Relaxation effects in graphite intercalation compounds

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The ac susceptibility bridge technique is applied to the measurement of a long spin-lattice relaxation time associated with the magnetic anomaly which has been reported for $FeCl_3$ graphite intercalation compounds at 1.75 K. Investigations of this relaxation mechanism show that the specific heat of the spin system at low temperatures contributes to an anomaly in the relaxation time near the temperature of the magnetic anomaly. Our results indicate that the graphite layers between the magnetic intercalant layers act as nonmagnetic spacing layers allowing the c-axis spin-spin coupling to be varied.

INTRODUCTION

In graphite intercalation compounds (GIC's) the electrical resistivity is one of the properties most drastically changed by intercalation of both acceptor and donor materials,[1,2] it is also one which holds the greatest promise for technological applications.[3] If one wants to use the conventional four-probe technique to measure the resistivity of these materials, the high anisotropy of GIC's is expected to introduce difficulties in the measurements. As a result of these difficulties, experimentalists had thought of alternative means to measure the resistivity for these highly anisotropic compounds.

One of the widely-used approaches in the measurements of the electrical resistivity in GIC's is the low-frequency eddy-current technique.[4–6] The basic concept of this method is that when a sample is inserted into an ac field, the induced currents in the conductor reduce the magnetic flux which penetrates the conductor. If the signal is detected by a standard susceptibility bridge[7] the induced eddy current, which is proportional to the resistivity of the sample, is related to the out-of-phase or quadrature component of the magnetic susceptibility.[8]

Because relaxation effects which induce an out-of-phase signal are also associated with low-temperature magnetic anomalies, which have been reported for a variety of GIC's,[9,10] one has to be careful in relating the out-of-phase component of the susceptibility to the resistivity of the system. Relaxation effects, therefore, which might contribute to the out-of-phase signal should not be ignored near a magnetic anomaly.

In our system, near the temperature of the magnetic anomaly, a spin-lattice relaxation mechanism is suggested as the contributor to the quadrature component of the magnetic susceptibility. When a spin system (magnetic ions) is disturbed from its thermal equilibrium by an external source, such as an applied magnetic field, the heat developed in this spin system has to be given to the lattice. We assume that the spins are in thermal equilibrium with each other and at a temperature slightly different from the lattice temperature. The transfer of heat between the spin system and the lattice is associated with a relaxation time (τ), which depends on the thermal conduction between the spins and the lattice and the specific heat of the spin system. Relaxation effects for GIC's in which low-temperature magnetic phase transitions were reported have not yet been explored. As shown in the following sections, investigation of such effects can provide information about the heat capacity of the system and also about the nature of the mentioned magnetic anomaly in these compounds.

In this work we have measured the long relaxation time in the $FeCl_3$-GIC system, using the susceptibility bridge technique. We have also used the conventional four-probe technique to investigate the electrical resistivity at the low-temperature anomaly which has been observed in the out-of-phase component of $FeCl_3$-intercalated graphite.[5] In fact, no anomaly in the resistivity along the c axis was observed at any temperature. These resistivity results, which will be shown in this work for comparison and whose details are presented elsewhere, are in qualitative agreement with the theory reported by Sugihara.[11] Therefore, it is clear that the anomaly of the out-of-phase component of the susceptibility of $FeCl_3$-intercalated graphite compounds is due to the relaxation effects in the system. Although we have concentrated on the measurements of the relaxation time of stage-6 $FeCl_3$ GIC, because of the similarity in the magnetic anomaly between the various stages, we can draw analogies from samples other than that stage. Thus we have chosen stages 5 and 9 for the comparison between the maximum in the out of phase susceptibility and the c-axis resistivity.

The crystal structure of $FeCl_3$ is a repeated sequence of three layers of hexagonally arranged atoms,[12] these layers are displaced relative to each other so that every iron atom is surrounded by an octahedron of chlorine atoms. Upon intercalation of $FeCl_3$ into the graphite, one electron is donated by the graphite host for every four iron atoms.[13] It is not yet clear what site these donated electrons occupy, room temperature Mössbauer data[14,15] and Raman spectroscopy[16] do not support the existence of $FeCl_2$ as a result of the acceptance by $FeCl_3$ of the donated electron.[17] However, there is a discrepancy in the low temperature Mössbauer data for $FeCl_3$. Millman and Kirczenow[18] have reported the existence of Fe^{2+} ions at temperatures as high as 100 K which is contradictory to the work of Ohhashi *et al.*[15] More theoretical and experimental work is necessary to understand the intercalation

mechanism and the associated charge transfer in this system.

