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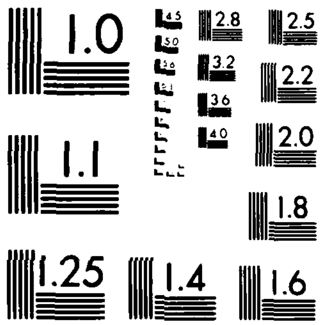

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: AFOS[illegible]229
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER:
4. TITLE (and Subtitle): INVESTIGATION OF ELECTRIC AND MAGNETIC PROPERTIES OF INTERCALATED GRAPHITE
5. TYPE OF REPORT & PERIOD COVERED: Annual — 12 MOS. STARTING SEP. 30 '83
6. PERFORMING ORG. REPORT NUMBER: 20-219-6340-5
7. AUTHOR(s): GEORGE O. ZIMMERMAN
8. CONTRACT OR GRANT NUMBER(s): AFOSR 82-0286
9. PERFORMING ORGANIZATION NAME AND ADDRESS: PHYSICS DEPARTMENT, BOSTON UNIVERSITY, BOSTON, MA 02215
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 2306/C3, 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS: AFOSR/NE, BUILDING 410, BOLLING AFB, DC 20332
12. REPORT DATE: NOVEMBER 15, 1984
13. NUMBER OF PAGES: 21
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):
15. SECURITY CLASS. (of this report): UNCLASSIFIED
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:
16. DISTRIBUTION STATEMENT (of this Report): UNLIMITED

[illegible]

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report):

DTIC ELECTE JAN 23 1985 D

[illegible] SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

INTERCALATED GRAPHITE
MAGNETISM
ELECTRICAL CONDUCTIVITY
IRON CHLORIDE

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

THIS YEAR, BECAUSE OF THE MOVE OF THE PHYSICS DEPARTMENT OF BOSTON UNIVERSITY TO NEW QUARTERS, THE RESEARCH FACILITIES AND THE LABORATORY HAVE BEEN SIGNIFICANTLY UPGRADED. THE UPGRADING INCLUDED NEW PUMPING SYSTEMS AS WELL AS CONTROL AND DATA ACQUISITION DEVICES, SO THAT NOW THE DATA CAN BE SAMPLED, COLLECTED AND ANALYZED BY COMPUTER.

ALTHOUGH THE UPGRADING TAKES SOME TIME, THE IMPROVED FACILITIES ALLOWED CER-

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TAIN MEASUREMENTS, SUCH AS THE CONDUCTIVITY MEASUREMENT WHICH WOULD HAVE BEEN IMPOSSIBLE BEFORE. THE MOST SIGNIFICANT DISCOVERIES DURING THE PAST YEAR WERE THE DISCOVERY OF A CONDUCTIVITY MAXIMUM IN $FeCl_3$-INTERCALATED GRAPHITE ALONG THE C-AXIS. THE MAXIMUM COULD BE SUPPRESSED BY A MAGNETIC FIELD AS SMALL AS 0.4MT. AN ACCOMPANYING SUSCEPTIBILITY MAXIMUM OBEYS THE SCALING LAW WITH AN EXPONENT OF APPROXIMATELY TWO.

Scientific

Annual

[redacted] Report on

Investigation of Electric and Magnetic Properties of Intercalated Graphite

Grant No. AFOSR 82-0286

Grant Period 12 Months Starting 83 Sept. 30

Project Task 2306/C3

November 15, 1984

By George O. Zimmerman

Principal Investigator

Physics Department

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Abstract

This year, because of the move of the Physics Department of Boston University to new quarters, the research facilities and the laboratory have been significantly upgraded. The upgrading included new pumping systems as well as control and data acquisition devices, so that now the data can be sampled, collected and analyzed by computer.

Although the upgrading takes some time, the improved facilities allowed certain measurements, such as the conductivity measurement in appendix 2 which world have been impossible before. The most significant discoveries during the past year were the discovery of a conductivity maximum in $FeCl_3$-intercalated graphite along the c-axis. The maximum could be suppressed by a magnetic field as small as 0.4mT. An accompanying susceptibility maximum obeys the scaling law with an exponent of approximately two.

