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Magnetic properties of graphite intercalation compounds

A. K. Ibrahim and George O. Zimmerman
Physics Department, Boston University, Boston, Massachusetts 02215
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Comprehensive measurements of the magnetic properties of $FeCl_3$ graphite intercalation compounds are presented with an emphasis on the low-temperature region where a susceptibility maximum is observed in all stages. This maximum, which varies in size according to stage, occurs in a very narrow temperature range and is attributed to the two dimensionality of the intercalate system. It obeys the power law of a second-order phase transition with an exponent γ which has a value between 1.8 and 2.0. The maximum occurs only in the in-plane direction with no corresponding c-axis-susceptibility response. The application of an external magnetic field drastically suppresses the susceptibility maximum and shifts it to higher temperatures. Both in-plane and out-of-plane measurements are presented and the magnetic properties of stages 1–6, as well as stage 9, are compared.

I. INTRODUCTION

Graphite intercalation compounds (GIC's) are naturally layered[1] and are of interest because electronically, only the graphite layers next to the intercalant change significantly upon intercalation.[2] For a magnetic intercalant, the inner layers can be a controlling factor in the magnetic interactions between different magnetic intercalant layers. The systematic change of the number of graphite layers between two adjacent intercalant magnetic layers can provide two-dimensional magnetic systems by shielding the intercalant layers from each other until their interaction is insignificant.

Magnetic compounds have been widely used in the intercalation of highly ordered pyrolytic graphite (HOPG) and generally one observes magnetic anomalies in the GIC, even in high stages (stage index refers to the number of graphite layers between two consecutive intercalant layers). It has been reported[3] that for all the magnetic compounds which have a low-temperature phase transition there exists a corresponding transition when these compounds are intercalated into graphite. Additional transitions due to the magnetic two dimensionality of the systems were also reported.[4,5] Thus intercalation of magnetic species into graphite provides very useful model systems for the study of two-dimensional magnetism.

In this work we present a systematic study of the low-temperature phase transition of $FeCl_3$-intercalated graphite compounds and its behavior as a function of the stage of the sample. We also investigate the dependence of these transitions on an external dc magnetic field. Our data for $FeCl_3$ GIC are compared with reported data for similar GIC systems. The standard low-frequency ac-susceptibility bridge technique[6] is used to obtain the experimental data.

The crystal structure of $FeCl_3$ is a repeated sequence of atoms of chlorine, iron, and chlorine, hexagonally arranged[7] such that every iron atom is surrounded by an octahedron of chlorine atoms. The iron atoms in subsequent layers are displaced with respect to each other by one-third of the unit cell and thus three $FeCl_3$ layers are encompassed by the cell vector in the **C** direction. Upon intercalation of $FeCl_3$ into the graphite, one electron is donated by the graphite host for every four iron atoms.[8] It is not yet clear what site these donated electrons occupy; room-temperature Mössbauer data[9,10] and Raman spectroscopy[11] do not support the existence of $FeCl_2$ as a result of the acceptance by $FeCl_3$ of the donated electron.[12] However, there is a discrepancy in the low-temperature Mössbauer data for $FeCl_3$. Millman and Kirczenow[13] have reported the existence of Fe^{2+} ions at temperatures as high as 100 K which is contradictory to the work of Ohhashi and Tsujikawa.[10]

Magnetic susceptibility measurements on $FeCl_3$ graphite intercalated compounds were performed by Karimov *et al.*[14] and by Hohlwein *et al.*[15] The interest there was the nature of magnetic behavior of the $FeCl_3$ which in its pristine state undergoes a magnetic phase transition at 8 K.[16] Those measurements concentrated mainly on the properties of stages 1 and 2. Although the results of those measurements disagreed on the details, the authors reported a phase transition in the temperature region of their measurements. The method used in those measurements was the Faraday balance supplemented by an ac method; the samples consisted of small crystallites. More recent measurements of the magnetic properties of stages 1 and 2,[17,18] prepared from HOPG, revealed that the samples undergo a magnetic phase transition with long-range order; however, the transition temperatures are depressed from those of the pristine $FeCl_3$. The measurement of Millman *et al.*[17] was performed by means of the Mössbauer effect, while Millman *et al.*[18] measured the magnetic susceptibility of the system; the latter method has a better temperature resolution. Both measurements found that stage 1 undergoes a phase transition at 4.3 K while stage 2 undergoes a transition at 1.3 K. Moreover, the Curie-Weiss Θ indicated that stage 1 orders antiferromagnetically in plane and ferromagnetically between planes while stage 2 orders antiferromagnetically both in plane and between planes.