Studies of the magnetic properties of low stage $FeCl_3$ GIC, as well as other systems, have shown a low-temperature phase transition and different mechanisms were proposed[9,10,19] to describe the origin of this transition. Limited transport measurements have been reported for low-stage $FeCl_3$ GIC. In-plane thermal conductivity data[20] show a dominant electronic contribution at low temperatures, while high-temperature data indicate a phonon contribution. The c-axis thermal conductivity, however, is driven by phonons at all temperatures. The authors[20] have also shown that the anisotropy of the thermal conductivity is much smaller than that of the electrical conductivity. It has been reported[21] that the in-plane resistivity data of stage-1 and -2 $FeCl_3$ GIC exhibit a low-temperature phase transition while stage 3 or 4 did not show any anomaly. It is the purpose of this work, which was initiated a few years ago at Boston University, to investigate in a full and comprehensive way the properties of the $FeCl_3$-GIC system.

EXPERIMENTAL

The $FeCl_3$-GIC samples were prepared using a standard two-zone furnace technique[3] where stage index was controlled by the temperature difference between the graphite host [highly-oriented pyrolytic graphite (HOPG)] and the $FeCl_3$ powder. The graphite 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 using x-ray (001) diffraction. 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 showed that the cycling did not affect this staging distance.

A standard ac bridge technique[7] was employed to probe the signal which is in-phase with the exciting field (related to the relaxation of the system or the out-of-phase susceptibility χ'') and the signal which is out-of-phase with the exciting field (related to the in-phase magnetic susceptibility of the system χ'). These components were 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—1000 Hz.

A computer-controlled system, via analog-to-digital (A/D) and digital-to-analog (D/A) 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 He vapor pressure. 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 (room to nitrogen temperature), the coils were immersed in liquid nitrogen.

An ac current in the primary circuit of magnitude about 4 mA was used to keep the amplitude of the exciting ac field below 0.1 G, thus nonlinear susceptibility effects were excluded. To investigate the relaxation as a function of the magnetic field, an external dc field in the range of (0—50 G) was applied to the samples. The magnetic dc and ac fields configurations are shown in Fig. 1. It shows schematically several layers of GIC's with the probing ac and the external dc magnetic fields parallel to the a-b plane, thus the induced eddy currents would be normal to that plane along the c axis. 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.

The four-probe method was used to probe the out-of-plane resistivity, and an on-off current technique enabled us to subtract out any ambient or spurious voltage from that created by the measuring current. A special computer program was made to transfer the data from a Symbolics, Inc. MACSYM-350 (ANALOG DEVICES) computer, which monitors the apparatus and collects the data, to a Digital Equipment Corporation VAX11 minicomputer for routine analysis.

RESULTS AND ANALYSIS

The most striking result in this work is the temperature dependence of the out-of-phase component of the magnetic susceptibility which exhibits an anomaly in the form of a sharp peak at temperatures near 1.75 ± 0.05 K in zero dc magnetic field. This anomalous behavior is correlated with the same anomaly which we have seen in the in-phase component of the magnetic susceptibility.[9] Figure 2 shows the correlation between the in-phase and the out-of-phase component as a function of temperatures for stage-6 $FeCl_3$ GIC at $f=39.7$ Hz and in zero dc field. As shown in the figure, both the in-phase part (χ') and the out-of-phase part (χ'') exhibit anomalies in the form of sharp peaks with the maximum in χ'' shifted to lower temperatures.

The samples were oriented inside the coils in such a way as to probe the in-plane susceptibility and the out-of-plane resistivity as explained in the preceding section. To

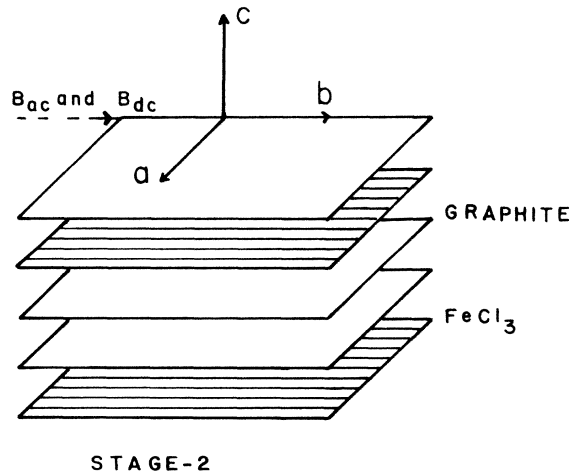

FIG. 1. Layered structure for stage-2 $FeCl_3$ GIC. B_{ac} and B_{dc} are the applied ac and dc magnetic fields along the b axis.