Progress Report

During the investigation of $FeCl_3$ incalated graphite at this laboratory, several important discoveries were made about the electric and magnetic properties of these substances. It was found that in well characterized $FeCl_3$ samples there was a magnetic susceptibility maximum indicating a magnetic transition at 6.5 K in stage one and at 1.72 K in stage two. At higher temperatures the magnetic susceptibility of these samples obeyed the Curie-Weiss law with the theta indicating an antiferromagnetic interaction within the layers and a ferromagnetic one between layers in stage one and antiferromagnetic interactions both within and between layers in stage two. Figure 1 shows the susceptibilities as a function of temperature while Figure 2 shows the inverse susceptibility and the Curie-Weiss law. Table 1 lists the various parameters for the transitions.

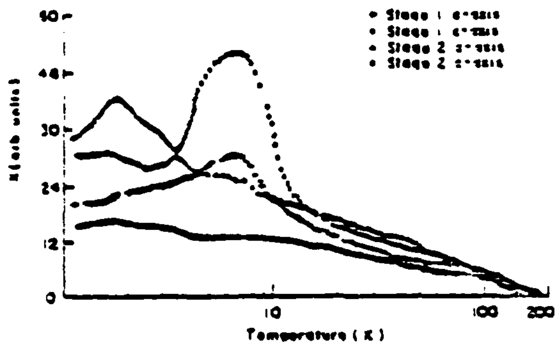

Figure 1. susceptibility (X) versus temperature (T), plotted on a semi-logarithmic scale, for the stage 1 and 2 compounds. The measuring field was fixed both parallel (a-axis) and perpendicular (c-axis) to the basal plane. Notice the small amount of stage 1 (undetectable in the x-ray diffractograms) which can be detected in the stage 2 curve.

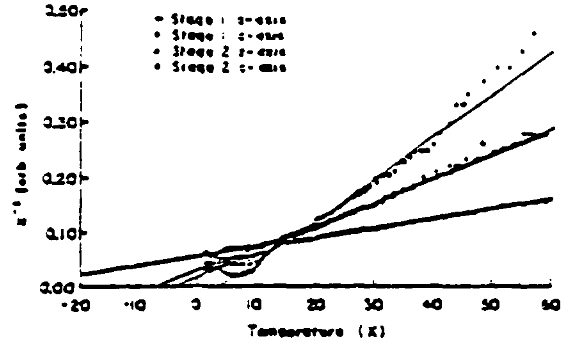

Figure 2. Inverse susceptibility (X^{-1}) versus temperature (T) for the curves shown in Figure 1. The solid lines represent least squares fits to the data.

TABLE 1 This table lists the magnetic properties of the compounds.

STAGE	DIRECTION	TRANSITION TEMPERATURE	SUSCEPTIBILITY MAXIMUM	θ	CURIE CONSTANT (ARBITRARY UNITS)	NEAREST NEIGHBORS TO IRON VACANCIES
1	a-axis	4.3	6.5	-3.3	222	54%
1	c-axis	4.3	6.5	-3.3	132	54%
2	a-axis	1.3	1.72	-7.6	242	9%
2	c-axis	1.3	1.72	-33.0	375	9%

Possibly a more important discovery was that of a susceptibility maximum which occurs in $FeCl_3$ intercalated graphite at 1.7 K. That maximum occurs in each stage at the same temperature but its size becomes significantly greater with stage. Figure 3 shows this maximum in stage 1,2,4 and 6. The size of this maximum depends

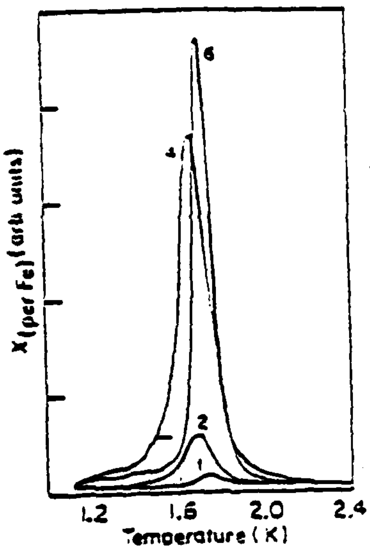

Figure 3. Measurements of susceptibility for magnetic fields perpendicular to the c-axis, $\chi_\perp$, vs temperature for graphite-$FeCl_3$ stages 1, 2, 4, and 6.

sensitively on the applied magnetic field. Figure 4 shows this maximum as a function of temperature, which is in zero (higher peak) magnetic field for a stage 6 sample.