A Mössbauer investigation of higher stages[19] revealed that no long-range order existed in stages 4 and 6 down to temperatures of 65 mK. Subsequent susceptibility measurements on those samples and others revealed a magnetic susceptibility maximum which occurred in all the samples at a temperature between 1.7 and 1.8 K, depending on stage.[20] Although the maxima occurred seemingly at the same temperature for all stages, the size of the maximum varied widely from stage to stage, becoming generally greater as the stage increased. In fact, this investigation reveals that the size of the maximum increases by a factor of 55 from stage 1 to stage 5. Moreover, the susceptibility maximum was suppressed by relatively low magnetic fields, of the order of 10 G, which may have accounted for the fact that it was not seen by other investigators prior to that time. Since the maximum increased in intensity with stage, it was assumed that it was a consequence of the two dimensionality of the system. Within the same stage, the height of the susceptibility peak increased with the number of iron atoms next to iron vacancies.[21]

Phase transitions in other GIC's such as $CoCl_2$ and $NiCl_2$ were also reported by Karimov *et al.*;[22,23] recently these transitions were also confirmed by Elahy *et al.*[24] The authors of Ref. 24 have concluded that the magnetic intercalants exhibit a very general type of magnetic behavior, independent of species or of stage. More recently low-temperature magnetic phase transitions were reported for $MnCl_2$,[25] and also for stage-1 C_6Eu.[26] Qualitatively most of the reported phase transitions have shown similarities in both magnetic field and temperature dependence, differences exist only in the location of the transition points and the dc magnetic field needed to quench the peaks in the measured magnetic susceptibility. Most of the reported experimental data have been analyzed on the basis of a two-dimensional *XY* model with a low temperature transition to a two-dimensional antiferromagnetic phase.[24,25]

II. EXPERIMENTAL

A. Characterization of samples

The $FeCl_3$ GIC samples were prepared by use of a standard two-zone furnace technique where stage index was controlled by the temperature difference between the graphite host (HOPG) and the $FeCl_3$ powder. The samples were in the form of thin rectangular plates of dimensions $1.5\times0.5\times0.1$ cm^3. Well-staged samples were achieved by controlling the pressure of Cl_2 gas inside the intercalation tube, as well as the partial pressure of $FeCl_3$ through rigid temperature control. After intercalation, the samples were characterized for identity and uniformity of staging by use of x-ray (001) diffraction. Only single-stage, well-staged samples were used in the magnetic measurements. The x-ray diffractograms were also used to determine the *c*-axis repeat distance I_c after cycling the samples from room to liquid-helium temperature, and showing that the cycling did not affect this staging distance.

Most of the samples measured were characterized by means of the Mössbauer effect, which can reveal the ratio of iron atoms next to iron vacancies to that of the total number of iron atoms in the intercalant layer, as well as that of Fe^{2+} to that of Fe^{3+}.[17,19] The initial measurements were performed on the same samples used in the Mössbauer investigations. The same measured samples were characterized periodically, before and after the measurements, over a time span of over a year, having been stored at room temperature in a dry-nitrogen environment. No deterioration was observed in the samples during the period of measurements.[27] Once deterioration was observed, the samples were discarded. In higher-stage samples, where stage disorder is expected,[28] the Hendricks-Teller[29] and Metz-Hohlwein[30] analysis techniques, were used to calculate the intensity, width, and location of the x-ray reflections. We find that our experimental x-ray data on the stage-9 samples reported in this article are in good agreement with that calculated for the pure and well-staged stage 9. Although a small admixture of stage 10 cannot be excluded, this stage serves as an example of a high-stage sample.

As shown in Table I of Ref. 19, the Mössbauer analysis of our initial samples showed that $(17\pm3)\%$ of the iron sites were next to vacancies (ISNV) in stages 1 and 2 while this number was $(19\pm3)\%$ and $(13\pm3)\%$ for stages 4 and 6, respectively. The Fe^{2+} sites comprised $(23\pm3)\%$ in stages 1 and 2 at low temperatures, while only $(3\pm1)\%$ in stages 4 and 6. In a similar set of measurements it was also shown that the amount of Fe^{2+} increased systematically with a decrease in temperature from about 100 to 10 K, and was constant below that temperature.[13] In some of the subsequent samples the percentage of iron atoms next to vacancies was reduced to 7% or lower.

If one assumes that most of the sites near vacancies come from the atoms at the boundary of the intercalate islands, one can calculate the minimum average diameter of an island to be 64 Å for a 19% ISNV and 175 Å for 7% ISNV corresponding to clusters of 200 and 1500 atoms, respectively. If, however, most of the ISNV's were to come from the island boundaries, one would observed two ISNV sites. One would come from the ISNV next to one vacancy and another next to two vacancies. Only the ISNV next to one vacancy was observed.[31] It is therefore argued that since only one kind of ISNV was observed, the ISNV's were within the islands. Because on a honeycomb lattice there would be three ISNV's near one vacancy, the vacancy percentage would be one-third that of the ISVN percentage and the island size would be much bigger than the above limits. On the whole, there was consistency in the magnetic measurements between the samples within one stage. This is true with the exception of several samples which significantly deviated from the norm and upon further examination turned out to be $FeCl_2$-intercalated compounds. In each case, more than one sample was used in our magnetic measurements, and in some cases as many as five or six.

B. Measurement techniques

A standard ac bridge technique[6] was employed to probe the magnetic susceptibility (χ') of the system. The signal was picked up by a two-phase lock-in analyzer which can detect signals down to 1 μV. The data were taken at several frequencies ranging between 40 and 1000 Hz.

A computer-controlled system, via analog-to-digital and digital-to-analog converters, was used to operate the apparatus at all desirable conditions. The temperatures of the samples above 2 K were measured by a calibrated silicon-diode thermometer, while temperatures below 2 K were determined by means of the ^{4}He vapor pressure. This allowed for an accuracy of ± 1 mK at 2 K. When greater resolution was required, a carbon resistor was employed. The resistance of certain carbon resistors, in our case an International Resistor Corporation brand, is very temperature sensitive at low temperatures. This method enabled us to detect temperature changes of less than 0.1 mK.

