical temperature the divergence corresponds to a transition from the bound vortex state to a state with conventional long-range order.

The JKKN analysis is based on the Villain model[47] in which one approximates the action for the xy model by a different function, known as the Villain action, whose Fourier expansion matches that of the xy model up to the second term. Thus, the JKKN results can only describe the xy model in the limit of short wave vector k, or long correlation length, i.e., near T_{KT}. The range of validity of such an analysis has been estimated[48,49] to correspond to values of t as small as 10^{-1} or 10^{-3}.

However, for most physically realizable quasi-two-dimensional magnetic systems, their behavior in such a narrow temperature region in the immediate neighborhood of the critical point could be masked by the finite size of the magnetic domains[50] or the effect of the magnetic interlayer interaction. Also, in the case of the susceptibility or magnetization measurements, the effect of a uniaxial excitation field h very close to T_c can become significant.

In particular, in our experimental system all of these effects are present. Nevertheless, in the preliminary analysis of our susceptibility results, we obtained a good fit of our data to a function of the form

$$\chi=\chi_0+\chi_1\exp(b'/t^{1/2})\ , \qquad (6)$$

where $t=T/T_{cu}-1$. In this form χ_0 includes other contributions to the susceptibility and is generally quite small. The range of the fitting and the values of the fitting parameters were previously reported.[51] The fit obtained was better than for any power law previously discussed. The value of $b'=1.39$ found from this fitting is smaller than

the theoretical[46] value 2.625 or the value of 1.70 found for the Monte Carlo simulation.[52]

Agreement between the experimental data and the theoretical exponential function beyond the range of validity of the theoretical analysis has been also reported for $NiCl_2$-GIC (Ref. 41) and K_2CuF_4 (Ref. 53). In the case of $NiCl_2$-GIC (Ref. 41), the zero-field susceptibility in the upper temperature side of the susceptibility peak has been fitted with the function $\exp(b'/t^{\nu})$, where $t=T/T_{\max}-1$ for $t \geq 1.5\times10^{-1}$, and the values $b'=1.73$ and $\nu=0.50$ have been obtained as best-fit values. These values of b' and ν are in good agreement with the Monte-Carlo-simulation results of Tobochnik and Chester.[52] As for K_2CuF_4, which has a Heisenberg spin interaction with only 1% xy anisotropy, the temperature dependence of the correlation length, ξ, agrees with the KT exponential function for t even larger than 0.8.[53] A more detailed comparison of the K_2CuF_4 system with our $CoCl_2$-GIC system is presented in Sec. V B.

B. Stage dependence of zero-field susceptibility

Figure 1 shows the in-plane susceptibility for stage-2, -4, and -5 $CoCl_2$-GIC. In stages 4 and 5, instead of a single peak, the susceptibility anomaly consists of two closely spaced peaks which are separated by a local minimum. In our data for the stage-2 compound, as in the data reported by Karimov *et al.*,[10] no shoulder is present on the high-temperature side of the anomaly. In contrast, the data of Suzuki and Ikeda for a stage-2 compound[41] has a very clearly observable shoulder around T_{cu}. It is clear from Fig. 1 that the separation of the peaks is larger for stage 5 than it is for stage 4. If we assume that the shoulder in the stage-2 compound of Suzuki does not appear in our data (due perhaps to the smaller size of our intercalate islands), one can plot the double-peak separation as a function of stage, as in Fig. 2(a); the plot displays a monotonic increase of the peak separation with increasing stage. Alternatively one can plot the stage dependence of the width at half maximum of the anomaly, also shown in Fig. 2(a). Here also the same trend is observed. This indicates that the temperature range of the intermediate phase increases with stage. Considering the fact that JKKN predict a much wider intermediate phase, $T_{cu}/T_{cl}=\frac{9}{4}$ for $n=\infty$ ($J'=0$), the observed experimental trend within the limitations of the available data is consistent with the theory.