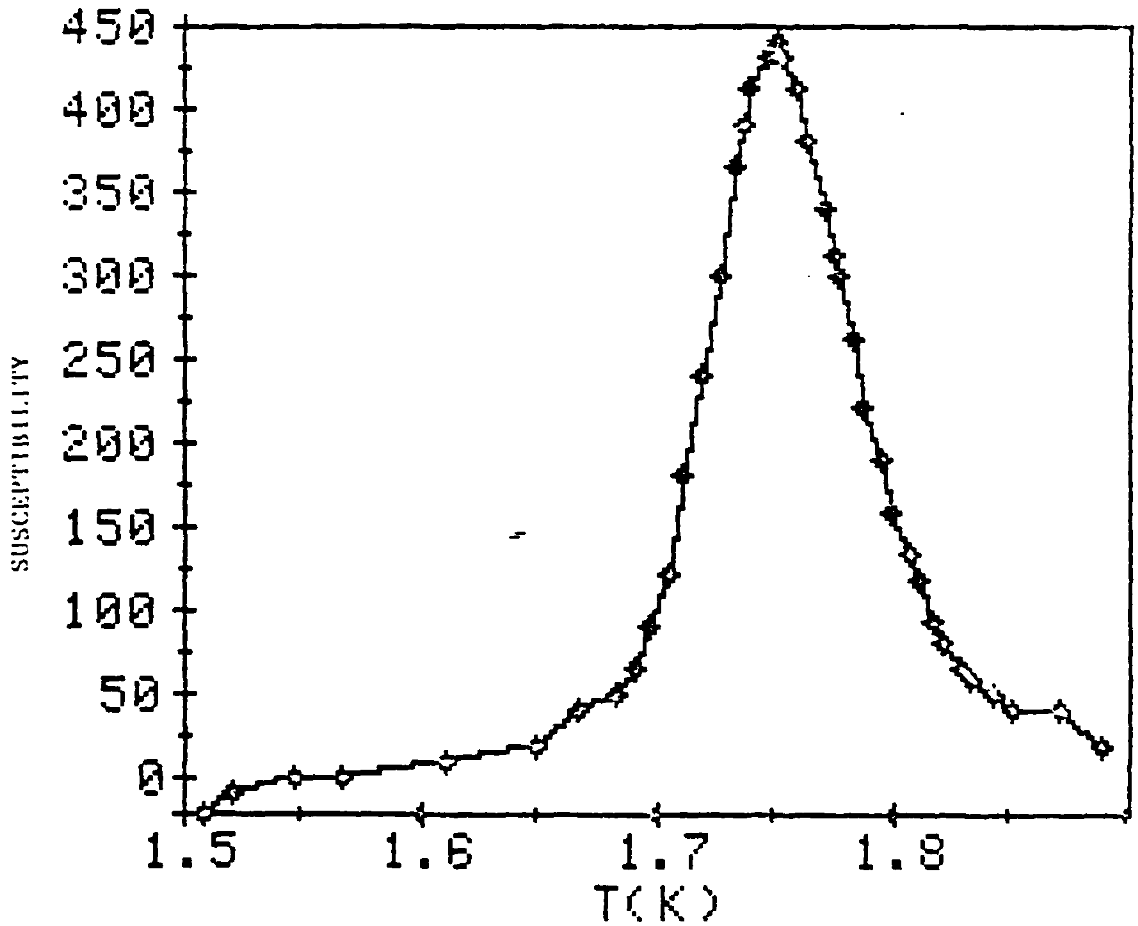

FIGURE 4

Figure 4

The magnetic susceptibility of stage 6 $FeCl_3$ intercalated graphite as a function of temperature. The peak occurs at T = 1.749 K.

Figure 5 shows the maximum in different magnetic fields applied along the c-axis while Figure 6 shows the field dependence along the a-axis.

