Magnetic and structural properties of stage-1 NiCl₂-graphite intercalation compounds

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Stage-1 NiCl₂-graphite intercalation compounds (GIC’s) have been prepared under conditions of high temperature and high Cl₂ pressure. These compounds have a c-axis repeat distance of \( I_c = 9.36 \pm 0.05 \text{ Å} \), and the intercalate has a rhombohedral interplanar stacking sequence similar to pristine NiCl₂. Just as with stage-1 CoCl₂-GIC’s, the magnetic behavior of stage-1 NiCl₂-GIC’s appears always to be three dimensional. We interpret the magnetic phase transition at \( T = 22.0 \pm 0.5 \text{ K} \) as the Neél temperature \( T_N \). At lower temperatures, the ac susceptibility shows two magnetic field-induced transitions when a magnetic field is applied in the x-y plane. At \( T = 11.5 \text{ K} \), a temperature much less than \( T_N \), the transition field values are \( H_{c1} = 380 \text{ Oe} \) and \( H_{c2} = 780 \text{ Oe} \). Compared with similar measurements in stage-2 NiCl₂-GIC’s and pristine NiCl₂, we estimate that the ratios of the interplanar antiferromagnetic couplings \( J^\text{pristine} = J_{\text{stage-1}} = J_{\text{stage-2}} \) are 720:24:1. These new results now provide us with two families, stage-1 and stage-2 CoCl₂-GIC’s and NiCl₂-GIC’s, from which some general trends about quasi-two-dimensional systems can be inferred.

I. INTRODUCTION

In this paper we report on the magnetic and structural properties of nearly pure stage-1 NiCl₂-GIC’s (graphite intercalation compounds). This first-stage compound, which has not been investigated before in any detail, provides an important link between pristine NiCl₂ and stage-2 NiCl₂-GIC’s; the latter is considered a good candidate for observing two-dimensional planar magnetic (2D XY) behavior. To facilitate the comparison of the magnetic properties of stage-1 NiCl₂-GIC’s with other GIC’s, it is useful to review the properties of CoCl₂-GIC’s and stage-2 NiCl₂-GIC’s, as well as their parent pristine metal chlorides.

Pristine NiCl₂ and CoCl₂ have been studied as possible XY magnets because the crystal field anisotropy favors the spins lying down in the x-y plane. In these metal chlorides, the in-plane exchange interaction \( J \) is strong and ferromagnetic, whereas the interplanar exchange interaction \( J' \) is weak and antiferromagnetic. Upon intercalation, the NiCl₂ and CoCl₂ layers retain their in-plane properties (e.g., in-plane lattice constants, in-plane exchange constants), but the interplanar parameters will be changed. A dramatic decrease of \( J' \) is expected. However, small \( J' \) becomes, these systems will eventually order into a three-dimensional (3D) magnetic state at a sufficiently low temperature. Below the 3D ordering temperature, there are sheets of ferromagnetically aligned spins, and these sheets are ordered antiferromagnetically along the c axis.

Using neutron scattering, Ikeda et al.\(^1\) reported that stage-1 CoCl₂-GIC’s have a Neél temperature of 9.9 K, which is close to the upper of the two maxima that are observed in temperature-dependent ac susceptibility measurements. For the stage-1 CoCl₂-GIC the c-axis antiferromagnetic coherence length \( \xi_c \) is about 20 magnetic layers.\(^1\) For the stage-2 CoCl₂-GIC, the three-dimensional order is found to set in at a lower temperature, \( T_{cl} = 8.0 \text{ K} \). At a slightly higher temperature, \( T_{cu} = 9.1 \text{ K} \), another magnetic transition is observed, and it is thought that in the region \( T_{cl} < T < T_{cu} \), the stage-2 compound is in a 2D XY Kosterlitz-Thouless phase. Later neutron work\(^2\) provided some support for this identification of the transition temperatures. Although the values of \( T_{cu} \) and \( T_{cu} \) vary from group to group (often using different experimental techniques to probe these magnetic properties), it is always found that the 3D ordering temperature in the stage-1 compound is higher than \( T_{cu} \) and \( T_{cl} \) of the stage-2 compound. Additionally, the 3D magnetic order in the stage-2 compound is not long range as in the stage-1 compound, \( \xi_c \) being equal to two or three layers.\(^2\)