The susceptibility coils were always kept in a cryogenic bath, thus changing the temperature of the sample did not change the temperature of the coils. At high temperatures (nitrogen to room temperature), the coils were immersed in liquid nitrogen.

An ac current in the primary circuit, of magnitude 4 mA and below, was used to keep the amplitude of the exciting ac field below 0.1 G, thus nonlinear susceptibility effects were excluded. To investigate the susceptibility as a function of the magnetic field, a dc magnetic field in the range of 0—150 G was applied to the samples. Figure 1 shows schematically several layers of GIC with the intercalant (striped layers). Generally the probing ac and the external dc magnetic fields are parallel to the a-b plane, thus the in-plane magnetic susceptibility component was measured in this configuration. Other configurations were used in the various measurements and will be mentioned as appropriate. Our sample holder was designed so that the orientation of the sample can be adjusted to any desired configuration relative to the exciting field direction. The c-axis susceptibility data were taken when the a-b plane aligned perpendicular to the exciting field. Configurations where the dc field was perpendicular to the measuring ac field, either along the c axis or along the a-b plane, were also used.

Mechanical vibrations can cause serious problems in this kind of experiment, thus careful attention has been paid to ensure that the sample was firmly attached to the sample holder and in a rigid configuration with the susceptibility coils. A special computer program was made to transfer the data from a MACSYM-350, Analog Devices, Inc., computer, which monitors the apparatus and collects the data, to a Digital Equipment Corporation VAX11 minicomputer for routine analysis.

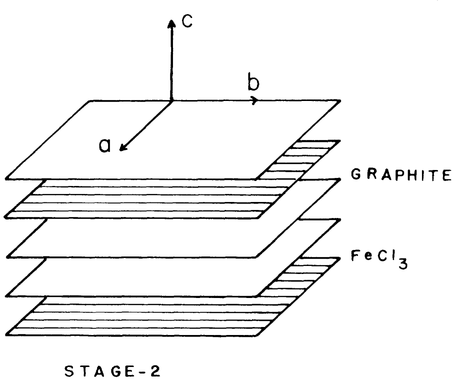

FIG. 1. Layered structure for stage-2 $FeCl_3$ GIC; the striped layers are the intercalant.

III. RESULTS AND ANALYSIS

A. In-plane susceptibility

The susceptibility results in zero external dc magnetic field of stages 1—6, and nine samples, are presented in Fig. 2. In this configuration the measuring ac field was perpendicular to the c axis, thus in-plane susceptibility data are shown in the figure. The susceptibility is given in arbitrary units; however, it is normalized for the amount of iron in each sample and at a frequency of 397 Hz. Also, all the susceptibility data are subtracted from the value at the lowest measured temperature, 1.1 K. At low frequencies and away from the transition (at the transition the relaxation times can be very long, $\tau = 6\times10^{-3}$ s; see Ref. 32), the arbitrary unit is equal to 1.0 emu/mol of iron. However, the susceptibility varies with the measuring frequency and thus we give our data in "arbitrary" units. For a more detailed analysis of this we refer the reader to Ref. 32. As shown in the figure, all the stages have low-temperature susceptibility maxima at about the same temperature but the relative size of the peaks is different; stage 5 has the largest peak.

As shown in the inset to Fig. 2, where the logarithm of the peak size, χ_m, is plotted as a function of stage, n, the peak size for stages 1—5 follows an exponential law. More exactly,

$$\chi_m = 0.028\exp(n) \tag{1}$$

for $1 \le n \le 5$. This suggests that the graphite layers shield

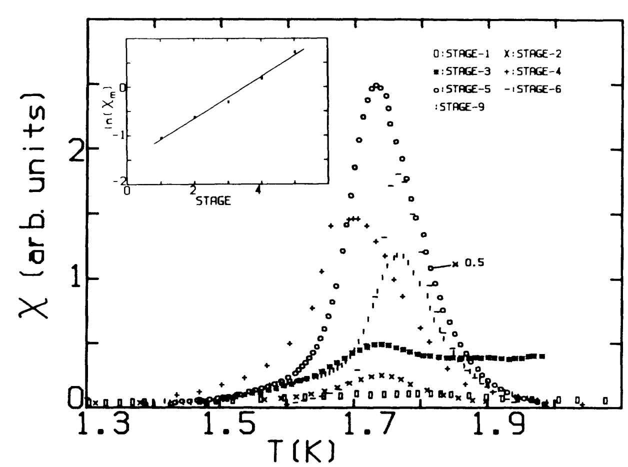

FIG. 2. In-plane magnetic susceptibility vs temperature for different stages of $FeCl_3$ GIC near the transition temperature. The data of stage 5 is multiplied by 0.5. The inset shows the logarithm of the peak height (χ_m) as a function of the stage index (n) to emphasize the exponential behavior for $1 \le n \le 5$.

the intercalant-layer interaction exponentially, similar to the shielding of electromagnetic radiation from the interior of a conductor due to the skin depth. The conducting graphite layers between the intercalant layers shield the interplanar intercalant interaction, and thus control the dimensionality of the magnetic system. In stage 5 the magnetic intercalant layers are 22.7 Å apart. The sharp increase of the peak size from stage 1 to stage 5 indicates that five stages of the graphite layers between the intercalant layers are sufficient to completely reduce the interlayer interactions and produce a two-dimensional magnetic system. As shown in Fig. 2, the peak sizes started to decrease for samples of stages higher than stage 5.

