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Magnetic properties of $CoCl_2$-graphite intercalation compounds under pressure

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We report ac magnetic susceptibility ($\chi = \chi' - i\chi''$) measurements of stage-1 and stage-2 $CoCl_2$-graphite intercalation compounds (GIC's) carried out under hydrostatic pressures of 0–15 kbar. For stage-1 $CoCl_2$-GIC's, it is found that the three-dimensional ordering temperature $T_{c2}=T_N=9.7$ K, where the ferromagnetic planes of Co^{2+} spins become ordered into an antiferromagnetic arrangement along the *c* axis, shifts to a higher temperature with increasing pressure. Additionally, the transition field H_t, measured when a magnetic field is applied in the *x*-*y* plane, shifts to a higher field value with increasing pressure. From the increase of the transition field, we can estimate the pressure dependence of the antiferromagnetic interlayer coupling J'. For stage-2 $CoCl_2$-GIC's, it is found from measurements of χ' and χ'' that the transition temperatures T_{cl} and T_{cu} increase with applied pressure.

I. INTRODUCTION

While earlier high-pressure studies of graphite intercalation compounds (GIC's), reviewed in Ref. 1, have studied the effect of pressure on structural transformations, transport properties, and superconductivity, no measurements have been made of the effect of pressure on the magnetic properties of GIC's.

The $CoCl_2$-GIC's are regarded, at least in their high stages, as showing two-dimensional (2D) magnetic behavior and relative to other magnetic GIC's they demonstrate the clearest *XY* spin anisotropy. Stage-1 and stage-2 $CoCl_2$-GIC's are the easiest compounds to synthesize and their magnetic properties are well documented. Except for a small amount of published data on the stage-3 compound,[2] there is no other information on the trends in the magnetic behavior of these pure compounds as the intercalate layer separation is varied. One method of decreasing the three dimensionality of these systems is through the synthesis of the bi-intercalation compound $CoCl_2$-$GaCl_3$-GIC,[3] where a $GaCl_3$ layer is introduced in between the remaining adjacent graphite layers of a stage-2 $CoCl_2$-GIC. This demonstrates the effect of decreasing J', the interlayer antiferromagnetic coupling parameter, keeping all other exchange parameters constant.

We shall show that the application of pressure also provides a controlled method for varying some of the magnetic interactions. We can use these pressure-induced changes to elucidate the magnetic behavior at the various transition temperatures. We show in this work that at a pressure of 15 kbar there are significant changes in the magnetic transition temperatures, comparable to those resulting from decreasing the stage index from 3 to 1.[2] Furthermore, the use of pressure provides the opportunity for changing the magnetic properties of a single well-characterized sample. This is important because of the differences in the transition temperature observed in the susceptibility $\chi(T)$ from one sample to another with the same nominal stage. The remainder of this introduction will review the magnetic properties of $CoCl_2$-GIC's at ambient pressure. Before discussing the magnetic properties in detail, it is worth emphasizing that the magnetic properties of stage-1 and stage-2 $CoCl_2$-GIC's must be explained by different mechanisms. This difference in mechanism is substantiated in these pressure-dependent studies.

The magnetic properties of stage-1 $CoCl_2$-GIC's at ambient pressure and in zero magnetic field are well established. As a function of temperature, the ac susceptibility $\chi = \chi' - i\chi''$, where χ' and χ'' are the real and imaginary components of the susceptibility, shows two transitions at temperatures T_{c1} and T_{c2}. For the stage-1 compound, the peak in $\chi'(T)$ is at $T_{c2}=9.7$ K, close to the three-dimensional (3D) antiferromagnetic ordering temperature $T_N=9.8$ K, as observed from the $(00\frac{1}{2})$ magnetic neutron scattering peak.[4] The nature of the transition at T_{c1} is harder to explain; an in-plane magnetostriction effect is observed[5] to disappear just below T_{c1} suggesting that some domain alignment effect occurs at this transition temperature. When a magnetic field is applied in the x-y plane for temperatures less than T_N, the field sweeps of the susceptibility $\chi'(H)$ show a field-induced maximum at H_t. The transition at H_t occurs when the applied field is just able to overcome the interplanar antiferromagnetic coupling J'. In the low temperature limit H_t=380 Oe. As the temperature is raised, this field structure shifts to lower field and eventually disappears just above T_{c2}. The magnitude of the susceptibility peak maximum at the transition field $\chi'(H_t)$ is largest at $\sim 0.8T_{c2}$.