Stage-2 NiCl₂-GIC’s have magnetic properties\(^2\) similar to those of stage-2 CoCl₂-GIC’s, where the values of \( T_c \) are scaled appropriately by \( JS' \), with \( T_{cl} \approx 18 \text{ K} \) and \( T_{cu} \approx 21 \text{ K} \). In this paper we show evidence suggesting that stage-1 NiCl₂-GIC’s order into a 3D antiferromagnetic state at \( 22.0 \pm 0.5 \text{ K} \), a temperature greater than \( T_{cu} \) for stage-2 NiCl₂-GIC’s. This evidence is in part inferred from comparative studies with CoCl₂-GIC’s.
In Sec. II of this paper we report results on the structural characterization of the new stage-1 NiCl$_2$-GIC samples and in Sec. III on magnetic investigations, including ac susceptibility, magnetotransport, and magnetization studies. The magnetic studies are preliminary because we have not yet been able to synthesize stage-1 samples with less than $\sim 10\%$ stage-2 contamination. One major objective of the magnetic experiments is to obtain an approximate value for the interplanar antiferromagnetic coupling constant $J'$ as discussed in Sec. IV.

II. SAMPLE PREPARATION AND STRUCTURAL CHARACTERIZATION

The reaction kinetics and sample preparation conditions for stage-2 NiCl$_2$-GIC’s have been extensively investigated. Like other transition-metal chlorides, the intercalation reaction requires the presence of a Cl$_2$ atmosphere; in general, the higher the chlorine pressure $P_{\text{Cl}_2}$, the lower the stage obtained. In their study, Flandrois et al. state that when the reaction temperature was raised to 690°C, keeping $P_{\text{Cl}_2}$ fixed at one atmosphere, it was not possible to make stage-1 NiCl$_2$-GIC’s.

We have successfully made stage-1 samples using significantly higher Cl$_2$ pressures, about four atmospheres at room temperature, and high temperatures (660°C), using a method previously applied to prepare stage-1 CoCl$_2$-GIC’s of high staging fidelity and homogeneity. The greater difficulty in making stage-1 NiCl$_2$-GIC’s compared to stage-1 CoCl$_2$-GIC’s is probably due to the higher melting point of the former $T_m$ (NiCl$_2$) = 1001°C, and $T_m$ (CoCl$_2$) = 724°C, which causes slower kinetics at a given reaction temperature (e.g., 560°C). Stumpf has recently synthesized nominally stage-1 NiCl$_2$-GIC’s starting with a stage-1 CdCl$_2$-GIC and proceeding with a displacement reaction to yield a mixed compound C$_2$NiCl$_2$(CdCl$_2$)$_{10.14}$; for these samples a c-axis repeat distance of $I_c = 9.36$ Å was obtained. Chieu et al. intercalated benzene-derived graphite fibers, heat treated to 2900°C, and by characterizing these fiber samples using Raman scattering, they were able to demonstrate the presence of stage-1 NiCl$_2$-GIC within the optical skin depth of the fiber. To our knowledge, the present work is the first report of the magnetic properties of stage-1 NiCl$_2$-GIC’s.

In this study, kish graphite, highly oriented pyrolytic graphite (HOPG), and natural flake graphite have been intercalated with NiCl$_2$; it was always easier to intercalate the thinner and smaller pieces of host material. The magnetic results shown in this paper were obtained using natural graphite flakes from Alfa Products, and each flake had a typical weight of 0.1 mg prior to intercalation. The intercalation reaction was carried out in a quartz ampoule and took 1–2 months, after which the samples were blue, typical of stage-1 acceptor compounds. The (00l) x-ray diffraction scan, Fig. 1, using Cu $K\alpha$ radiation shows that the single crystals are not pure stage-1, but are contaminated with weak stage-2 peaks [the (003) peak marked in Fig. 1 at 2$\theta$ = 21.1° being particularly strong]. From the stage-1 peak positions, the value $I_c = 9.36 \pm 0.05$ Å was obtained. The scans show little evidence of shifting or broadening of the x-ray peaks; such broadening effects would suggest random-layer stacking of the different stages according to the Hendricks-Teller model.

X-ray precession studies of small single crystals have allowed us to elucidate the crystallography of this GIC system. Zero-level x-ray precession photographs recorded along c and a are shown in Fig. 2. These zero-level photographs represent two-dimensional “slices” of the reciprocal lattice (normal to the real-space-zone axis) which include the origin of reciprocal space. Upon intercalation, the NiCl$_2$ and graphite maintain their pristine in-plane symmetries and lattice constants within $\sim 1\%$. Hence the NiCl$_2$ layers are translationally incommensurate with respect to the carbon layers. The intercalate layer in stage-1 NiCl$_2$-GIC’s (as with all of the incommensurate MCl$_2$-GIC’s, where $M$ denotes a metal atom) exhibits rotational epitaxy with $a_{\text{NiCl}_2}$ centered about $a_{\text{graphite}}$ with a FWHM linewidth of $\sim 4^\circ$ as shown schematically in Fig. 2(c). This range of misorientation accounts for the circumferential arcing of the intercalate $(hk0)$ reflections shown in Fig. 2(a).