We surmise that the decrease in the relative peak size beyond stage 5 is related to the in-plane density of the magnetic ions, because the in-plane intercalant density of graphite-$FeCl_3$ compounds decreases as the stage is increased.[31] As shown in Ref. 31, the in-plane density varies within stage at low stages from 100% to 95%. This variation was not observed in our susceptibility measurements. The variation of the in-plane density can be attributed to the existence of large islands[33,34] in the intercalant compound; a decrease in the number of iron ions in these islands is expected when the stage index is increased. Therefore we suggest that the maximum in the relative peak size of the susceptibility versus the stage index, presented in Table I, is due to the competition between the dimensionality of the system and the intercalant in-plane density. Moreover, it is interesting to note that, as shown in Table I, the transition temperatures also vary with the stage index and stage 4 has the lowest transition temperature. This indicates an additional aspect of the competition between dimensionality and in-plane density, since otherwise all the transitions would have occurred at the same temperature for all the stages.

The magnetic anomaly in this system depends strongly on the external applied dc magnetic field. The susceptibility data versus the external applied dc magnetic field for stages 6 and 3, as examples, are presented in Figs. 3 and 4, respectively. Note that the scales of Figs. 3 and 4 are different from those of Fig. 2 at the maximum. The reason is that because of the relaxation times[32] the susceptibility varies with frequency. Figure 2 represents the peak sizes at 397 Hz while Fig. 3 is at 39 Hz and Fig. 4 is at 197 Hz. In these figures the exciting field is perpendicular to the c axis, thus the in-plane susceptibilities are the measured data. In this paper we have adopted the convention that B stands for the exciting ac magnetic field and H stands

TABLE I. Stage index vs the relative peak size and the peak temperature of the susceptibility for $FeCl_3$ GIC.

Stage	Peak size	T (K)
1	0.0846	1.793
2	0.2256	1.745
3	0.4650	1.746
4	1.4381	1.710
5	4.9300	1.735
6	1.7800	1.761
9	1.1610	1.768

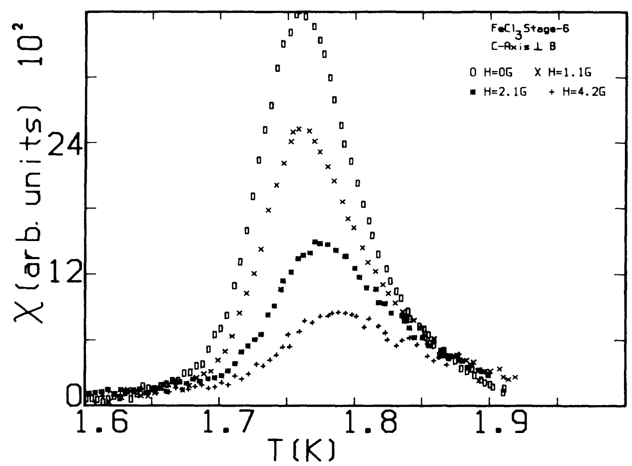

FIG. 3. In-plane magnetic susceptibility vs temperature for stage-6 $FeCl_3$ GIC. H denotes the applied dc magnetic fields in gauss in the a-b direction.

for the external applied dc magnetic field. In this case H is applied parallel to B. As shown in the figures, the peak size is drastically reduced when a magnetic field of the order of 5 G is applied to the sample. One would expect that, in three dimensions, a phase transition would be quenched by a magnetic field at least in the order of $k_B T$ or 1.6 kG. Therefore we suspect that the increase in the number of graphite layers between two successive intercalant layers, which reduce the intercalant interaction, contributes to the strong field dependence. Spin glasses also exhibit strong low-field dependence and there may be a relation of our system to that of a two-dimensional spin glass.

In Figs. 5 and 6 the in-plane susceptibility at constant temperature, normalized to the zero field value, is shown as a function of the external applied dc magnetic field H

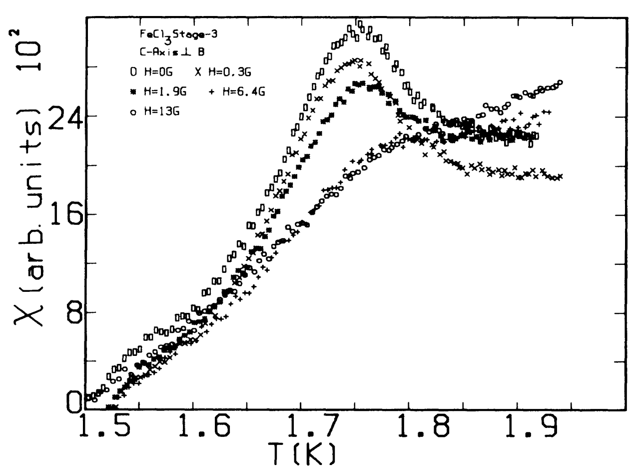

FIG. 4. In-plane magnetic susceptibility vs temperature for stage 3 $FeCl_3$ GIC. H denotes the applied dc magnetic fields in gauss in the a-b direction.