The ac susceptibility of the stage-2 $CoCl_2$-GIC is much stronger per Co^{2+} ion than in the stage-1 compound,[2] indicative of the more 2D nature of the magnetic behavior of the higher stage compounds. Because of the quasi-2D nature of the magnetic properties of stage-2 $CoCl_2$-GIC's, the upper critical temperature T_{cu} has been identified as the Kosterlitz-Thouless transition temperature. T_{cl} has been identified as the onset of 3D ordering. At low temperatures, the 3D antiferromagnetic order in stage-2 $CoCl_2$-GIC's is not long range and the antiferromagnetic coherence length along the c axis is only 20 Å.[6] At low temperatures, field-dependent susceptibility measurements reveal a "spin-flop" transition at H = 10–15 Oe. However, the transition field diminishes and disappears at T_{cu}=9.1 K, not T_{cl}, at odds with the identification of T_{cu} as a 2D transition temperature. This spin-flop transition is weaker in magnitude than the peak observed at 380 Oe in the $\chi'(H)$ plots of stage-1 compounds. The spin-flop transition has also been observed with field-dependent neutron scattering measurements at 6.0 K;[7] however, H_t has not been followed as a function of temperature by this technique.

The remainder of this paper is organized as follows. The characterization of the samples at various pressures is described in Sec. II. The magnetic results for stage-1 and stage-2 $CoCl_2$-GIC's under pressure are presented in Sec. III. The magnetic Hamiltonian and the pressure properties of pristine $CoCl_2$ are presented in Sec. IV, providing a reference for the pressure-dependent effects of $CoCl_2$-GIC's discussed in Sec. V.

II. SAMPLE CHARACTERIZATION

The magnetic measurements reported in this paper were performed on one highly oriented pyrolytic graphite (HOPG)-based stage-1 sample and one kish-based stage-2 $CoCl_2$-GIC sample. The (00ℓ) x-ray diffraction scans of the samples were checked before and after the pressure experiments; no changes in the diffraction patterns were observed. The θ-2θ traces, measured using Cu K_α radiation, of the two samples after the pressure experiments are shown in Figs. 1(a) and 1(b).

To relate the effect of pressure to the change in the distance between the magnetic intercalate layers, structural measurements under pressure were carried out on a powder stage-1 $CoCl_2$-GIC sample of particle diameter 0.01 mm. High-pressure x-ray diffraction studies were performed utilizing a diamond anvil cell (DAC) with a conventional x-ray generator, and by energy dispersive techniques, with a cubic anvil-type apparatus (MAX80) using the intense synchrotron radiation source in the Photon Factory of the National Laboratory for High Energy Physics (KEK) in Japan.[8] Figure 2 shows a typical spectrum using the MAX80 at pressure P=12.7 kbar. From the shift in the (002), (003), (004), and (006) Bragg peak positions, see Fig. 3, we determine the c-axis compressibility k_c, defined by

$$-\frac{\partial \ln I_c}{\partial P} = k_c \qquad (1)$$

to be $k_c=(1.1\pm0.1)\times10^{-3}$ kbar^{-1} at room temperature. In the zero pressure limit $k_c \approx 1/C_{33}$, where C_{33} is the usual elastic constant for hexagonal systems. No structural phase transitions have been observed up to 50 kbar, and the c-axis compressibilities measured in this pressure range with the DAC and the MAX80 agree to within 1%.

Pristine $CoCl_2$ and graphite are layered materials, with highly anisotropic Young's moduli: C_{11}/C_{33}=29 for graphite[9] and 2.5 for $CoCl_2$.[10] GIC's are also layered materials and when subjected to pressure are expected to have an in-plane compressibility close to that of pristine graphite, $\partial \ln a_{\text{graphite}}/\partial P \approx -1 \times 10^{-4}$ kbar^{-1}.[9] In the powder diffraction patterns, see Fig. 2, the (00ℓ) peaks are the most intense and the only information on the in-plane intercalate structure is contained in the weak $(1\,0\,\frac{7}{3})_{CoCl_2}$ peak. The denominator of 3 in the ℓ index of $\frac{7}{3}$ arises from the rhombohedral stacking of the

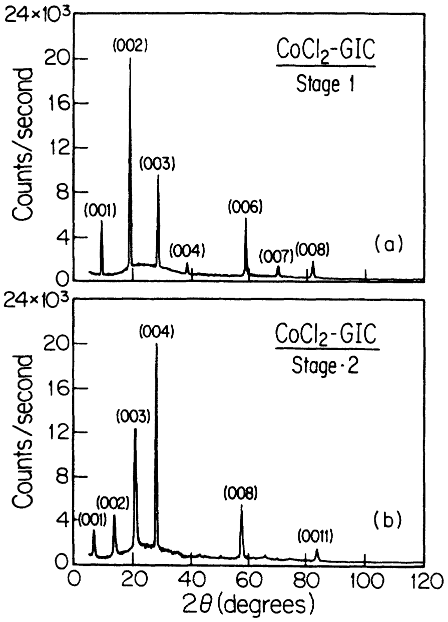

FIG. 1. (00ℓ) x-ray diffraction scans of (a) HOPG-based stage-1 and (b) kish-based stage-2 $CoCl_2$-GIC's taken after the pressure measurements.