The temperature of the susceptibility peak $T_{\max}$ at the lower-temperature peak is relatively independent of stage as seen in Fig. 2(b), indicating that the transition to the ordered phase is only slightly influenced by the variation of J' from stage 2 to stage 5 and is mainly controlled by the in-plane magnetic parameters. The small drop in the peak value is consistent with the expectation that the lower effective number of nearest neighbors should result in a lower transition temperature. In contrast, the Kosterlitz-Thouless transition seems to be much more sensitive to the intraplanar interaction, as has been theoretically predicted.[54] The direction of the shift is opposite to what has been proposed by Kosterlitz and Thouless for a ferromagnetic interplanar interaction. They have argued that a ferromagnetic coupling constant J'

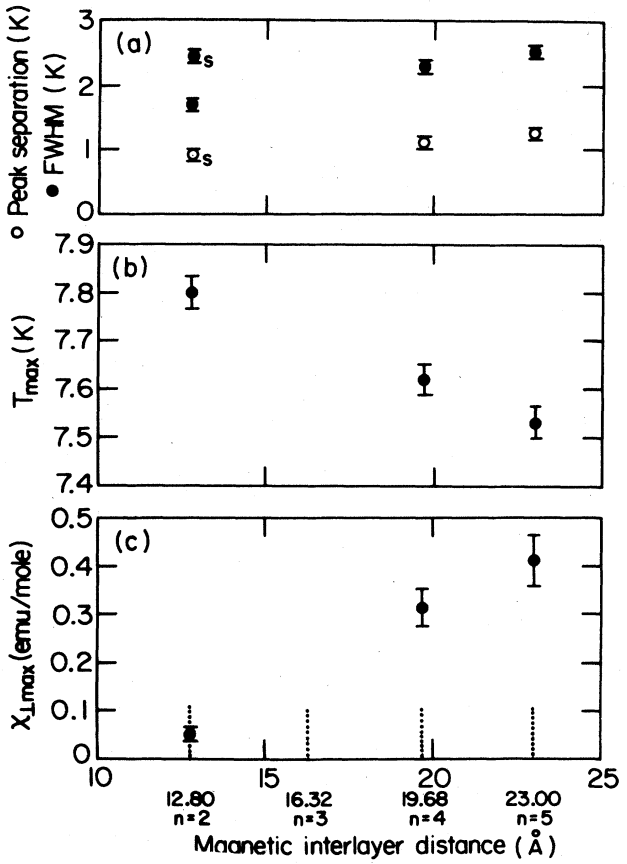

FIG. 2. Dependence of various parameters on the magnetic interlayer distance for stages $2 \leq n \leq 5$. (a) Stage dependence of the width at half maximum (●) and the double-peak temperature separation (○) for the in-plane susceptibility of $CoCl_2$-GIC's. The points marked with s are from Ref. 41. (b) Stage variation of the $T_{\max}$ critical temperature T_{cl} at the lower-temperature susceptibility peak. (c) Stage variation of the amplitude of the susceptibility peak $\chi_{\perp\max}$ at T_{cl}.

shifts the vortex unbinding transition temperature according to the following relation,[54]

$$\frac{T_{\mathrm{KT}}(J')}{T_{\mathrm{KT}}(0)}-1 \cong 9[\ln(z_c J/J')]^{-2}, \tag{7}$$

where z_c is a finite constant ~ 1.

The effect of variation of the interplanar interaction on the phase transition in quasi-two-dimensional systems has been investigated in a systematic way for $(C_2H_{2n+1}NH_3)_2CuCl_4$ and $(C_nH_{2n+1}NH_3)_2CuBr_4$.[27] In these systems which undergo phase transitions to a ferromagnetic state, the J'/J ratio can be varied from 10^{-3} to less than 10^{-5} by varying n which results in increasing the separation of the adjacent magnetic layers while leaving the magnetic in-plane structure relatively unchanged. The critical temperature correspondingly is reduced by 30% in the bromide compounds and by 20% in the chloride compounds. The change in kT_c/J seems to be even smaller. For our system the shift in the position of the shoulder corresponding to T_{cu} in Fig. 2(a) is less than 5% of T_{cu}. However, the absence of the shoulder from

our stage-2 sample and the upward direction of the shift as a function of stage, is not understood at this point.