The stacking sequence is determined by indexing precession photographs along the in-plane axes. To successfully index the a-axis precession photographs, a domain twin model must be incorporated to account for the fact that the three-dimensional intercalate structure possesses lower symmetry ($R\bar{3}m$) than an individual carbon (graphene) layer (6mm). Assuming that the NiCl$_2$ layers have $R\bar{3}m$ symmetry, there are two unique possible orientations of the intercalate layer. Using these two lattices, all of the intercalate reflections satisfy the condition $-h + k + l = 3m$, where $m$ is an integer. These two sets of reflections are indicated in Fig. 2(d) by solid and partially closed circles in the schematic interpretation of the a-axis precession photograph. This condition results in rhombohedral (· · · $a\bar{b}f\gamma a\bar{b}f$ · · ·) stacking for the inter-
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FIG. 2. Zero-level x-ray precession photographs from stage-1 NiCl₂-GIC (a) zone-axis along c and (b) zone-axis along a. (c) A schematic interpretation of the photograph (a) showing both the graphite and intercalate reciprocal unit cells. (d) Schematic interpretation of (b) showing the \( hkl \) reciprocal lattice point identifications. The indexing scheme used is that of the full three-dimensional lattice; hence the \( l \) values are three times larger than used in the indexing of Fig. 1. The large solid circles indicate \( hOl \) reciprocal lattice points from one of two possible intercalate orientations. The partially open circles indicate \( 0kl \) reciprocal lattice points from the other intercalate orientation.

calate layers, similar to the stacking in pristine NiCl₂. The diffuse nature of the intercalate \( (hOl) \) or \( (0kl) \) reflections in Fig. 2(b) is attributed to both the large mosaic spread in the crystal and the small 3D crystallographic coherence length. A more complete report of this structural work will be published elsewhere.⁸

Further evidence for 3D ordering of the intercalate layers comes from x-ray diffraction results measured on a four-circle diffractometer. In Fig. 3 we show a radial scan \( (\theta-2\theta) \) through the \( (113)_{NiCl₂} \) peak (see inset of Fig. 3 for scan direction). The first peak encountered as \( 2\theta \) increases is \( (110)_{NiCl₂} \) at \( 2\theta=52.35^\circ \). The shoulder on the high \( 2\theta \) side of the \( (110)_{NiCl₂} \) peak is the \( (113)_{NiCl₂} \) peak \( (2\theta=53.31^\circ) \). The large mosaic spread in the crystal smears the 110 and 113 reciprocal lattice points into spherical caps. A portion of the 110 spherical cap lies in the path of a vector connecting the origin of the reciprocal lattice to the center of the \( 113_{NiCl₂} \) reciprocal lattice position. Hence the first peak measured in a scan from the origin to \( 113_{NiCl₂} \) is the \( (110)_{NiCl₂} \) peak. The scan in Fig. 3 clearly shows a distinct \( (113)_{NiCl₂} \) peak. The presence of discrete \( (hkl) \) reflections is a clear indication of 3D ordering of the intercalate.
III. Experimental Results

In-plane ac susceptibility measurements $\chi^{\text{ac}}$ were performed on a mosaic array of six intercalated natural graphite pieces mounted on a glass coverslip. The modulating field of amplitude 0.3 Oe, frequency 300 Hz, is parallel to the applied field $H$. The $\chi^{\text{ac}}$ versus $T$ data, see Fig. 5, show a stage-1 shoulder at $T=23.0\pm0.5$ K. The much larger peak observed at $T=18.5$ K is the susceptibility maximum for the stage-2 NiCl$_2$-GIC's and higher stage regions of the sample. The higher-stage susceptibility contributions are much stronger than the stage-1 contribution (even though the higher stages are minority phases as determined by x rays), because the susceptibility signal per Ni$^{2+}$ ion increases rapidly with increasing stage number $n$. This conclusion is inferred from the rapid increase of the susceptibility maximum versus stage $n$ that was observed in the CoCl$_2$-GIC's (Ref. 11) and in the FeCl$_2$-GIC's. When the $\chi^{\text{ac}}(T)$ measurements on the NiCl$_2$-GIC sample (see Fig. 5) were repeated in the presence of a magnetic field, the lower-temperature peak was completely suppressed by a field of $H=300$ Oe. The upper peak was also slightly attenuated and this peak was shifted to a lower temperature ($\sim 22.0$ K). Figure 6 shows a series of $\chi^{\text{ac}}(H)$ plots, the data being taken at different temperatures $T$. At $T=11.5$ K (plot $a$), the lowest temperature at which two peaks could be clearly observed, the field values of the maxima (interpreted as field-induced phase transitions) were $H_{\text{a1}}=380$ Oe and $H_{\text{a2}}=780$ Oe. As the temperature increases, the two transitions move towards lower field values, as shown in plots $b$ to $h$. These peak structures persist up to $T=21.4$ K (plot $i$), but disappear by $T=22.5$ K (plot $j$). In the low-field region $H<100$ Oe, we observed the susceptibility contribution of the stage-2 regions of the samples; here there were low field transitions, as were previously observed by Suzuki et al. The low field transi-