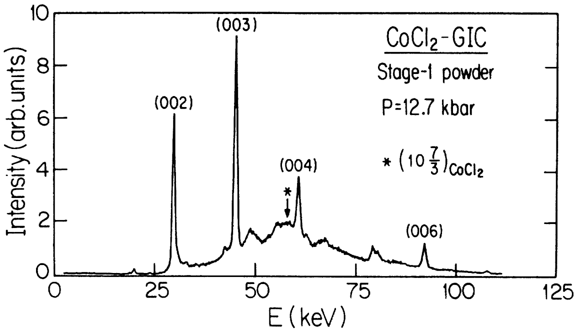

FIG. 2. Typical (00ℓ) energy x-ray diffraction pattern of the powder stage-1 $CoCl_2$-GIC sample at 12.7 kbar. The unlabeled peaks are due to either the sample cell or are used for pressure calibration. The peak labeled by * denotes the $(10\frac{7}{3})_{CoCl_2}$ intercalate reflection.

intercalate,[11] which was not taken into account when the (00ℓ) peaks were indexed. Using k_c and the pressure dependence of the $(1\,0\,\frac{7}{3})_{CoCl_2}$ peak we estimate $\partial \ln a_{CoCl_2}/\partial P \approx -(2 \pm 1) \times 10^{-4}$ $kbar^{-1}$. Therefore, as in other pressure studies of GIC's,[1] we shall assume that the effect of hydrostatic pressure is to change the c-axis properties predominantly.

Graphite has a c-axis compressibility of approximately 2.7×10^{-3} $kbar^{-1}$,[9] whereas pristine $CoCl_2$ has a volume compressibility of 5×10^{-3} $kbar^{-1}$ at 4.2 K and 9×10^{-3} $kbar^{-1}$ at room temperature.[12] The value for $k_c(\text{stage } 1)=1.2 \times 10^{-3}$ $kbar^{-1}$ at room temperature is smaller than either of the constituent materials and its surprisingly low value may be due to several factors. First, in the stage-1 $CoCl_2$-GIC there are no weak interplanar interactions such as the Cl-Cl layer or C-C layer couplings that are present in pristine $CoCl_2$ and graphite, respectively. Second, there is a relatively strong bonding between the intercalate and graphite layers that is responsible for the rhombohedral stacking of both the $CoCl_2$ and the graphite layers in the stage-1 compound.[11] By the same reasoning it is expected that $k_c(\text{stage } 2)$ will be larger than $k_c(\text{stage } 1)$, though we have not performed structural measurements of stage-2 $CoCl_2$-GIC's under pressure. k_c is expected to decrease at lower temperatures, in accordance with the behavior observed in pristine $CoCl_2$.[12]

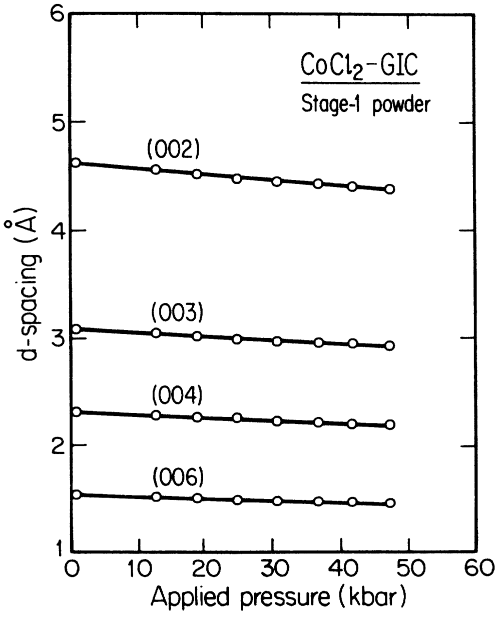

FIG. 3. The variation with applied pressure of the d spacings determined from the (002), (003), (004), and (006) Bragg peak positions of a powder stage-1 $CoCl_2$-GIC sample. The data were obtained using the MAX80.

It is unlikely that the sample will undergo a staging transition as pressure is applied; the temperature at which the pressure is applied (300 K) is low in comparison to that of intercalation (830 K). $CoCl_2$ is not a molecular species like some other acceptor GIC's that have been subjected to pressure. The strong ionic bonds within the Cl-Co-Cl sandwich are expected to make it energetically unfavorable for the intercalate to diffuse at room temperature. Brandt[13] studied the effect of 15-kbar pressure on stage-2 $CuCl_2$-GIC's, compounds that have similar intercalation conditions to $CoCl_2$-GIC's, and found no evidence for a pressure-induced staging transition.