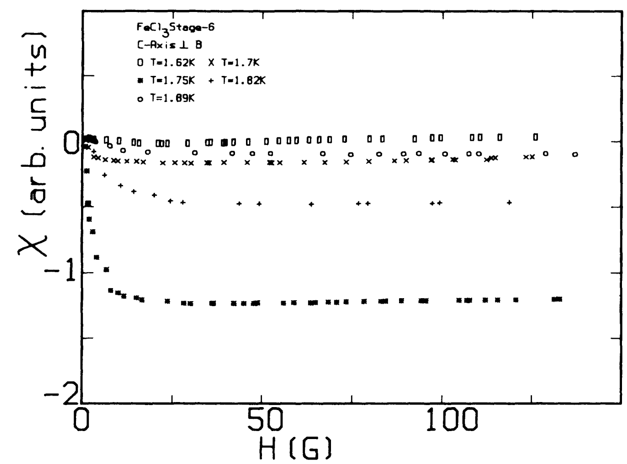

FIG. 5. The change in the in-plane magnetic susceptibility vs applied magnetic field for stage-6 $FeCl_3$ GIC near the transition temperature.

for different temperatures for stages 6 and 3, respectively. Here H is again parallel to B. The remarkable features in these figures are the low field local minima in the susceptibility, more pronounced for stage 3, which steeply decrease on the left-hand shoulder near the transition temperature. This rapid turnover of the susceptibility at very small magnetic fields and its subsequent increase is in qualitative agreement with the results of mean-field calculations for two-dimensional dipoles on a honeycomb lattice.[35]

In these mean-field calculations, we considered a system of dipoles on a two-dimensional honeycomb lattice. Dipolar interactions are inherently anisotropic since they depend on both $\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j$ and $\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij}$, where $\boldsymbol{\mu}_i$ denotes the magnetic moment of the dipole and $\mathbf{r}_{ij}$ is the distance between the two interacting dipoles. The dipoles were constrained to rotate about an axis normal to the plane and thus to point along the plane. That system has a continuously degenerate ground state whose energy is -1.0 K per dipole if the dipole moment and separation of the dipoles is that of the iron in $FeCl_3$. There is a phase transition in zero field which takes place at 1 K and is lowered in an applied field. In a perfect lattice, the magnetic susceptibility increases with an applied magnetic field at low fields. If, however, defects are taken into account, the susceptibility has a minimum with the application of an external field at a constant temperature. Since the results calculated for this model system are of the same order of magnitude and qualitatively similar to those measured for $FeCl_3$ GIC, we assume that in-plane dipolar interactions play a significant role in the behavior of our measured systems. As will be seen below, in the c-axis measurements at low temperatures, the spins tend to rotate in the plane, thus approximating the configuration of the model system above.

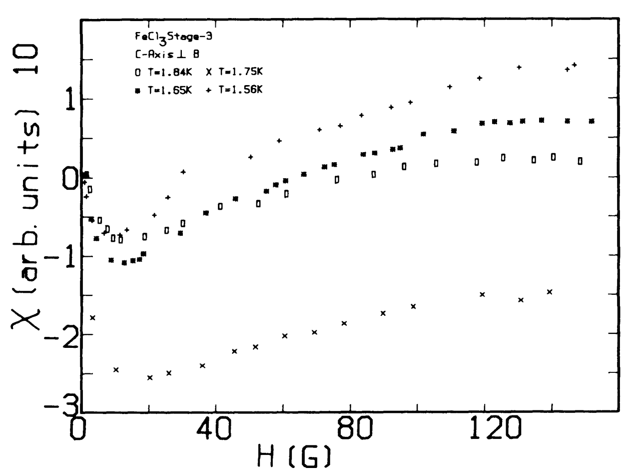

FIG. 6. The change in the in-plane magnetic susceptibility vs applied magnetic field for stage-3 $FeCl_3$ GIC near the transition temperature.

It is of interest to note the relative large increase in the susceptibility on the high-field side of the minima for stage 3, compared with that for stage 6, where the susceptibility exceeds the zero field value. This emphasizes the still-existing interplanar interactions in the lower stages. Stage 2 exhibits similar behavior to that of stage 3.[18] As we have shown, the interplanar interactions decrease as the stages increase, thus the in-plane magnetic phase of stage 3, where three-dimensional effects are still significant, is affected by the applied field in a way as to reduce the interplanar interaction and increase the in-plane interactions of the system. In stage 6 the interplanar interactions are already quenched by the graphite layers and the external field is not expected to increase the in-plane magnetization significantly in this low magnetic field.

The explanations of other susceptibility peaks[24] were based on a two-dimensional XY model,[36] however, the existence of a spin-glass transition was also suggested.[21] The model calculations mentioned above[35] have the XY symmetry. Lundgren *et al.*[37] have suggested a three-dimensional spin glass model to relate the in-phase and out-of-phase parts of the magnetic susceptibility. We have tried their approach to the analysis of the magnetic anomaly in our system in the frequency range of our data and found no quantitative agreement between the suggested model and our data. Therefore we again conclude that the magnetic anomaly in this system is two dimensional in nature. The spins are locally locked in layered planes and contribute to the two-dimensional anomaly. The fact that the spins are confined to the a-b plane is confirmed by our c-axis susceptibility measurements.

B. c-axis susceptibility

The c-axis susceptibility was measured over wide temperature range. For stages 3 and 6 we did not observe any magnetic anomaly at low temperatures; however, the susceptibility showed a steep decline as the temperature decreased thus indicating that the spins are locked in the planes as temperature is lowered. Apparently the Curie law is not applicable for these data in any temperature range.