Additional structural evidence for the existence of stage-1 NiCl$_2$-GIC was obtained from Raman characterization. Figure 4 shows a single Raman peak at 1624 cm$^{-1}$, with HWHM = 4.0 cm$^{-1}$; this spectrum was obtained from the edge of an HOPG-based sample, where the edge was visibly thicker than the rest of the sample. In the center of this sample, the Raman spectrum showed two peaks (1583 cm$^{-1}$, 1608 cm$^{-1}$) that are characteristic of a much higher stage ($n \geq 3$). The first-order Raman peak centered at 1624 cm$^{-1}$ occurs at a lower frequency than the Raman shift of 1633.5 cm$^{-1}$ observed in the intercalated fibers, but is still within the range of values that has been reported for several stage-1 acceptor compounds.

FIG. 3. Radial scan ($\theta - 2\theta$) of single-crystal stage-1 NiCl$_2$-GIC through the 113$_{\text{NiCl}_2}$ reciprocal lattice point. The inset shows the direction of the scan. The circumferential arcing of the reciprocal lattice points is due to the mosaic spread in the crystal. Because of the large mosaic spread of the crystal used for this experiment, the (110)$_{\text{NiCl}_2}$ peak is also measured in this scan (see text for further details).

FIG. 4. Raman spectrum of a stage-1 region of a HOPG-based NiCl$_2$-GIC sample.

FIG. 5. $\chi^{\text{ac}}(T)$ data for the nominal stage-1 NiCl$_2$-GIC sample showing a stage-1 maximum at 23 K and a stage-2 (and higher stage) peak at about 18 K. The lower temperature peak can be essentially eliminated by the application of a field of 300 Oe.
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FIG. 6. In-plane ac susceptibility $\chi^a$ vs $H$ of a mosaic of stage-1 NiCl$_2$-GIC samples at different temperatures: a, 11.5 K; b, 16.1 K; c, 16.9 K; d, 17.8 K; e, 18.8 K; f, 19.7 K; g, 20.2 K; h, 21.2 K; i, 21.4 K; j, 22.5 K; k, 23.3 K. No demagnetization corrections were made, and the traces in the figure are displaced so that the various sweeps do not overlap. The peaks $H_{c1}$ and $H_{c2}$ are indicated.

FIG. 7. The $H$-$T$ phase diagram derived from $\chi^a(H)$ data, showing data points for the $H_{c1}$ and $H_{c2}$ transitions. The solid lines are a guide to the eye.

FIG. 8. SQUID magnetization trace taken at $T$=7.5 K on the same mosaic sample as in Fig. 6.

FIG. 9. Resistivity $\rho_a$ vs temperature $T$ of a single flake of intercalated (stage-1 NiCl$_2$ GIC) natural graphite in applied in-plane magnetic fields of 0, 300, 600, and 1200 Oe.

FIG. 10. Temperature dependence of the magnetization as a function of field in 051 (a) and 051 (b) for different values of field as indicated. The susceptibility $\chi$ is given in arbitrary units.

The susceptibility values of $H_{c1}$ and $H_{c2}$ for various temperatures are plotted in Fig. 7, as shown in Fig. 8. Similar susceptibility results were obtained for larger HOPG-based nominal stage-1 samples, for which an overall stronger signal was obtained, but the HOPG samples showed proportionally larger stage-2 regions. The size of the anomaly at $H_{c1}$ was also found to be relatively smaller in the HOPG-based samples.

Magnetization measurements, Fig. 8, were also carried out, using the SQUID magnetometer at the Francis Bitter National Magnet Laboratory. The measurements of $M(H_{lc})$ confirm the $\chi^a(H)$ measurements presented in Fig. 6 and check that there are no higher field transitions (up to 10 kOe) than those accessible in the susceptibility measurements in our traces disappeared at $T$=20 K. Unfortunately, there are no field traces reported above 19.4 K for stage-2 NiCl$_2$-GIC (Ref. 13) with which we can compare our data.