In Fig. 2(c) we have plotted the stage dependence of the amplitude of the susceptibility peak $\chi_{\perp\max}$ at the lower temperature. A clear monotonic increase in $\chi_{\perp\max}$ is observed with increasing stage. Since the amplitude of the peak primarily depends on the average size of the intercalation islands,[55] the obvious implication is that the intercalate islands could be larger in our higher-stage samples. However, no simple explanation for the mechanism behind such a behavior is available at this point, nor has a systematic experimental investigation of the stage dependence of the intercalate island size been carried out so far.

IV. CORRELATION ALONG THE c AXIS

From the results presented in the preceding section it is clear that in the absence of an external magnetic field, the interplanar interaction does play an observable role in the magnetic behavior. However, at least in the high-temperature and the intermediate-temperature phases, the effect of nonzero J' seems to be secondary, i.e., it does not seem to change the nature of these phases, nor the phase transition temperature T_{cu}. The KT exponential function was found also to fit well to the susceptibility data, for the stage-4 and -5 compounds.[51]

For the low-temperature phase with long-range order, however, the situation seems to be different. The data of Karimov[14] on the low-temperature phase was indicative of a metamagnetic phase for stage-2 $CoCl_2$-GIC as in the pristine compound (although Karimov himself had reached a different conclusion). This explains the small spontaneous magnetization at $T=1.44$ K and a relatively small saturation field of 1 T.[14] Our low-field-dependent susceptibility results are indicative of a weak antiferromagnetic interplanar coupling. Finally, recent neutron data in low-stage $CoCl_2$-GIC established an in-plane ferromagnetic and a c axis antiferromagnetic order.[43] These results clearly indicate that in the case of stage-2 $CoCl_2$-GIC using Kish single crystals as the host material, the low-temperature phase is three-dimensionally antiferromagnetic in nature. As for the nonzero residual magnetization found in this region, Suematsu *et al.* have proposed an explanation based on the islandic nature of the intercalate.[42]

For the $CoCl_2$-GIC system the interplanar interaction can be considered as being either of the dipole-dipole type or due to indirect exchange coupling through two chlorine and n graphite layers. The interaction energy of two dipoles of moments $m=\mu_B g S$ separated at distance $r=I_c$ to first order is

$$u=\frac{(\mu_B g S)^2}{4\pi\mu_0 I_c^3}\ , \tag{8}$$

which for $g=2$ and $S=\frac{1}{2}$ yields an energy u in units of mK

$$u(\mathrm{mK})=\frac{632}{I_c^3}\ , \tag{9}$$

where I_c is expressed in Å. The estimated dipole-dipole interaction energy and the corresponding effective interplanar interaction coupling J'_{eff} values for stage-2 through -5 compounds are listed in Table II. The simple calculation given above yields a lower bound for the interplanar magnetic interaction. As the in-plane correlation increases and more spins in the plane align, a larger moment is formed and a larger interplanar coupling results. On the other hand, if the size of the intercalate island is much larger than the adjacent magnetic interlayer distance, I_c, the average interaction per spin will decrease with increasing in-plane correlation length. In particular, in the limit of $\xi\to\infty$, we know that the magnetic field due to an infinite ferromagnetic plane is zero at any distance r away from it.[16] So the size of the magnetic intercalate islands plays a crucial role in determining the average interplane coupling per spin in the dipole-dipole—interaction model. In any case, the dipole-dipole picture, although it might not be the full story, is a good starting point for understanding the coupling of magnetic planes at such large separations. This interaction particularly favors the antiferromagnetic ordering along the c axis because of the lower energy for this configuration.

TABLE II. Interplanar dipole-dipole interaction for stages 2 through 5 for I_c values as determined by $(00l)$ x-ray diffraction. For the spin-$\frac{1}{2}$ system $J'_{\mathrm{eff}}=4u$.