III. MAGNETIC MEASUREMENTS UNDER PRESSURE

The magnetic measurements under pressure were carried out using a clamp-type piston-cylinder cell at the Institute for Solid State Physics in Tokyo. The experimental details of this set up are briefly described here. A heater and a primary coil are wound on the outside of the pressure cell, the primary provides an excitation field of less than 0.1 Oe. Inside the pressure cell is a compressible Teflon cell which contains a lead manometer and the sample mounted in two pick-up coils, all immersed in a pressure medium (Fluorinert made by 3M). The sample is centered inside one of the secondary coils (sample coil), and the other coil serves as the background coil. The magnetic susceptibility χ is proportional to the imbalance signal from the secondary coils, V_{sample}-$V_{\text{background}}$. If detected by a lock-in amplifier which is properly phase shifted, the real χ' and imaginary χ'' components of the susceptibility can be measured. When the pressure medium freezes at low temperatures, the pressure was determined by measuring the shift of the superconducting transition temperature of the lead manometer placed in the background coil. The zero-field χ measurements were carried out in a glass dewar away from any possible remanent magnetic fields. The magnetic field measurements were carried out in a superconducting magnet. The temperature was varied by either placing the pressure cell into an evacuated stainless-steel jacket immersed in liquid helium, or using the Varitemp insert of the superconducting magnet. To ensure thermal equilibration of the pressure cell, the temperature sweeps were limited to a rate slower than 2 K/h. The zero pressure mag-

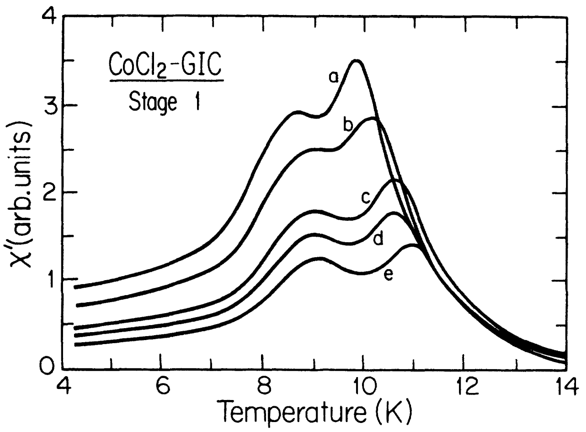

FIG. 4. The zero field temperature-dependent susceptibility $\chi'(T)$ of stage-1 $CoCl_2$-GIC under pressures of (a) 0, (b) 3.1, (c) 8.6, (d) 12.5, and (e) 15 kbar.

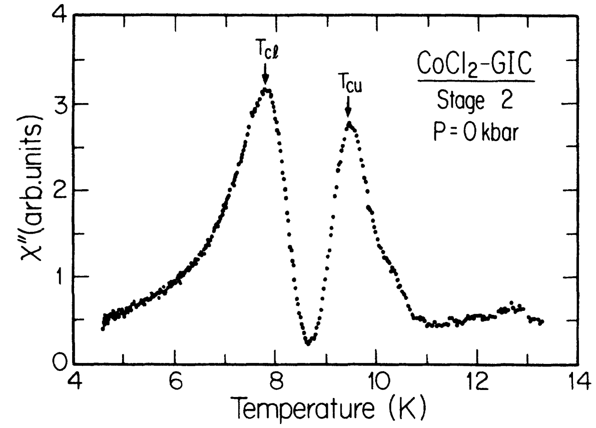

FIG. 6. The zero field measurements of the imaginary part of the susceptibility $\chi''(T)$ of stage-2 $CoCl_2$-GIC at zero pressure.

netic behavior of the samples is in good agreement with measurements in other setups.

To interpret the pressure dependence of χ it is necessary to track some characteristic feature of the susceptibility curves. For stage-1 $CoCl_2$-GIC's, the real part of the susceptibility $\chi'(T)$ shows a double-peak structure as a function of the temperature (see Fig. 4); the position of the lower and upper peaks are designated as T_{c1} and T_{c2}, respectively. The imaginary part of the susceptibility $\chi''(T)$ shows a single peak at T_{c2}. In contrast, $\chi'(T)$ of stage-2 $CoCl_2$ GIC's has only a single peak (see Fig. 5) and the positions of T_{cl} and T_{cu} are determined from the double-peak structure of $\chi''(T)$, see Fig. 6. The magnitude of the peak in $\chi''(T)$ is ~15 times smaller than the peak in $\chi'(T)$ and its magnitude is more severely depressed by pressure than that for $\chi'(T)$. The position of the various transition temperatures for the stage-1 and stage-2 compounds with respect to pressure are plotted in Figs. 7(a) and 7(b), respectively. As previously stated, the transition temperatures of the stage-1 and stage-2 compounds do not have the same interpretation. This is illustrated in Fig. 7 where the lower transition temperature T_{cl} of the stage-2 compound at 15 kbar is approaching the value of T_{c1} of the stage-1 compound at ambient pressure; at the given pressures the I_c values for the two compounds differ by about 3 Å.