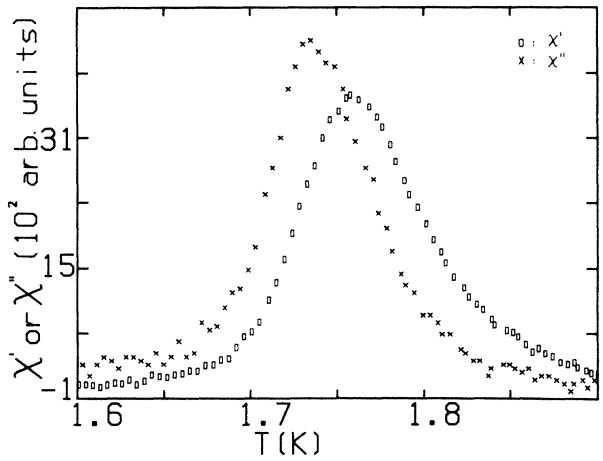

FIG. 2. The in-phase and out-of-phase components of the magnetic susceptibility versus temperatures near the transition point for stage-6 $FeCl_3$ GIC.

determine whether the correlation between χ' and χ'' is due to a resistivity anomaly or due to the long relaxation time in the system, the four-probe resistance measurement technique was engaged simultaneously with the susceptibility measurements. Figure 3 shows the out-of-phase components χ'' as a function of temperature for stages 5 and 9, and Fig. 4 shows the out-of-plane resistivity for the same samples and in the same temperature range. As shown in the figures, there is no anomaly in the electrical resistivity measured by the four-probe method and the resistivity basically behaves as predicted by Sugihara.[11] Therefore, we can conclude that the low-temperature maximum in χ'' cannot be ascribed to an anomaly in the resistivity, but is related to the relaxation of the spin system.

Based on the above results and the theoretical descriptions of Casimir and Du Pré,[22] we have made a detailed investigation of the relaxation mechanism for stage-6 $FeCl_3$ GIC. The real and imaginary parts of the complex susceptibility are related to the relaxation time of the system and the frequency by the following equations:[23]

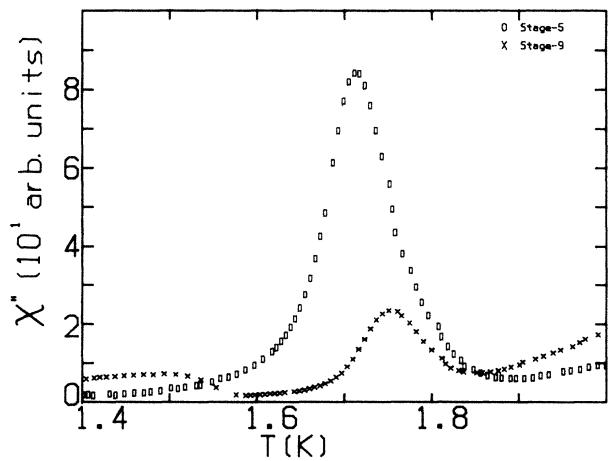

FIG. 3. The out-of-phase susceptibility component versus temperature for stage-5 and -9 $FeCl_3$ GIC's near the transition temperature.

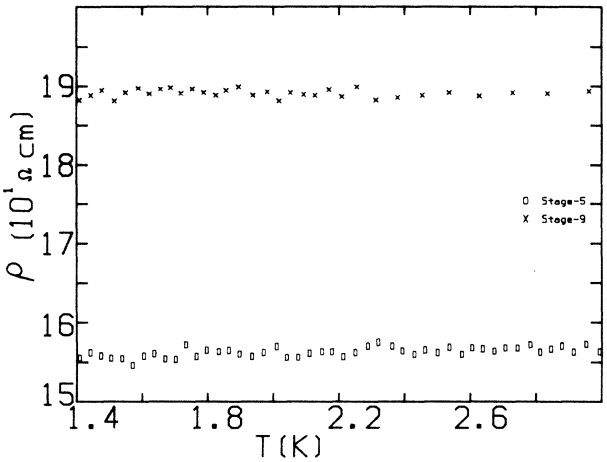

FIG. 4. The c-axis resistivity versus temperature in the vicinity of the magnetic anomaly for stage-5 and, -9 $FeCl_3$ GIC's.