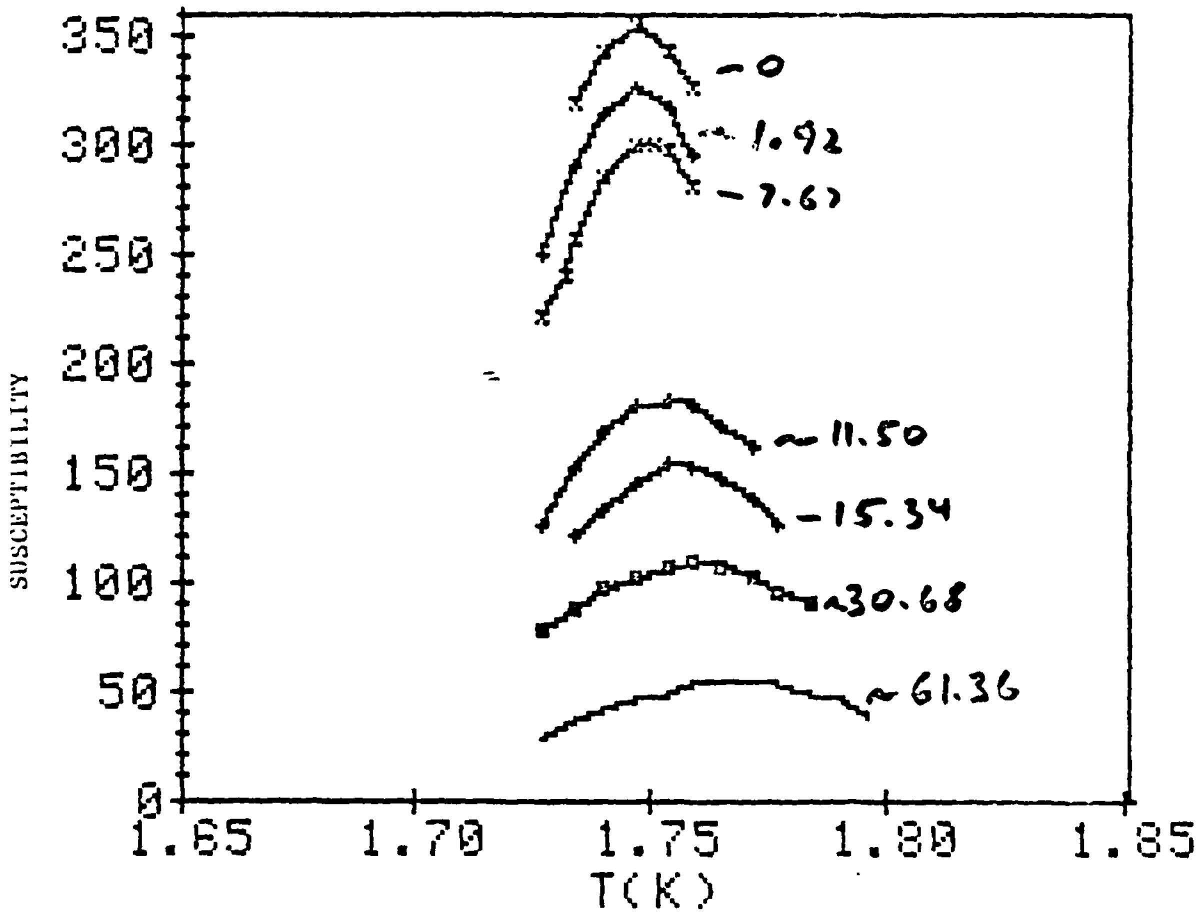

FIGURE 5

Figure 5

The magnetic susceptibility of stage 6 $FeCl_3$ intercalated graphite in the temperature region of the susceptibility maximum as a function of the applied external magnetic field. The field is applied along the c-axis while the measuring field is along the a-axis.