All of the transition temperatures show increases with increasing pressure, and these have been fitted with straight lines:

$$T_i(P) = T_i(0)(1+\alpha_i P) , \tag{2}$$

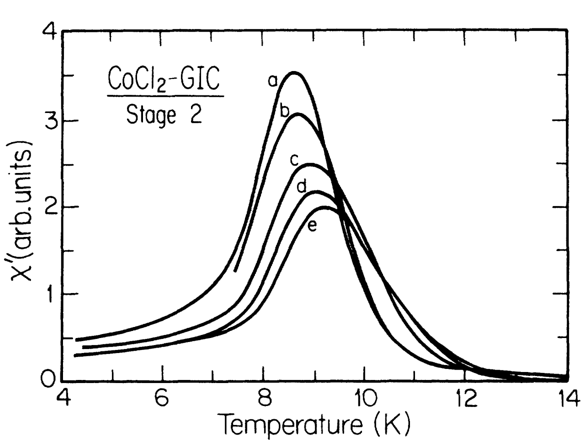

FIG. 5. The zero field temperature-dependent susceptibility $\chi'(T)$ of stage-2 $CoCl_2$-GIC under pressures of (a) 0, (b) 3.1, (c) 8.6, (d) 12.5, and (e) 15 kbar.

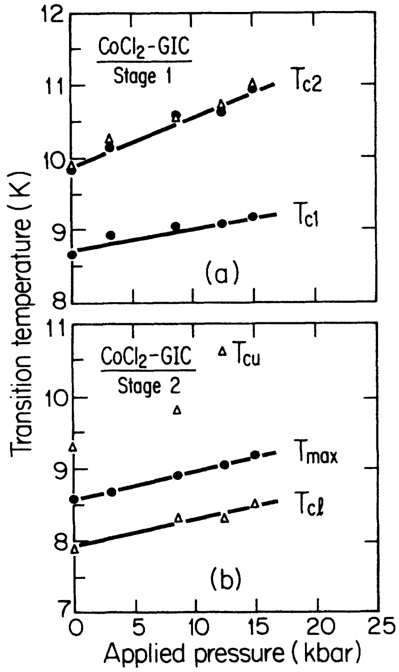

FIG. 7. The position of the transition temperatures under pressure of (a) stage-1 and (b) stage-2 $CoCl_2$-GIC's. The solid bullets (●) are obtained from $\chi'(T)$ data, and the triangles (Δ) are derived from $\chi''(T)$ data. The solid lines are fits to a linear pressure dependence with coefficients given in Table I.

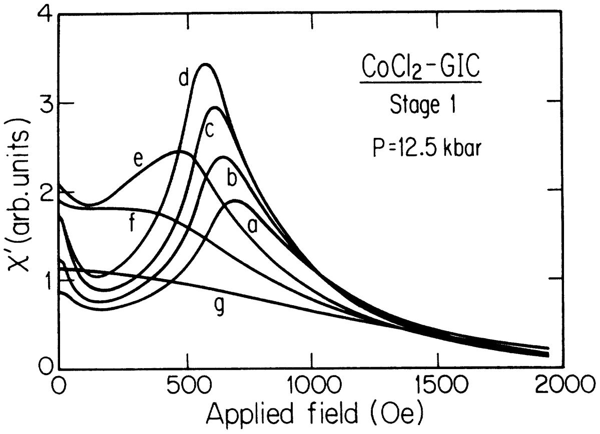

FIG. 8. In-plane susceptibility $\chi'(H)$ field sweeps of stage-1 CoCl$_2$-GIC at 12.5 kbar measured at temperatures (a) 7.28 K, (b) 8.10 K, (c) 8.70 K, (d) 9.23 K, (e) 10.48 K, (f) 11.09 K, and (g) 12.12 K.

where the subscript i=$c1$ and $c2$ refer to the transitions at T_{c1} and T_{c2} in the stage-1 compound. For the stage-2 compound, i=cl, cu, or max; here "cu" and "cl" denote the upper and lower transitions, and "max" refers to the temperature of the $\chi'(T)$ maximum. Referring to Fig. 7(b), the results for T_{cu} and T_{cl} obtained from $\chi''(T)$ are not shown (nor used in the fits) in those cases where the background signal and pressure-induced smearing makes its position ambiguous. We have not attempted to fit the three data points for T_{cu}. The results of the fits are summarized in Table I.