The low-temperature data are presented in Fig. 7. The figure shows the c-axis susceptibility of stage 6 versus the temperature at different external dc magnetic fields. As

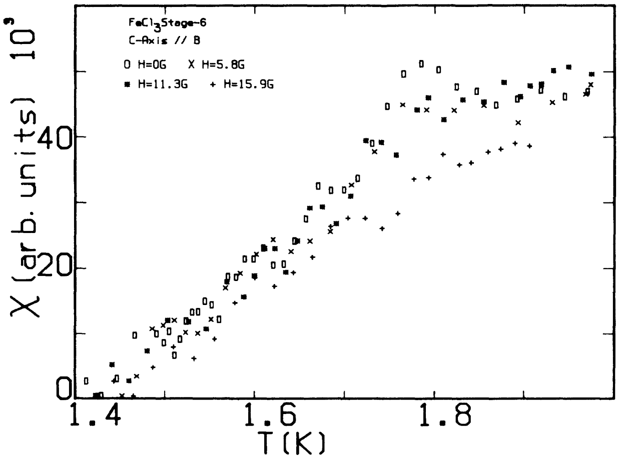

FIG. 7. Low-temperature c-axis magnetic susceptibility vs temperature near the transition temperature for stage-6 $FeCl_3$ GIC. H denotes the applied dc magnetic fields in gauss.

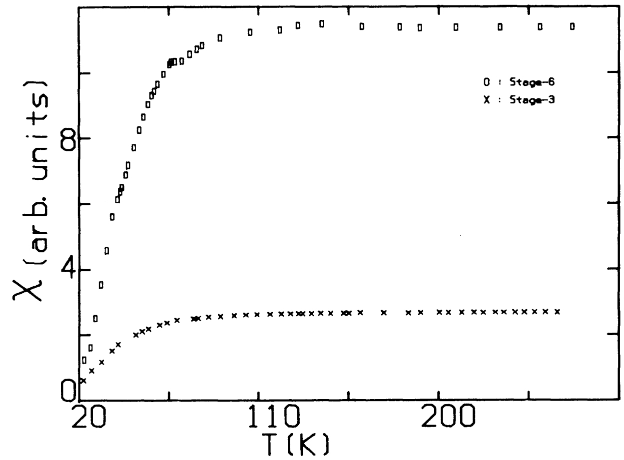

FIG. 8. c-axis susceptibility vs temperature for stages 3 and 6 $FeCl_3$ GIC extended to high temperatures.

shown in the figure, the susceptibility in this direction is down by a factor of 100 from the in-plane value. No significant anomaly exists in this direction. Experimentally, perfect orientation of the sample is very difficult and in addition the graphite planes may be out of parallel by as much as a few degrees, thus we expect a small contribution from the in-plane anomaly to the c-axis data. This contribution due to misorientation appears as a small peak in the c-axis susceptibility data near the transition temperature.

As shown in Fig. 7, the applied dc magnetic field does not change the c-axis susceptibility significantly as it does in the in-plane case which is shown in Fig. 3. In this high-stage—low-temperature limit the spins are expected to be confined to a plane parallel to the graphite layers, and thus are free to realign themselves along the applied field only in the in-plane directions. Therefore, in this small magnetic field limit and for the higher stage samples, the c-axis susceptibility is less sensitive to the applied magnetic field than the in-plane data.

Since the c-axis susceptibility data at low temperature were continuously increasing as a function of temperature, we decided to extend our measurements to higher temperatures where a high-temperature magnetic susceptibility maximum might exist. As shown in Fig. 8, the stage-3 susceptibility increases monotonically while the stage 6 susceptibility has a shoulder at about 65 K and a small maximum at a temperature of about 140 K. At 65 K the c-axis susceptibility of stage 6 is a factor of 200 greater than that at 2 K and below. We take this as evidence that the spins are locked in the plane at low temperatures. This is contrasted with stages 1 and 2 where above 15 K the magnetic susceptibility obeys the Curie-Weiss law both along the a-b and along the c direction.

The large size of stage-6 c-axis susceptibility versus the temperatures relative to that for stage 3, shown in Fig. 8, is another manifestation of the two dimensionality at low temperatures. In stage 6 the spins are locked in the plane at low temperatures and as the temperature is raised the spins are released from the planar orientation and are free to respond to the field in the **c** direction. In stage 3, the interaction between planes hinders the response of the spins in the **c** direction, and thus the susceptibility is smaller. Stage 3 is not completely two dimensional, and interplane interactions play a role in this stage.

C. Critical behavior

A maximum in the magnetic susceptibility often denotes a magnetic phase transition which, if it is a second-order transition, can be analyzed in terms of critical exponents.[38] As mentioned above, similar transitions were analyzed in terms of the Kosterlitz and Thoules XY model[39,40] and thus we decided to subject our data to a similar analysis. Before this analysis, however, the measured susceptibility has to be modified so as to account for the shape of the sample.[41]

Because of the high susceptibility at the maximum, each spin does not see the externally applied field, but a field which is modified by the field of the surrounding dipoles. This modification or shielding depends on the shape of the sample. In what follows we designate the externally measured susceptibility by χ_{ext}, and the actual susceptibility of the spin as χ_{int}. The relation between the two susceptibilities is

$$\chi_{int}=\chi_{ext}/(1-\epsilon\chi_{ext}) , \quad (2)$$

where ϵ is the shape factor. The shape factor can be exactly calculated only for homogeneous substances of ellipsoidal shape. Neither of these conditions applies to our substance since it is an inhomogeneous substance in the form of thin rectangular plates. Because of that one has to resort to experiment.