For $T$=7.5 K the in-plane magnetization saturated at $\sim$3 kOe. Magnetotransport experiments were carried out on a single flake of NiCl$_2$ intercalated natural graphite with an area of about 1 mm$^2$. The standard four-probe method was used; a dc current of 1 mA was used and the magnetic field was applied in the x-y plane. There was no noticeable difference in the transport results when, keeping $H_{lc}$, the geometry was changed from ($j||H$) to ($j\bot H$), where $j$ is the current density. Although the transport measurements are sensitive to scattering contributions from differently staged parts of the sample, the magnetic scattering contributions to the transport properties of a pure stage-2 sample were measured to be less than the experimental noise level, so we assume that the stage-1 NiCl$_2$-GIC is the predominant magnetic scatterer of conduction electrons in our mixed phase sample.

In the zero-field resistivity trace shown in Fig. 9, the temperature $T$ was swept from 30 to 5 K. The most striking feature of the zero-field data is the sharp increase of the resistivity for temperatures less than 21.5 K. The magnitude of the maximum scattering from the magnetic fields 0, 300, 600, and 1200 Oe are also indicated.

The results presented here show that the susceptibility measurements are sensitive to the magnetic properties of the sample. The susceptibility measurements provide a clearer picture of the magnetic transitions in the sample, especially when compared to the magnetization measurements.
species compared to the “background” resistivity 
\[ \rho_a = a + bT + cT^2 \] is expected for typical nonmagnetic 
GIC’s (Ref. 14)) \( \Delta \rho_a / \rho_a \) varies from 1% to 10%, depend-
ing on the sample. The most likely cause of this variation 
is the lack of homogeneity in the samples and the resultant 
mixing of \( \rho_a \) and \( \rho_c \). The previously mentioned sharp 
increase in resistivity can be reduced by application of a 
magnetic field, e.g., at 600 Oe, the size of \( \Delta \rho_a / \rho_a \) at low 
temperatures is halved. In a field of 1200 Oe, the magnetic 
scattering is nearly quenched. Figure 10 shows field 
sweeps for \( \rho_a(H) \) at different temperatures. The data 
have been displaced to show clearly that upon approaching 
\( T = 21.5 \) K the magnetoresistance becomes flatter. 
Within experimental error, the traces at \( T = 21.6 \) K 
(trace 6) and \( T = 21.9 \) K (trace 7) are identical, from 
which we conclude that \( T_N \sim 21.5 \) K at a field of \( \sim 300 \) 
Oe. Furthermore, \( T_N \) predicted in this way is lower than 
for the \( H = 0 \) experiments because \( T_N \) depends on \( H \). 
This behavior is consistent with the \( H-T \) phase diagram 
in Fig. 7 and with the magnetic field-induced shift in the 
peak in \( \chi^\alpha(T) \) shown in Fig. 5.

The field dependence of the resistivity \( \rho_a(H) \), at fixed 
temperature \( T \), has fewer features than the corresponding 
susceptibility \( \chi^\alpha(H) \) traces. We can define the transition 
field \( H_T \) as the point at which \( |\partial \rho_a / \partial H| \) is maximum in 
the traces of Fig. 10; this maximum is shown for \( T = 4.2 \) 
K in the lower half of Fig. 11 in relation to the \( \rho_a(H) \) 
trace shown in the upper half of the figure. The values of 
\( H_T \) thus obtained for different temperatures are plotted in 
Fig. 12. The resistivity (in the upper half of Fig. 11) is 
found to be featureless above 3 kOe, a field value that can 
be interpreted as the saturation field \( H_{sat} \).

IV. DISCUSSION

In all the transition-metal chloride GIC’s investigated 
to date, the intercalate does not completely fill the layers 
between the graphite sheets,\(^3,4\) we assume that the stage-1 
NiCl\(_2\)-GIC’s are no exception. The in-plane lattice 
constants of pristine NiCl\(_2\) and CoCl\(_2\) (both have the CdCl\(_2\) 
structure) differ by less than 0.5% and the rotational epitaxial 
angles and layer-stacking arrangements for stage-1 
NiCl\(_2\)-GIC’s are the same as for stage-1 CoCl\(_2\)-GIC’s. 
The consistency of these structural results with other 
transition metal MCl\(_2\)-GIC’s is explained elsewhere.\(^8,15\)
The value of the repeat distance \( I_c = 9.36 \pm 0.05 \) Å is 
consistent with the \( I_c \) (stage-2) = 12.67 \pm 0.03 Å result\(^3\) 
and application of the formula \( I_c = (n - 1)c_0 + d_{2l} \), where 
\( d_{2l} = I_c \) (stage-1), \( n \) is the stage number, and \( c_0 = 3.35 \) Å. 
Our value of \( I_c \) also agrees with that obtained by 
Stumpp.\(^3\)