$$\chi' = \frac{G}{(1+\omega^2\tau^2)} + \chi_0 - G \,, \tag{1}$$

$$\chi'' = \frac{G\omega\tau}{(1+\omega^2\tau^2)}, \; G = \chi_0(1 - C_m/C_h) \,, \tag{2}$$

where C_m and C_h are the heat capacities at constant magnetization and at constant field respectively, and χ_0 is the static susceptibility. τ is the relaxation time of the spin system, and ω is the angular frequency of the exciting field.

The out-of-phase magnetic susceptibility component data were taken as function of frequency and at temperatures between 1.1 and 2.4 K. Since that component varied significantly with frequency only in the temperature range between 1.65 and 1.85 K, constant temperature cuts were made in this temperature range and the measured values of the quadrature component of the magnetic susceptibility at constant temperature fit to the function given in Eq. (2). We used a nonlinear least-squares computer fitting program allowing G and τ to be varied to achieve the best

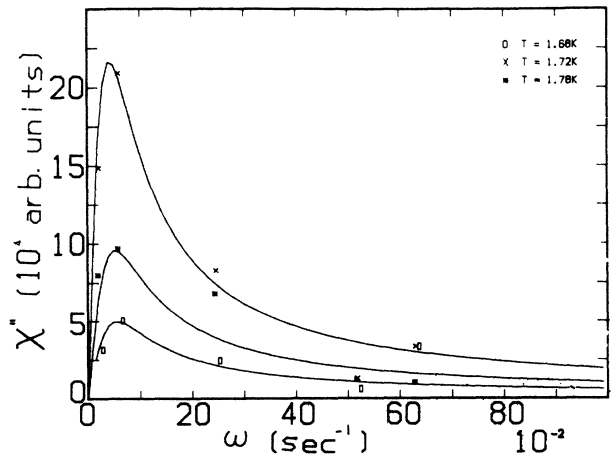

FIG. 5. The out-of-phase component of the magnetic susceptibility versus the angular frequency for stage-6 $FeCl_3$ GIC. The continuous lines are the theoretical functions and the symbols are the experimental data.

fit. Figure 5 shows the fits of the measured data at temperatures 1.68, 1.72, and 1.78 K. As shown in the figure, the data indicate a good fit to the Casimir—Du Pré relation in the low-frequency region and a somewhat worse fit at frequencies near 1 kHz. This is due to the fact that in the high-frequency region, it is difficult to decouple the two components of the measured susceptibility from each other because capacitive and skin effects impose an upper limit on the sensitivity of the bridge. The high-frequency points, however, were given a lower weight.

The fitting parameters τ and G were found to be temperature dependent and, in fact, both of them exhibit maxima near the temperature of the susceptibility anomaly. In Fig. 6 the values of these parameters are represented as a function of the temperature and, as shown in the figure, the peak of the relaxation time is shifted towards lower temperature from that in G. It is interesting to note that the out-of-phase component of the susceptibility, as shown in Fig. 2, shifts towards lower temperatures as the relaxation time does, while the in-phase component as well as the fitting parameter G are shifted towards higher temperatures.

The parameter G can be also written as

$$G=\chi_0(1-\chi_s/\chi_t)\ , \tag{3}$$

where χ_t and χ_s are the susceptibility at constant temperature and entropy, respectively. In the low-frequency region and at low temperature, one can assume that χ_s is small and expect G to have a maximum which coincides with that of the in-plane susceptibility which is proportional to χ_0. This explains the correlation between the graphs in Fig. 2 and Fig. 6 which showed a shift towards higher temperatures for χ' and G relative to χ'' and τ, respectively. Measurements at low-frequency provide an isothermal spin system so that the spin-spin relaxation can be ignored. The relaxation time, on the other hand, depends on the temperature through the specific heat at constant field of the spin system and the heat conduction between the spin system and the lattice system. Thus, in order to extract useful information, careful examination has to be carried out in this case.