	$n=2$	$n=3$	$n=4$	$n=5$
I_c (Å)	12.80	16.15	19.50	22.85
J'_{eff} (mK)	1.20	0.60	0.36	0.20

Calculation of the indirect exchange coupling between intercalate layers has not yet been attempted. Our experimental study of the magnetic field dependence of the susceptibility and the neutron diffraction measurements by Suzuki *et al.*[43] give estimates for J' which both agree with each other and are roughly of the same order of magnitude as that of the dipole-dipole interaction. This suggests that even if an indirect exchange interaction is present in the $CoCl_2$-GIC system, it cannot greatly exceed the dipole-dipole coupling.

V. MAGNETIC BEHAVIOR IN THE PRESENCE OF AN EXTERNAL MAGNETIC FIELD

Based on what we already know about the $CoCl_2$-GIC system, we can expect that the behavior of the system in the presence of an in-plane external magnetic field, $H\perp c$, can be divided into three regions. First, in the very-low-field region with $H<100$ Oe, the physics is very complicated because the in-plane sixfold symmetry-breaking field H_A^I, the interplanar antiferromagnetic field, H', and the external magnetic field H are all of the same order of magnitude. Second, in the intermediate-field region where $100<H<3000$ Oe, we note that H dominates over both H_A^I and H'. In the second field regime, the system becomes simpler and the hope is that we are still fairly close to the region of critical behavior to be able to indirectly acquire information about this critical behavior. In fact the upper bound of 3000 Oe is experimentally determined by such a criterion, as we will see later. In particular, we will experimentally examine the validity of the scaling

laws in this intermediate-field region and try to see whether it is possible to learn about the critical exponents at the magnetic phase transitions. Finally, the high-field region with $H > 3000$ Oe denotes the regime where the external magnetic field tends to completely align the spins and the magnetic parameters tend to saturate. We proceed with discussions of the behavior of the system in each of the forementioned magnetic field regimes.

A. Low-magnetic-field range

Figure 3 shows the in-plane susceptibility of stage-4 $CoCl_2$-GIC as a function of temperature for several values of external magnetic field applied parallel to the basal plane. Despite the relative complexity of the behavior, several trends can be easily distinguished.

First, the amplitude and the shape of the susceptibility anomaly is extremely sensitive to fields as small as a few Oersteds. At less than 3 Oe the susceptibility anomaly has a totally different shape than for $H = 0$ and its amplitude is down by about 50%. This points to the need for making the measurements in a system shielded from the earth's magnetic field and using very small amplitudes for the probing ac field.

Second, the peak at 7.6 K shifts to lower temperatures for very small fields and splits into a double bump at about 1 Oe. The lower bump continues to shift downward in temperature and quickly reduces in amplitude until it disappears in the background between about $H = 10$ and 20 Oe. The upper bump shifts upward in temperature and decreases in amplitude with a slower rate.

Third, the zero-field shoulder of the susceptibility anomaly at higher T shifts downward in temperature as its amplitude decreases until it is unified with the upper bump to form a single peak at $H = 11$ Oe. The position of this peak clearly moves upward in temperature only for fields larger than 21 Oe.

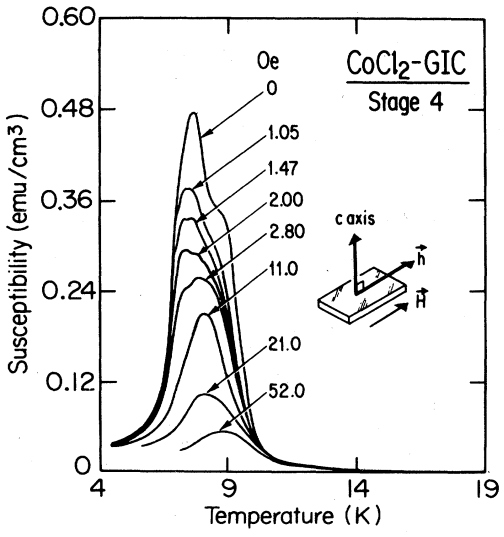

FIG. 3. In-plane susceptibility of stage-4 $CoCl_2$-GIC as a function of temperature for constant in-plane external magnetic fields, H, of magnitudes (a) 0, (b) 1.05 Oe, (c) 1.47 Oe, (d) 2.00 Oe, (e) 2.80 Oe, (f) 11.0 Oe, (g) 21.0 Oe, and (h) 52.0 Oe. The inset shows the geometry of the static field $\vec{H}$ and the ac probing field $\vec{h}$.