The magnetic properties of stage-1 NiCl\(_2\)-GIC’s are 
expected to lie between those of pristine NiCl\(_2\) and stage-2 
NiCl\(_2\)-GIC’s. The Hamiltonian for pristine NiCl\(_2\) may be

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**Fig. 10.** In-plane resistivity \( \rho_a(H) \) of intercalated (stage-1 
NiCl\(_2\)-GIC) natural graphite single crystal at various temperatures: 
\( a, 4.2 \) K; \( b, 9.4 \) K; \( c, 12.2 \) K; \( d, 16.4 \) K; \( e, 17.8 \) K; \( f, 18.7 \) K; \( g, 19.5 \) K; \( h, 20.0 \) K; \( i, 20.4 \) K; \( j, 21.0 \) K; \( k, 21.6 \) K; \( l, 21.9 \) K.

**Fig. 11.** The resistivity and its derivative at \( T = 4.2 \) K as a 
function of magnetic field.

**Fig. 12.** The \( H-T \) phase diagram derived from \( \rho_a(H) \) data, 
showing data points for the \( H_T \) transition. The solid line is a 
guide to the eye. Note the similarity of the \( H_T \) values compared 
with those of \( H_{c2} \) shown in Fig. 7.
written in the form

$$\mathcal{H} = -2J \sum_{i>j} S_i \cdot S_j - 2J' \sum_{i>k} S_i \cdot S_k + D \sum_i (S_i^z - S_i^{2z} - S_i^{2y}),$$

where the index \( j \) (\( k \)) is over nearest-neighbor intraplanar (interplanar) spins, and \(|S| = 1\). The values \( J = 21.7 \) K, \( D = 0.4 \) K, and \( J' = -0.8 \) K have been measured for pristine NiCl\(_2\) by magnetization\(^{7,16}\) and neutron scattering\(^{16}\) experiments. This Hamiltonian [Eq. (1)] was used to describe stage-2 NiCl\(_2\)-GIC's,\(^{19}\) which show quasi-two-dimensional behavior at \( J_S^2/k_B \approx 20 \) K, suggesting that \( J \) (and other in-plane magnetic properties) is not strongly affected by intercalation. The value of the anisotropy of the \( g \) value, \( g_{an} - g_{ee} = -2.156 - 2.096 = 0.06 \) obtained in the stage-2 compound\(^{16}\) gives rise to a calculated anisotropy (using the theory of Lines\(^{20}\) as a rough estimate) of \( D/J = 0.021 \), close to that of the pristine material (0.018) and suggesting \( XY \) behavior. It is expected that a similar value for \( D/J \) will be found in the intermediate stage-1 compounds, and it is further assumed that the above Hamiltonian will also describe stage-1 NiCl\(_2\)-GIC's. The only stage-dependent quantity in \( \mathcal{H} \) is the antiferromagnetic interaction \( J' \), which we estimate below.

The zero-field susceptibility peak at \( T = 23 \) K occurs at a higher temperature than any other magnetic feature observed in the ac susceptibility of the stage-2 compounds.\(^{13}\) The relatively weak sensitivity of the magnitude of the 23 K peak to an applied field (see Fig. 5) supports its identification with the stage-1 phase of the sample. We can tentatively interpret the Neel temperature \( T_N \) as being close to 23 K; the peak structure in \( \chi^{xy}(H) \) and in \( \langle \partial \rho_{xy} / \partial H \rangle \) disappears at 22.0±0.5 K. This is usual behavior for a conventional antiferromagnet, i.e., the temperature of the ac susceptibility maximum is found to be higher than the actual 3D ordering temperature as determined by neutron scattering. Within the accuracy of our susceptibility and resistivity experiments, we obtain \( T_N = 22.0 \pm 0.5 \) K for stage-1 NiCl\(_2\)-GIC's. By comparison, the susceptibility maximum in stage-1 CoCl\(_2\)-GIC's also occurs at higher temperatures than the maxima of the higher-stage CoCl\(_2\)-GIC's.