In Fig. 8, we present $\chi'(H)$ data for a stage-1 CoCl$_2$-GIC sample at 12.5 kbar for various temperatures. In the low temperature limit, the field-dependent anomaly in $\chi'(H)$ occurs at H_t=690 Oe, in good agreement with that obtained from resistivity measurements at a similar pressure.[5] The data in Ref. 5 have been reexamined using the maximum of the derivative $|\partial\rho_a/\partial H|$ to determine the transition field H_t. This method of relating the transport results with susceptibility measurements has been shown to give consistent results for a similar field-induced transition in stage-1 NiCl$_2$-GIC's.[14] As the temperature increases, the value of H_t decreases, and the magnitude of $\chi'(H_t)$ is at a maximum at ~9.3 K which is approximately 80% of the Néel temperature T_N=11 K. The latter temperature, being determined from the extrapolated temperature at which the field structure disappears, roughly agrees with T_{c2} at the same pressure.

TABLE I. Pressure-dependent properties of CoCl$_2$-GIC's determined from the results presented in Figs. 7(a) and 7(b). The α_i are defined in the text, and are given in units of 10^{-3} kbar^{-1}.

stage-1 CoCl$_2$-GIC	stage-2 CoCl$_2$-GIC
α_{c1}=3.4±0.7	α_{cl}=4.7±0.8
α_{c2}=6.9±0.5	$\alpha_{\max}$=4.6±0.2

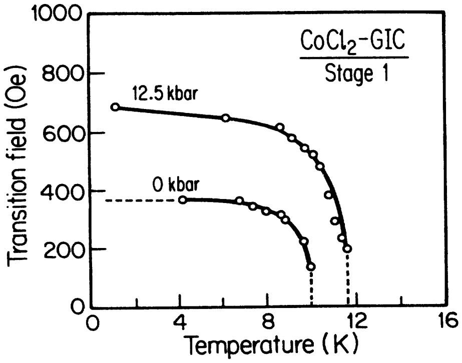

FIG. 9. The H-T phase diagram, derived from $\chi'(H)$ data, for stage-1 CoCl$_2$-GIC's at 0 and 12.5 kbar. The data points show the position of the transition field H_t at various temperatures.

The H-T phase diagram obtained from the measurements at 12.5 kbar is shown in Fig. 9; also included in this figure are the corresponding data for ambient pressure.

IV. REVIEW OF PRISTINE CoCl$_2$ PROPERTIES

The magnetic properties of pristine CoCl$_2$ are discussed using a Hamiltonian $\mathcal{H}$ of the form[15]

$$\mathcal{H} = -J\sum_{i>j}\mathbf{S}_i\cdot\mathbf{S}_j + J_A\sum_{i>j}S_{iz}S_{jz} + J'\sum_{i>k}\mathbf{S}_i\cdot\mathbf{S}_k - g_\perp\mu_B S H_6\sum_i\cos(6\theta_i)\ , \qquad (3)$$

where the subscripts j (k) denote the nearest intraplanar (interplanar) neighbors. The strong in-plane ferromagnetic exchange J between two neighboring Co^{2+} ions is due to a superexchange mechanism mediated by two Cl$^-$ ions in the adjacent chlorine layer.[15] The value of J is very sensitive to the degree and the angle of overlap of the Co^{2+} d orbitals with the Cl$^-$ p orbitals. The squashing of the octahedron of Cl$^-$ ions around the central Co^{2+} ion determines the in-plane anisotropy exchange J_A. As the trigonal distortion δ increases, the ratio J_A/J increases and the in-plane interaction become more XY-like.[16,17] J' is the weak interlayer antiferromagnetic exchange constant and $g_\perp \approx 6$, $S=\frac{1}{2}$, and μ_B is the Bohr magneton. The strength of the sixfold in-plane anisotropy field H_6 can be estimated from the pure electrostatic effect on the Co^{2+} ions of the Cl$^-$ ions treated as point charges. If the Cl-Co-Cl sandwich undergoes pure uniaxial compression, this is not expected to affect H_6 strongly.