If one assumes that at the maximum the χ_{int} is infinite then

$$\epsilon=1/\chi_{ext} \quad (3)$$

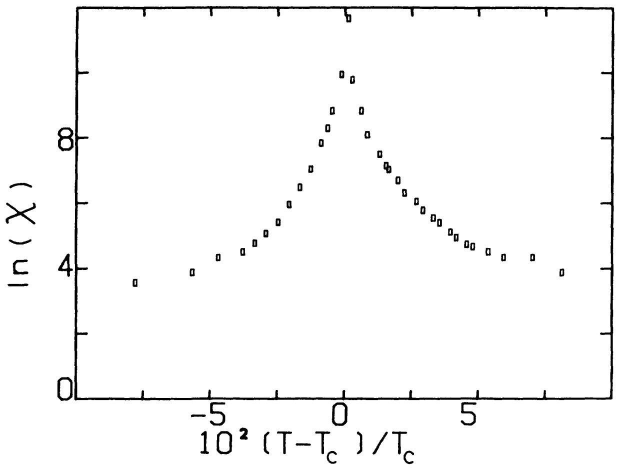

FIG. 9. Natural logarithm of the shape-corrected in-plane susceptibility at zero dc magnetic field vs the reduced temperature for stage-6 $FeCl_3$-graphite intercalation compound.

at that point. A finite but very large susceptibility does not change this result significantly.

If one uses the value obtained for ϵ from Eq. (3) and applies it to our data by use of Eq. (2) one obtains susceptibility values shown in Fig. 9. This figure shows the natural logarithm of $\chi_{\rm int}$ as a function of the reduced temperature $t=(T-T_c)/T_c$ where T_c is the temperature at the susceptibility maximum. Although this procedure introduces an infinity where only rounded maxima exist, it is justified by the fact that our data agree well with Eq. (4), below, over a wide range of temperature. Moreover, the best fit was found with $\chi_{\rm int}$ being finite and of the order of 400 rather than infinity.

Figure 10 shows the natural logarithm of the susceptibility as a function of the natural logarithm of the absolute value of the reduced temperature for stage 6. Similar data reduction was performed on stages 4, 5, and 9 with similar results. Stages 1–3 were not suited for this analysis because of interference from the high susceptibility due to three-dimensional interactions[18] which necessitated the subtraction of the field-sensitive component from the total susceptibility, with an accompanying loss in accuracy. The squares are for $T>T_c$, while X represent data for $T<T_c$. This graph suggests the usual power-law behavior of the susceptibility

$$\chi \propto |(T-T_c)/T_c|^{\gamma} , \quad (4)$$

with $\gamma=1.97$ for $T>T_c$ and $\gamma=1.85$ for $T<T_c$. The error in γ is ± 0.1. The slopes of the drawn lines denote γ. The value for γ is unusually large. For a three-dimensional system γ has the value between 1 and 1.25 while the calculated value for the two-dimensional Ising model is 1.75 [see Ref. 38(b)]. Our values appear to be higher than that and thus it appears that we are dealing with a somewhat different phenomenon. Our data were also fitted to an equation derived by Kosterlitz,[40]

$$\chi \propto \exp(bt^{-0.5}) , \quad (5)$$

where b is a constant. Our data fit Eq. (5) only in a very limited temperature region. The data shown in Fig. 10 are well within the accuracy of our experiment since $\ln|(T-T_c)/T_c| = -7.5$ represents a temperature difference of one millidegree.

Figures 11 and 12 show the magnetic-field dependence of the susceptibility. Two configurations were used. The measuring field was along the a-b plane while the applied dc magnetic field was normal to the measuring field either along the a-b, in-plane direction H_a, or along the c-axis direction H_c. Both the temperature shift of the maximum and the size show a high-field and low-field behavior. The horizontal axis is calibrated in terms of H_0 where H_0 has a value of 17 G for H_c and 7.5 G for H_a.

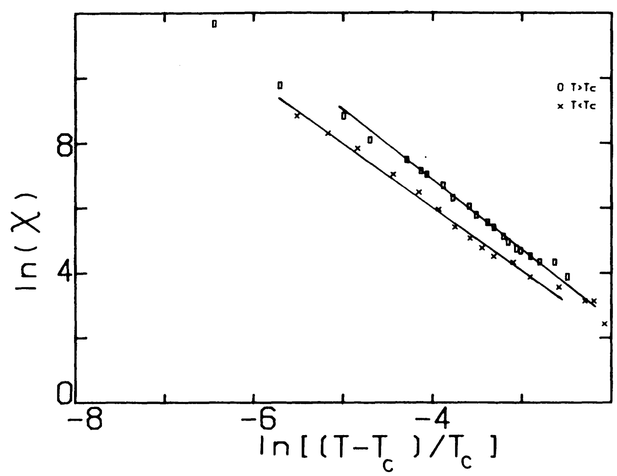

FIG. 10. Natural logarithm of the in-plane susceptibility at zero dc magnetic field vs natural logarithm of the reduced temperature showing the universal power-law behavior. The squares denote data for $T>T_c$ and the $\times$ denote data for $T<T_c$.