Although it is not possible to propose a unique and definitive model for the microscopic behavior of the system based on such limited and complicated macroscopic results, we suggest a mechanism that could account for the observed field dependence of the in-plane susceptibility.

The sensitivity of the susceptibility anomaly to an external magnetic field and its rapid attenuation with small applied fields could probably be understood if we remember that the large amplitude of the susceptibility in the intermediate-temperature region arises because the susceptibility is infinite below T_{KT} according to the KT theory and only remains finite in our system due to the finite size of the intercalate islands.[50] On the other hand, the JKKN analysis predicts that the intermediate KT phase is unstable against a uniaxially applied magnetic field. Thus, under the application of an external magnetic field, the intermediate phase disappears as T_{cu} and T_{cl} move towards each other, as described below.

We can interpret the splitting of the susceptibility peak and the formation of the intermediate phase to be due to a temperature difference between the interplane and the intraplane ordering. The external magnetic field facilitates the intraplane ferromagnetic ordering (moving the transition to higher temperatures) and inhibits the interplanar antiferromagnetic ordering (shifting this transition to lower temperatures). The antiferromagnetic "bumps" disappear at about $H \sim 11$ Oe, suggesting an interplanar coupling of $J' \sim 0.7$ mK, in rough agreement with the estimated dipole-dipole value $J'_{\text{eff}} \sim 0.36$ mK given in Table II for the stage-4 compound.

The in-plane ferromagnetic ordering transition at T_{cl} shifts upward in temperature until it meets the downward shifting shoulder associated with T_{cu}. For fields above 20 Oe, the situation becomes much simpler. Since $H > H'$ in this regime, we can neglect the interplanar interaction and essentially consider a two-dimensional system in this case. In the intermediate-field range $50 < H < 100$ Oe discussed in the next section, the external field dominates the in-plane symmetry-breaking field, since H_A^I has been estimated for pristine $CoCl_2$ to be ~ 100 Oe (Ref. 27) and for $CoCl_2$-GIC to be ~ 10 to 30 Oe (Ref. 14). The second estimate[14] for the $CoCl_2$-GIC is more approximate.

The direct confirmation of the model proposed above is possible by a detailed investigation of the temperature and field dependence of the neutron diffraction intensities. Such an experiment has not yet been done.

B. Intermediate-field range and scaling hypothesis

Figure 4 shows the temperature dependence of the in-plane susceptibility of stage-4 $CoCl_2$-GIC for fields ranging up to 3100 Oe. In this region, the susceptibility peak monotonically decreases in amplitude and shifts to higher temperatures. This intermediate-field region has relatively simpler physics than the low-field region, and it is possible to examine the validity of the static scaling hy-

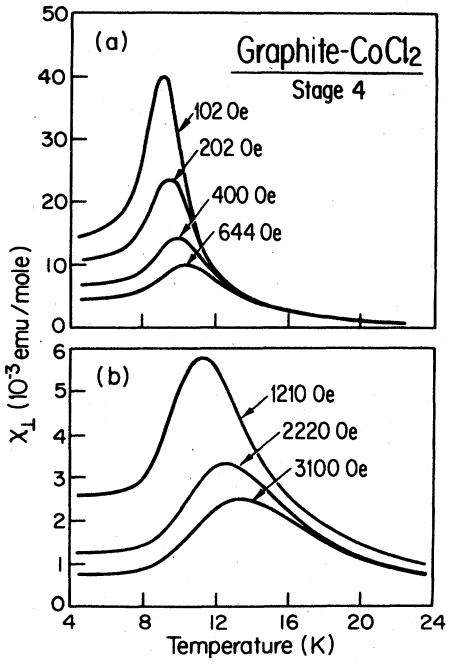

FIG. 4. In-plane susceptibility of stage-4 $CoCl_2$-GIC as a function of temperature for constant in-plane external magnetic fields of (a) 102 to 644 Oe and (b) 1210 to 3100 Oe, using the same geometry as in Fig. 3. Note the scale change resulting from the smaller susceptibility amplitudes at higher fields.