The effect of hydrostatic pressure on the magnetic properties of pristine CoCl$_2$ has been investigated by Lukin *et al.*[18] The saturation field H_{sat}, as measured by antiferromagnetic resonance at 4.2 K, is found to increase with pressure from 32 kOe (0 kbar) to 44 kOe (2.1 kbar). H_{sat} is related to the interlayer antiferromagnetic coupling J through the relation

$$2zS^2J' = g_\perp \mu_B S H_{\text{sat}} \,, \tag{4}$$

where $z = 6$ is the number of nearest-neighbor spins on the adjacent planes. Assuming that the volume compressibility of $CoCl_2$ is equal to its c-axis compressibility, then $J'_{\text{pristine}}(I_c)$ can be calculated[18] and the results are plotted in Fig. 10. The variation of J'_{pristine} with I_c was modeled by $J'_{\text{pristine}} \sim \exp(-\beta_{\text{pristine}} I_c)$; the overlap of the wave functions in a superexchange mechanism is expected to have this functional form. The decay constant is determined[18] to be $\beta_{\text{pristine}} \approx 5$ Å^{-1}.

V. DISCUSSION OF THE MAGNETIC PROPERTIES OF COCL$_2$-GIC'S UNDER PRESSURE

Upon intercalation, the Co^{2+} ions within the $CoCl_2$ layers retain their point-group symmetry D_{3d} (Ref. 11) and the form of the Hamiltonian in Eq. (3) will also describe the $CoCl_2$-GIC's. Of the various parameters in Eq. (3), the interlayer antiferromagnetic coupling J' is expected to be reduced most dramatically by intercalation. In fact, the reduction of J' by intercalation is so large that it is no longer possible to interpret the magnetic properties of $CoCl_2$-GIC's as a 3D magnetic system. For example, a 3D theory of Lines[19] predicts that the Néel temperature T_N is close to zero for a ratio $J'/J \sim 10^{-3}$, whereas we know that stage-1 $CoCl_2$-GIC's undergo a 3D ordering near the upper transition temperature T_{c2}. For quasi-2D magnets a more suitable prediction of the 3D ordering temperature is given by

$$k_B T_N \sim J' S^2 (\xi_a/a)^2 \,, \tag{5}$$

where ξ_a is the in-plane spin-correlation length and a is the in-plane lattice constant for the intercalate lattice. In Fig. 4 the magnitude of χ' in the upper temperature range $T > T_{c2}$ is the same at all the measured pressures. This suggests that in this temperature range the in-plane spin-correlation length is behaving in a similar fashion at all pressures. As the pressure and interlayer antiferromagnetic coupling constant increases, the 3D ordering temperature T_N, as predicted by Eq. (5), shifts to higher temperature.

For the stage-1 compound, it appears that the pressure-induced variations of the in-plane magnetic parameters J, J_A, and H_6 are not as important as the increase of $J'_{\text{stage-1}}$. If the hydrostatic pressure only affects the interlayer spacing I_c, we can use Eq. (4) with H_t substituted for H_{sat} to determine $J'_{\text{stage-1}}$ as a function of pressure. Using our measured value for the c-axis compressibility $k_c = 1.2\times10^{-3}$ kbar^{-1}, then $J'_{\text{stage-1}}$ can be estimated as a function of the c-axis spacing I_c. For convenience, the logarithm of $J'_{\text{stage-1}}$ is plotted versus the interplanar spacing I_c in Fig. 10, and from the relation $J'_{\text{stage-1}} \sim \exp(-\beta_{\text{stage-1}} I_c)$ we determine $\beta_{\text{stage-1}} = 4.7\pm0.7$ Å^{-1}. An additional point for the stage-2 compound is included in the figure using a reasonable value for the antiferromagnetic coupling $J'_{\text{stage-2}} = 0.003$ K.[14] In Fig. 10, it is not possible to extrapolate a line from the pristine $CoCl_2$ data points through the stage-1 data points. This suggests that the mechanism for interlayer exchange is different for the two compounds. The superexchange mechanism that is valid for pristine $CoCl_2$ is not appropriate to the stage-1 compound due to an intervening graphite layer containing delocalized electrons. The mechanism in stage-1 $CoCl_2$-GIC's probably has some indirect exchange characteristics, since the interaction is mediated by these graphitic electrons. However, our value of the characteristic length scale of the interaction $1/\beta_{\text{stage-1}} \approx 0.2$ Å is much shorter than the electronic screening length along the c axis $\sim$4 Å as predicted by theory.[20] Referring to Fig. 10, it is also not possible to extrapolate the fit of the stage-1 data points to go through the stage-2 point. This suggests that in the stage-2 compound yet another mechanism is important in determining the magnitude of $J'_{\text{stage-2}}$, probably a long-range classical dipolar force. The possible interlayer exchange mechanisms in $CoCl_2$-GIC's have been discussed by Yeh et al.[21]