In interpreting the magnetic field results, we know that the minority stage-2 phase is saturated at fields above 100 Oe.\(^{13,21}\) The phase transitions that we observe at \( H_{c1} \) and \( H_{c2} \) are too high in field to be confused with stage-2 (or higher stage) effects and are too small in field to be caused by pristine NiCl\(_2\). In the 3D ordered phase of this system, we would expect a number of transitions when a magnetic field is applied in the \( x \)-\( y \) plane. In zero field, the system is an antiferromagnet (AF); at a certain field the antiferromagnetic phase flops into the spin-flop (SF) phase, where the spins on alternate layers are aligned at angles of \( \pm \pi/3 \) with respect to the magnetic field applied along an easy direction.\(^{22}\) At even higher fields, there will be an eventual alignment of the spins along the applied field, leading to the spin-aligned paramagnetic (P) phase. The ratio \( H_{c2}/H_{c1} \approx 2 \) is similar to that observed in stage-1 CoCl\(_2\)-GIC's (300/160) (Ref. 22) and in stage-2 NiCl\(_2\)-GIC's (25/15) (Ref. 13) but cannot be explained by the mean-field theory proposed by Szeto et al.,\(^{22}\) where the ratio \( H(SF \rightarrow P)/H(AF \rightarrow SF) = 3.0 \) at \( T = 0 \) K. A value of 3 for this ratio is also found by Monte Carlo simulations.\(^{23}\) The peak structure at \( H_{c1} \) in \( \chi^{xy} \) versus \( H \) for stage-1 CoCl\(_2\)-GIC's is not observed in all samples; later work on better characterized samples found the peak at \( H_{c2} \) to be more dominant. The strong sample dependence of the \( H_{c1} \) structure in both stage-1 NiCl\(_2\) and CoCl\(_2\)-GIC's is not well understood, but may be due to the range of angles of the easy axes on the various magnetic layers with respect to the applied magnetic field.

To estimate the magnitude of the antiferromagnetic coupling \( J' \) we shall ignore the low field structure and assume that the in-plane anisotropy is small compared to \( J' \). We can estimate the magnitude of \( J' \) from the saturation field, which is the field that is required, at \( T = 0 \) K, to overcome the antiferromagnetic interplanar coupling, and is given by

$$H_{sat} \approx 2J'/g_{an} \mu_B H,$$

where \( \mu_B \) is the Bohr magneton. The number of next nearest neighbors on adjacent Ni\(_{2+}\) layers, \( z = 12 \), is the same for both the stage-1 and pristine compounds. From our studies of the magnetization \( M(H) \) and resistivity \( \rho_{xy}(H) \), we estimate that \( H_{sat} = 3.0 \) kOe for stage-1 NiCl\(_2\)-GIC's, and hence the value of \( |J'/J| = 1.5 \times 10^{-3} \)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pristine NiCl(_2)</th>
<th>Stage-1 NiCl(_2)-GIC</th>
<th>Stage-2 NiCl(_2)-GIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlayer distance(^a)</td>
<td>5.73±0.05 Å</td>
<td>9.36±0.05 Å</td>
<td>12.67±0.03 Å</td>
</tr>
<tr>
<td>NiCl(_2) stacking</td>
<td>rhombohedral</td>
<td>rhombohedral</td>
<td>random</td>
</tr>
<tr>
<td>( \theta^b )</td>
<td>0°±2°</td>
<td>0°±2°</td>
<td></td>
</tr>
<tr>
<td>( T_N )</td>
<td>54.5 K</td>
<td>22.0±0.5 K</td>
<td>25.0 K</td>
</tr>
<tr>
<td>( H_{c1}(0) )</td>
<td>380 Oe</td>
<td>15 Oe</td>
<td></td>
</tr>
<tr>
<td>( H_{c2}(0) )</td>
<td>380 Oe</td>
<td>25 Oe</td>
<td></td>
</tr>
<tr>
<td>( H_{sat}(0) )</td>
<td>3 kOe</td>
<td>100 Oe</td>
<td></td>
</tr>
<tr>
<td>(</td>
<td>J'/J</td>
<td>)</td>
<td>0.037</td>
</tr>
</tbody>
</table>

\(^a\)Interlayer distance denotes the separation between consecutive Ni\(_{2+}\) layers.
\(^b\)Rotational epitaxy angle.
\(^c\)Reference 13.
given in Table I can be calculated. In the same table this ratio is estimated for stage-2 NiCl₂-GIC's assuming that $H_{sat} = 100$ Oe. The ratio of $J'(\text{pristine})/J'(\text{stage-1})$ is $\sim 30$ for both NiCl₂ and CoCl₂-GIC's, suggesting that a similar mechanism is responsible for the reduction of $J'$ in both stage-1 compounds. If we extrapolate our reasoning to the stage-2 compounds, using $J'(\text{pristine})/J'(\text{stage-2}) = 720$ for stage-2 NiCl₂-GIC we estimate that $J'_{\text{stage-2 CoCl₂}} = 0.003$ K, close to the value obtained from high-temperature susceptibility measurements, where $J' = 0.007$ K.