pothesis in this field region. Our analysis follows the procedure used by Suzuki and Ikeda.[15]

First we show in Fig. 5 the field dependence of the amplitude of the susceptibility peak $\chi_{\perp\max}$ on a log-log scale. A linear fit to the data points yields the relation

$$\chi_{\perp\max}\sim H^{\gamma} \tag{10}$$

with a critical exponent $\gamma=0.8$. A similar log-log plot is shown in Fig. 5 for the field dependence of the normalized shift in $T_{\max}$, the temperature of the susceptibility

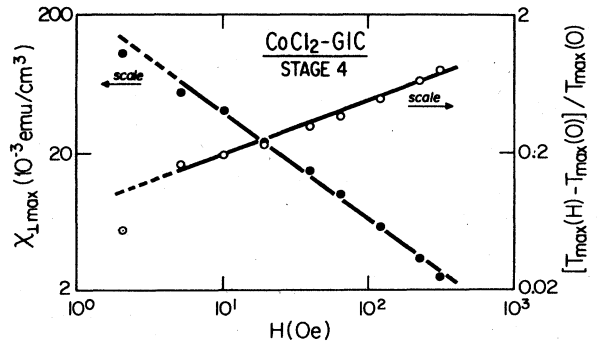

FIG. 5. Magnetic field dependence of the amplitude of the in-plane susceptibility peak $\chi_{\perp\max}$ on a log-log scale and the magnetic field dependence of the relative shift of the in-plane susceptibility peak position, $[T_{\max}(H)/T_{\max}(0)]-1$, on a log-log scale for a stage-4 $CoCl_2$-GIC.

peak. A linear fit to the data can again be obtained by the following relation,

$$[T_{\max}(H)-T_{\max}(0)]\sim H^{\mu}\ , \tag{11}$$

with $\mu=0.37$. To experimentally examine the validity of the scaling hypothesis in the field range under consideration, we have plotted $\chi/\chi_{\max}$ in Fig. 6 as a function of t/H^{x} for various values of J with $t=T/T_{cl}-1$. We find that for $x=\mu$ for all the susceptibility curves with $100<H<1000$ Oe coincide. As x deviates from μ, or H deviates from the aforementioned field range, the curves diverge from each other. This means that for $100<H<1000$ Oe, one can write

$$\chi_{\perp}(t,H)\sim\chi_{\perp\max}g_1(t/H^{\mu})\ , \tag{12}$$

where g_1 is some function of t/H^{μ}. Now remembering that we experimentally found $\chi_{\perp\max}\sim H^{\gamma}$ we can alternatively write the above equation as

$$\chi_{\perp}(t,H)\sim H^{\mu}g_2(H/t^{1/\mu})\ , \tag{13}$$

where g_2 is another function related to g_1 through their arguments. From comparison of Eq. (13) and the susceptibility equation derived from the scaling hypothesis,[56] we conclude that the scaling hypothesis is valid in this magnetic field region and we identify λ and μ through the following relations:

$$\lambda=\gamma/\Delta\ , \tag{14}$$

$$\mu=a/\Delta\ , \tag{15}$$

where Δ is the gap exponent. These relations along with the four scaling laws yield the following values for the critical exponents[57] of the system:

$$\alpha=1.20,\ \beta=0.54,\ \gamma=2.16\ ,$$

$$\delta=5.0,\ \nu=1.60,\ \text{and}\ \eta=0.35\ .$$

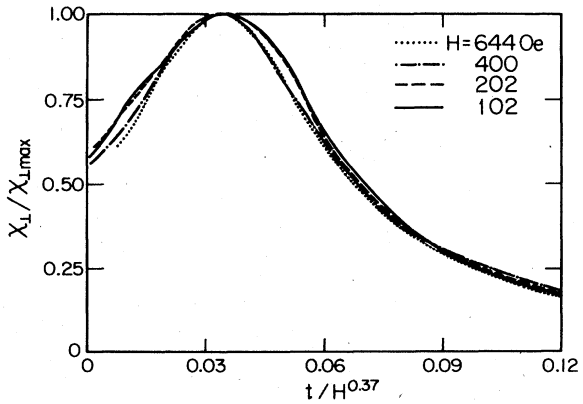

FIG. 6. Plot of $\chi_{\perp}/\chi_{\perp\max}$ as a function of t/H^{μ} with $\mu=0.37$. For this value of μ all the susceptibility curves within the range $100\le H\le 1000$ Oe coincide to within experimental error. This suggests the validity of the static scaling hypothesis in this field and temperature range. The curves represent 102 Oe (solid), 202 Oe (dashed), 400 Oe, (dashed-dotted), and 644 Oe (dotted).

These critical exponents, obtained experimentally for $CoCl_2$-GIC along with those for mean-field theory, the Ising model, and the Kosterlitz-Thouless (KT) theory are listed in Table III. In the KT theory $\nu=\infty$ and β is not defined since $M(t)=0$. However, $\gamma=\tilde{\gamma}/\nu$, $\alpha=\tilde{\alpha}/\gamma$, and δ obey the strong scaling laws,

$$\tilde{\gamma}=2-\eta\ , \tag{16}$$

$$\tilde{\alpha}=-d\ , \tag{17}$$

$$\delta=(d+2-\eta)(d-2+\eta)\ . \tag{18}$$

Although the critical exponents for $CoCl_2$-GIC do not agree with those of the KT theory,[46] many similarities are observed between the field-dependent behavior of the $CoCl_2$-GIC system and that for another two-dimensional system, K_2CuF_4.[56] We believe that valuable information can be obtained about both $CoCl_2$-GIC and K_2CuF_4 by comparative study of these two systems in this intermediate magnetic field range. As was mentioned before, K_2CuF_4 is a layered magnetic system, with $J'/J<7\times10^{-4}$, and a dominantly Heisenberg interaction, the xy anisotropy being only $\sim1\%$.[53] As was argued earlier, a small xy anisotropy in the limit of large correlation length can induce xy behavior in the system.

The first indication of KT-type behavior in the K_2CuF_4 system came from the field and temperature dependence of the magnetization and from comparison of the average susceptibility, M/H, with the KT theory.[58] These observations were later confirmed by neutron diffraction results.[53,59] It was proposed in accordance with the Hikami-Tsuneto theory[60] that the transition is principally caused by the KT interaction, with $T_{KT}=5.5$ K. However, the transition temperature is slightly modified by the three-dimensional interaction, giving rise to the observed $T_c=6.25$ K. The main differences between the K_2CuF_4 system and the $CoCl_2$-GIC's are the following. Firstly, in $CoCl_2$-GIC the relative xy anisotropy interaction is 60 times larger and, secondly, unlike K_2CuF_4, which has continuous in-plane symmetry, $CoCl_2$-GIC has a hexagonal in-plane symmetry-breaking field of ~100 Oe. However, one can expect the K_2CuF_4 in its two-dimensional xy regime,[59] and $CoCl_2$-GIC for $T_{cl}<T<28.5$ K and $H>H_A^I$ to behave similarly. This is, indeed, observed if we compare our susceptibility results in Fig. 4 with those of Suzuki and Ikeda[56] for K_2CuF_4. In fact, based on a similar analysis presented earlier for $CoCl_2$-GIC, they found that in the field range of $100<H<900$ Oe, the static scaling hypothesis is satisfied by K_2CuF_4. Furthermore, they found that for K_2CuF_4