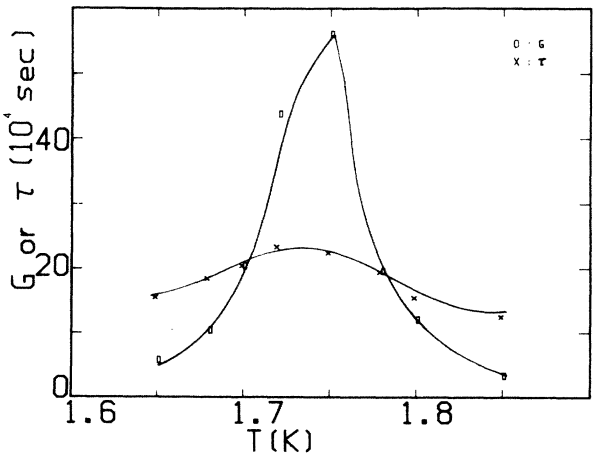

FIG. 6. The fitting parameters G and τ versus temperatures for stage-6 $FeCl_3$ GIC. The continuous lines are used to guide the eye.

We have also measured the spin-lattice relaxation time in stage-3 $FeCl_3$ GIC and found that the relaxation times in stage 3 were shorter by a factor of 4 compared to those of stage 6. According to the Casimir—Du Pré picture, relaxation occurs when heat is transferred from the spin-system, in our case $FeCl_3$ whose temperature changes in a sinusoidal fashion, to a lattice which is at a constant temperature and serves as a heat reservoir:

$$\tau=C/K\ , \tag{4}$$

where C is the spin specific heat and K is the thermal conductivity. If heat transfer were due to the electrons in the bounding layers, the relaxation time τ would be too short for us to measure by this method. It was also shown that the spacing between adjacent graphite layers is nearly independent of staging.[24,25]

Because of this, and the fact that near a magnetic transition the specific heat is related to the magnetic susceptibility χ by[26]

$$C=\frac{d(\chi T)}{dT}\ , \tag{5}$$

we can attribute the difference between the stage-3 and -6 relaxation times to the differences in their respective specific heats at the anomaly. Table I gives the relative magnitudes of the susceptibility, normalized per iron atom, of various stages of $FeCl_3$ GIC at the susceptibility maximum. As shown in Table I, stage 3 has a maximum whose size is approximately a factor of 4 smaller than that of stage 6.

Another possible mechanism for the difference in the relaxation times between the various stages could be the intercalate bounding layers of graphite. One imagines that the Fe^{3+} spins relax to the $FeCl_3$ lattice which then relaxes to the graphite layers mainly through the chlorine graphite interaction due to phonons. An enhancement in the low-frequency phonon spectrum of intercalated graphite over that of HOPG was actually calculated[27] and observed.[28] Since high stages have a smaller density of low-frequency phonons than low stages, according to equation (4) the conductivity K in the low stages would be enhanced and thus again lead to a shorter relaxation time. However, the changes in the relaxation times can be adequately accounted for by the relative size of the specific heats without considering the changes in the thermal conductivity. Thus we conclude that the change in thermal conductivity between different stages of $FeCl_3$ is small compared to the specific heat effect.

Therefore the maximum in the relaxation time is attributed to the specific heat of the spin system which is con-

TABLE I. Stage index versus the relative peak size of the in-phase magnetic susceptibility for $FeCl_3$ GIC.

Stage	Peak size
1	0.0846
2	0.2256
3	0.4381
4	1.4381
5	5.1877
6	1.8329
9	1.4706

sistent with theoretical calculations based on a model of two-dimensional interacting dipoles.[29] This model shows an increase in the specific heat of the system near the transition point which is similar to that exhibited by many other systems near their critical points and is attributed to critical fluctuations. Mössbauer studies[30] of anhydrous $FeCl_3$ describe the broadness of the resonance lines near the critical temperature as a result of the increase in fluctuations of the internal field direction which are caused by the spin relaxation in the system.

If the quantity $\omega\tau$ is eliminated between Eqs. (1) and (2), then another representation of χ' and χ'' can be given by the following equation:

$$(\chi'-\chi_0+\tfrac{1}{2}G)^2+(\chi'')^2=\tfrac{1}{4}G^2 . \quad (6)$$

As long as the relaxation is controlled by one relaxation time, Eq. (6) predicts that when χ' is plotted versus χ'' the points should lie on a circle. Figure 7 shows the experimental data of χ' versus χ'' at different frequencies at the peak temperatures and 1.72 K, which is about 30 mK below the peak temperature.