The transport properties of stage-1 NiCl₂-GIC's are very similar to their stage-1 CoCl₂ counterparts, where a careful comparison between $\chi^{(H)}$ and $\rho(\text{H})$ shows that $\rho_a(\text{H})$ is only sensitive to the transition at $H_{c2}$; no detailed comparison was carried out in Ref. 25. Figure 7 (susceptibility) and Fig. 12 (magnetoresistance) show similar behavior for the temperature dependence of $H_{c2}$ in stage-1 NiCl₂-GIC's.

The resistivity behavior can be explained by a model that accounts for the additional periodicity introduced in the $k_z$ direction by the antiferromagnetic ordering along the c axis; this causes a Fermi surface distortion that affects the transport properties. The theory was originally developed to explain resistance anomalies in the rare-earth metals, and predicts that

$$1/\rho_a = \sigma_a = \sigma_a(0)[1 + O(\Delta/E_F)]^2$$

and

$$1/\rho_c = \sigma_c = \sigma_c(0)[1 - O(\Delta/E_F)]^2,$$

where $\Delta$ is the new energy gap introduced at the Fermi level $E_F$ due to the AF order, and $\sigma_a(0)$ and $\sigma_c(0)$ are the $a$- and $c$-axis conductivities of the unperturbed system without Fermi-surface distortions. In the usual case we have $\Delta/E_F \ll 1$, and the change in $\sigma_a$ will be much larger than the change in $\sigma_c$. If there is strong mixing of $\sigma_a$ and $\sigma_c$ by staging defects or other inhomogeneities, then this theory may account for the unusual magnetic behavior observed in $\rho_a$. However, if the experimental measurements of $\rho_a$ are precisely in-plane, and if $\rho_a$ increases anomalously below $T_N$ (as indicated in Fig. 9), then the theory of Sugihara et al. 25 may be more suitable. Whichever theory is correct, both require long-range antiferromagnetic order along the c axis, a condition that is satisfied by stage-1 CoCl₂-GIC's. 1 The transport results suggest a similar long-range magnetic order in stage-1 NiCl₂-GIC's; however, neutron scattering measurements are needed to confirm this conjecture.

A number of factors may be responsible for the purely three-dimensional magnetic behavior of NiCl₂ and CoCl₂ stage-1 compounds compared to the quasi-two-dimensional behavior of their respective stage-2 compounds. First $J'(\text{stage-2})$ is reduced relative to $J'(\text{stage-1})$ because the distance between the metal-ion layers is increased due to the presence of an extra graphite layer. Second, these properties depend on the enhancement of the interplanar antiferromagnetic interaction in the stage-1 compound relative to stage-2 due to the in-plane spin-correlation length $\xi_0$ through the formula

$$J'S(\xi_0/a)^2 \sim k_B T_N,$$

where $T_N$ is the 3D ordering temperature and $a$ is the distance between adjacent spins in the x-y plane. For stage-1 NiCl₂-GIC's and CoCl₂-GIC's we estimate $J'$ from $H_{sat}$; from Eq. (5), this gives $\xi_0$ values of 90 and 40 Å, respectively. For the stage-2 CoCl₂-GIC's, $\xi_0$ saturates at 900±150 Å for $T < T_{cu}$, 27 and the value of $\xi_0$ calculated from Eq. (5) for a stage-2 NiCl₂-GIC is of the same order, i.e., 480 Å. These effects are under further investigation.

V. CONCLUSIONS

In conclusion, we have prepared stage-1 NiCl₂-GIC's and have characterized their magnetic and structural properties. We have found a large number of similarities between stage-1 NiCl₂-GIC's and stage-1 CoCl₂-GIC's. They both exhibit rhombohedral stacking of the intercalate layers which are oriented at 0° with respect to the graphite a axes. This structural three dimensionality also affects the magnetic behavior. Magnetically the two compounds appear to undergo a transition to an ordered 3D antiferromagnetic state. For $T < T_N$, this gives rise to field-induced transitions and strong conduction-electron scattering. We have also obtained a measure of how the interplanar coupling $J'$ decreases upon intercalation and a measure of the stage dependence of $J'$.

ACKNOWLEDGMENTS

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MAGNETIC AND STRUCTURAL PROPERTIES OF STAGE-1 . . .

FIG. 2. Zero-level x-ray precession photographs from stage-1 NiCl₂-GIC (a) zone-axis along c and (b) zone-axis along a. (c) A schematic interpretation of the photograph (a) showing both the graphite and intercalate reciprocal unit cells. (d) Schematic interpretation of (b) showing the hkl reciprocal lattice point identifications. The indexing scheme used is that of the full three-dimensional lattice; hence the l values are three times larger than used in the indexing of Fig. 1. The large solid circles indicate h0l reciprocal lattice points from one of two possible intercalate orientations. The partially open circles indicate 0kl reciprocal lattice points from the other intercalate orientation.