$$\chi_{\perp\max}\sim H^{-\lambda}\ \text{with}\ \lambda=0.82 \tag{19}$$

and

$$T_{\max}(H)-T_c\sim H^{\mu}\ \text{with}\ \mu=0.83\ . \tag{20}$$

Their value for λ is in very good agreement with our result $\lambda=0.80$. However, our value for μ is very different. Our analysis shows that μ is very sensitive to the choice of T_c. Furthermore, if in Eq. (20) one uses $T_{KT}=5.5$ K instead of $T_c=6.25$ K, their data yield

$$T_{\max}(H)-T_{KT}\sim H^{\mu}\ \text{with}\ \mu=0.36 \tag{21}$$

in excellent agreement with our result, and thereby yielding the same critical exponents for both systems.

We should point out here for the infinite-size xy model one does not expect ξ and χ to scale as powers of t. In fact, we first analyzed our results in terms of a KT-type exponential function for ξ but no such scaling was found for the field range under consideration. It is rather surprising that the conventional scaling theory with power laws holds for our xy system. We believe that this is not necessarily due to the finite size of the system. In fact, as we mentioned above, the same form of scaling holds for the K_2CuF_4 system which is essentially of infinite size. Rather we feel that when the external field dominates over the in-plane sixfold symmetry-breaking field, as predicted by JKKN, the intermediate xy phase becomes unstable and the KT functional form is not applicable.

C. Saturation field for $CoCl_2$-GIC

First we recall that for pristine $CoCl_2$ the in-plane saturation field, H_S^I, has been reported to be 33 kOe.[23] Such a relatively low H_S^I has been attributed to the layered nature of the compound, $J'/J\sim0.1$.[18] This means that the interplane nearest neighbors play a much smaller role, which results in the lower H_bS^I value. One therefore expects a slightly smaller in-plane saturation field for the stage-2 $CoCl_2$-GIC sample. Our experimental results yield $J'/J\sim10^{-4}$ and suggest a decreasing H_S^I with increasing n. Karimov's results of H_S^I $(n=2)\sim10$ to 20 kOe (Ref. 14) are consistent with this picture. However, the magnetic field dependence of the percentage downshift of the heat capacity $\Delta C_p(H)=C_p(T,0)-C_p(T,H)$ (Refs. 61 and 36) does not seem to saturate below $H\sim140$

TABLE III. Critical exponents for $CoCl_2$-GIC as determined from experiment, mean-field theory, two-dimensional Ising model, and two-dimensional xy model.

	α	β	γ	δ	ν	η
Experimental	−1.20	0.54	2.16	5.0	1.60	0.35
Mean field	0.0	0.5	1.00	3.0	0.50	0.0
2D Ising		0.125	1.75	15.0	1.00	0.25
2D xy	−2.0[a]		1.75[a]	15.0	∞	0.25

[a]According to the Kosterlitz-Thouless theory, at T_{KT} the exponents are given by $\alpha=\gamma=\nu=\infty$. We therefore list in the table $\tilde{\alpha}=\alpha/\nu$ and $\tilde{\gamma}=\gamma/\nu$ which are expected to obey the strong scaling laws.

kOe. This discrepancy is not understood at this time, but it could either be related to a large uncertainty in the measurement of a small specific-heat signal or due to lattice quenching (i.e., lowering the effective degrees of freedom of $CoCl_2$ ions) by the magnetic field.

VI. CONCLUSIONS

Our results for the in-plane magnetic susceptibility of stage-2, -4, and -5 graphite-$CoCl_2$ intercalation compounds are in good qualitative agreement with the predictions of the two-dimensional planar model with sixfold symmetry-breaking fields. Though the samples used in these studies are known to contain inclusions of $AlCl_3$, the magnetic properties are identical to those measured in samples synthesized with only $CoCl_2$.[62] Both types of samples have the same structure of the magnetic islands. For quantitative comparison more elaborate theories are needed in which the effect of small interplanar interactions, the c-axis component of the spins, and the islandic nature of the intercalated layers would be included.

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