The existence of the spin relaxation at the critical point for both anhydrous $FeCl_3$ and $FeCl_3$ GIC supports the correlation between the magnetic properties of these two systems. Thus, qualitatively, we suggest that the three-dimensional anomaly which is observed at about 8 K in anhydrous $FeCl_3$ is the source of the low-temperature anomaly in $FeCl_3$ GIC. The staging process decreases the interactions between the intercalant layers in such a way as to have a two-dimensional interacting spin system. Our data indicate that the graphite layers between the magnetic intercalant layers act as nonmagnetic spacing layers allowing the c-axis spin-spin coupling to be varied.

The application of a small dc magnetic field of the order of 5 G smears out the anomaly in the susceptibility[31] and thus no relaxation was observed at this field. The out-of-phase component (χ'') as a function of temperature and in different external dc magnetic fields is represented

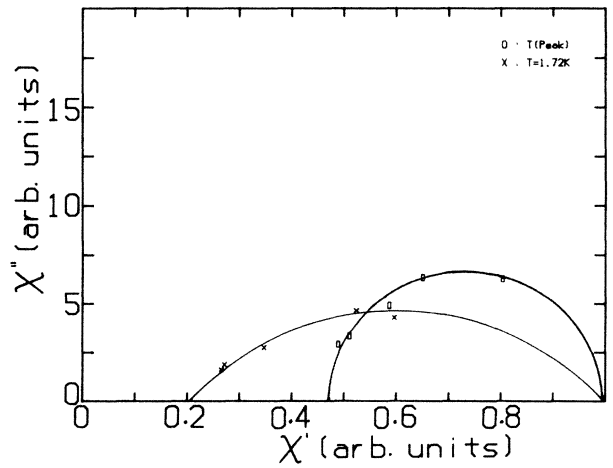

FIG. 7. The out-of-phase versus the in-phase components of the magnetic susceptibility at different frequencies and at the peak temperature and at $T=1.72$ K. The continuous lines are on a circle.

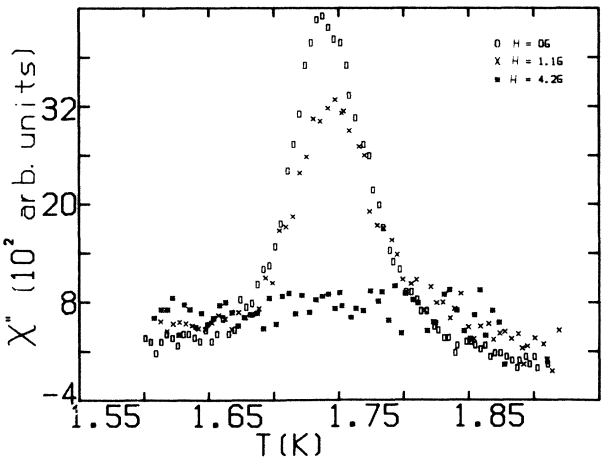

FIG. 8. The out-of-phase component of the magnetic susceptibility versus temperatures for stage-6 $FeCl_3$ GIC. The B's are the applied dc magnetic fields in Gauss.

in Fig. 8; as shown in the figure at a field of 4.2 G the anomaly has disappeared.

This anomaly, if it is a three-dimensional transition between two magnetic phases, is expected to exist in fields as high as 1 kG; however, the disappearance in such a small field emphasizes the two-dimensional nature of this phase transition. In addition, the stage dependence of this anomaly shows more pronounced peaks for higher stage samples in both components of the susceptibility.

CONCLUSION

We have shown that for systems which possess a magnetic anomaly the out-of-phase component of the susceptibility is dominated by spin-lattice relaxations, thus it would not be reliable to relate the electrical resistivity of these systems to the out-of-phase component. Fitting our data to a temperature-dependent relaxation shows that the relaxation time itself exhibits an anomaly near the transition temperature of the magnetic anomaly. On a qualitative basis, and in agreement with a two-dimensional mean-field calculation,[28] we have found that the relaxation anomaly is related to a similar one in the specific heat at constant field.

In agreement with reported thermal conductivity measurements[20] and phonon density calculations[27] at low temperatures, the out-of-plane phonon vibrations are determined to be the carriers of the heat from the spin system to the graphite lattice. The contribution of the conduction electrons is not significant in the temperature range over which our measurements were carried out. Finally, we have shown that the intercalant $FeCl_3$ controls the magnetic properties of the $FeCl_3$-GIC system and becomes more two dimensional as the stage is increased.

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