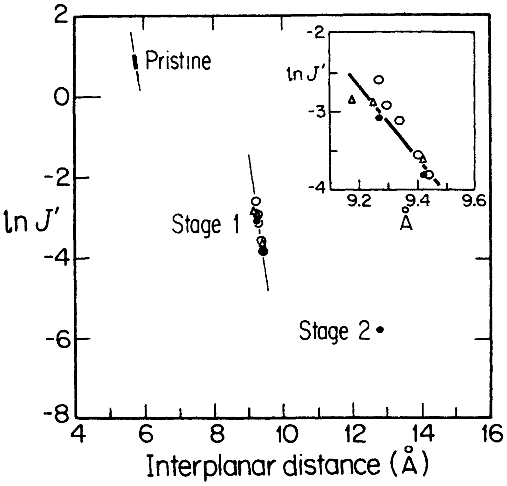

FIG. 10. The interlayer antiferromagnetic exchange ln J' as a function of the c-axis spacing I_c for pristine $CoCl_2$ (Ref. 18), stage-1, and stage-2 $CoCl_2$-GIC's. The fits are extrapolated beyond the experimental points with thin solid lines. The inset shows in detail the lnJ' data points derived from resistivity data (Ref. 5) (△), the magnitude of $1/\chi'$ at 4.2 K (○), and $\chi'(H)$ measurements (●) for the stage-1 compound.

For the stage-2 compounds the application of Eq. (5) with $J' = 0.003$ K yields a spin-correlation length $\xi_a \approx 400$ Å that is very close to the structural size of the "islands" or "lakes" that are presumed to exist in these acceptor compounds.[22] If the upper transition T_{cu} is a 2D transition, as has been suggested by many authors and experiments,[23] the increase in temperature of the upper transition would be controlled by the in-plane magnetic properties. However, it is difficult to determine which of the in-plane parameters is relevant; we shall therefore consider the effect of changing either J or J_A.

If the value of J is increased, the 2D transition temperature T_c will, through the relation $T_c \sim JS^2/k_B$, scale similarly. If the $\mathrm{CoCl_2}$-GIC's were to become more 2D, the susceptibility would diverge more rapidly for $T > T_{cu}$. Our results for the stage-2 compound, see Fig. 5, show that the magnitude of $\chi'(T > T_{cu})$ increases with increasing pressure. We also have some evidence, see Fig. 7(b), that T_{cu} shifts to a higher temperature with increasing pressure.

If the value of J_A is increased, as is expected when the $\mathrm{Cl^-}$ octahedron is compressed along the c axis, the spin anisotropy becomes more XY-like. Monte Carlo simulations of purely 2D systems[24] show that the 2D transition temperature T_c is given approximately by the relation

$$T_c \propto \frac{1}{A - B\ \ln(J_A/J)}\ , \tag{6}$$

where A=1.20 and B=0.08. In the regime where $0 \ll J_A < J$, the transition temperature has only a weak dependence on the anisotropy ratio J_A/J. For pristine $\mathrm{CoCl_2}$ and the $\mathrm{CoCl_2}$-GIC's, the ratio J_A/J is close to 0.5,[17] and from Eq. (6) a 20% increase in J_A/J will induce only a 2% increase in T_c. From these arguments, we therefore conclude that of the two exchange constants, J and J_A, it seems more likely that, upon the application of pressure, the increase in J causes the increase of T_{cu} of the stage-2 $\mathrm{CoCl_2}$-GIC's.

Our comments on the pressure dependence of stage-2 $\mathrm{CoCl_2}$-GIC's have been limited to the effects of pressure on the critical temperatures, since the magnetic field anomaly of stage-2 $\mathrm{CoCl_2}$-GIC's has not been measured as a function of pressure in this work.

VI. CONCLUSIONS

Upon application of hydrostatic pressure, the interplanar spacing of the $\mathrm{CoCl_2}$-GIC's is most significantly changed. For the stage-1 $\mathrm{CoCl_2}$-GIC's, we have shown that with increasing pressure the magnetic couplings become more three dimensional. We have estimated the interlayer exchange coupling parameter J' and its subsequent increase when the magnetic layers are forced closer together. For the stage-2 compounds, the transition temperatures increase with increasing pressure with coefficients that are comparable to those of the stage-1 compounds. Due to the lack of full 3D antiferromagnetic order in the stage-2 compounds, the variation of the in-plane exchange parameter J has been put forward as being responsible for the variation of the transition temperatures with hydrostatic pressure.

For the $\mathrm{NiCl_2}$-GIC's, the ratio of the single-ion anisotropy energy D (which has roughly the same meaning as J_A) to the ferromagnetic coupling J is much smaller: D/J=0.02.[14] For this reason [see Eq. (6)] we expect that, when $\mathrm{NiCl_2}$-GIC's are subjected to pressure, the changes of the transition temperatures will be strongly dependent on changes in D.

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