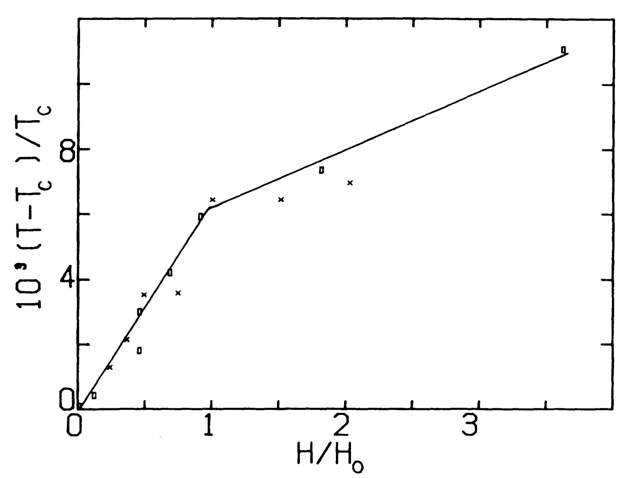

FIG. 11. Temperature dependence of the in-plane susceptibility maximum vs the applied dc magnetic field for stage 6 $FeCl_3$-GIC. The squares are for H along the c axis (H_c) and the $\times$ are for H along the a-b plane (H_a).

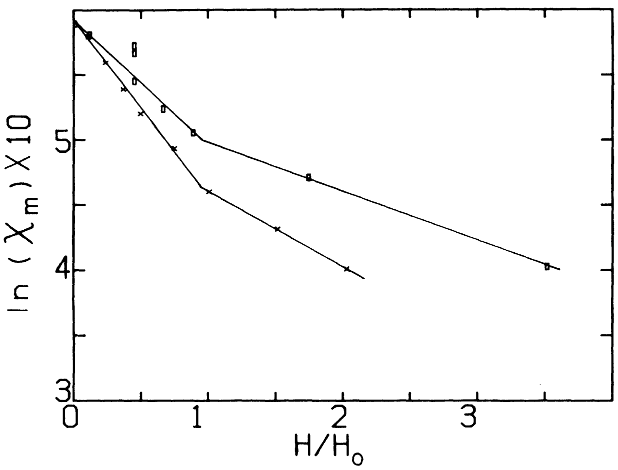

FIG. 12. Natural logarithm of the in-plane susceptibility maximum vs the applied dc magnetic field for stage 6 $FeCl_3$-GIC. The squares are for H along the c axis (H_c) and the $\times$ are for H along the a-b plane (H_a).

Figure 11 shows the temperature at which the peak occurs, in terms of the reduced temperature $(T-T_c)/T_c$ as a function of the applied field. Here T_c is the transition temperature at zero field. One sees that the maximum is shifted to higher temperatures as the magnetic field is applied. Moreover, two straight lines can be drawn through the points. One at low field with a steep slope and one at high field with a shallower slope. The slope at low field is a factor of 3 greater than that at high field. In addition, H_a is more effective in shifting the temperature of the maximum than H_c by a factor of 17/7.5, the ratio of H_0 in the respective directions. A similar low- and high-field behavior is seen if one plots the logarithm of the susceptibility peak size as a function of the applied magnetic field normalized to H_0, as shown in Fig. 12. One can fit the data in Fig. 12 with the expression

$$\chi_{max}(H)=\chi_{max}(0)\exp(-\phi H/H_0) , \quad (6)$$

with χ_{max} denoting the susceptibility at the maximum. For H_a the value of $\phi=1.3$ for the low field and $\phi=0.6$ at high field, while for H_c the value of $\phi=1$ for low field and $\phi=0.4$ for high field. Similar behavior was observed in other GIC samples.[24]

To summarize, our data obey the power-law behavior of general second-order phase transitions, with an exponent γ greater than that expected for a two-dimensional Ising model. In an externally applied magnetic field the susceptibility maximum exhibits a distinct low-field and high-field behavior.

IV. CONCLUSIONS

The in-plane magnetic susceptibility data of $FeCl_3$ GIC indicate that all the stages of this intercalant compound possess a low-temperature magnetic phase transition at temperature between 1.7 K and 1.8 K. This transition obeys the power-law dependence of second-order transitions. The data suggest that the transition is two dimensional in nature. Similarities in the behavior of the transition and calculations of the behavior of a two-dimensional dipolar system on a honeycomb lattice suggest that dipolar interactions play an significant role. The relative size of the anomaly in the magnetic susceptibility is maximum for stage 5. If the size of the low-temperature susceptibility maximum is taken as an indication of two dimensionality, then the shielding of the magnetic interaction by graphite layers is exponential. The variation in the size of the maximum is described as a competition between the staging mechanism which contributes to the two dimensionality and the in-plane density.

As shown in GIC, the graphite layers between the intercalant layers screen the intercalant interplane interactions in a way as to provide a two-dimensional magnetic system. The low-dimensional nature of this phase transition is supported by the dependence of the susceptibility peaks on the magnetic field; the application of a small dc magnetic field in the order of 10 G smears out the peak completely, whereas one would expect this to happen at fields of the order of 1.6 kG in three dimensions. The c-axis susceptibility does not show any anomaly at low temperature. Moreover, the susceptibility in this direction is not sensitive to the small dc external magnetic fields, which implies the confinement of the intercalant magnetic spins to the planes parallel to the graphite layers.

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