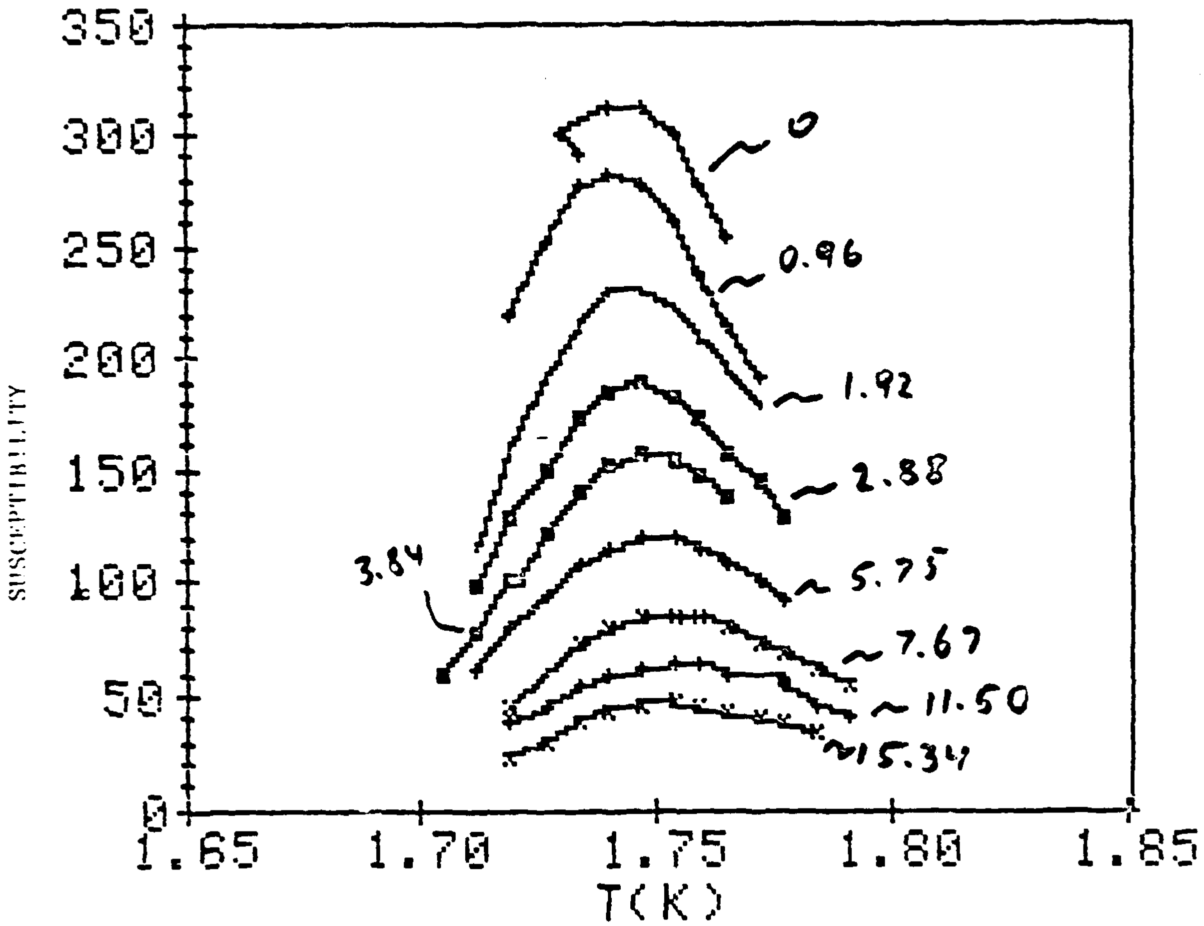

FIGURE 6

Figure 6

The magnetic susceptibility of stage 6 $FeCl_3$ intercalated graphite in the temperature region of the susceptibility maximum as a function of the applied external magnetic field. The field is applied along the b-axis while the measuring field is along the a-axis.

The notations near the various traces indicate the magnetic field in gauss. One notes that a field applied along the a-axis is much more effective in suppressing the maximum than a field along the c-axis. The measuring field was always along the a-axis. In order to explore the critical properties of the system one needs to apply the shape correction. since the susceptibility at the maximum in zero applied magnetic field is very large. When such a correction is applied the peak becomes very large and sharp. Fig. 7 shows the natural logarithm of the corrected maximum as a function of the reduced temperature $t = (T - T_c)/T_c$. The units are arbitrary but one notes the sharpness of the maximum. Fig. 8 shows that the susceptibility obeys a power law near the critical point.

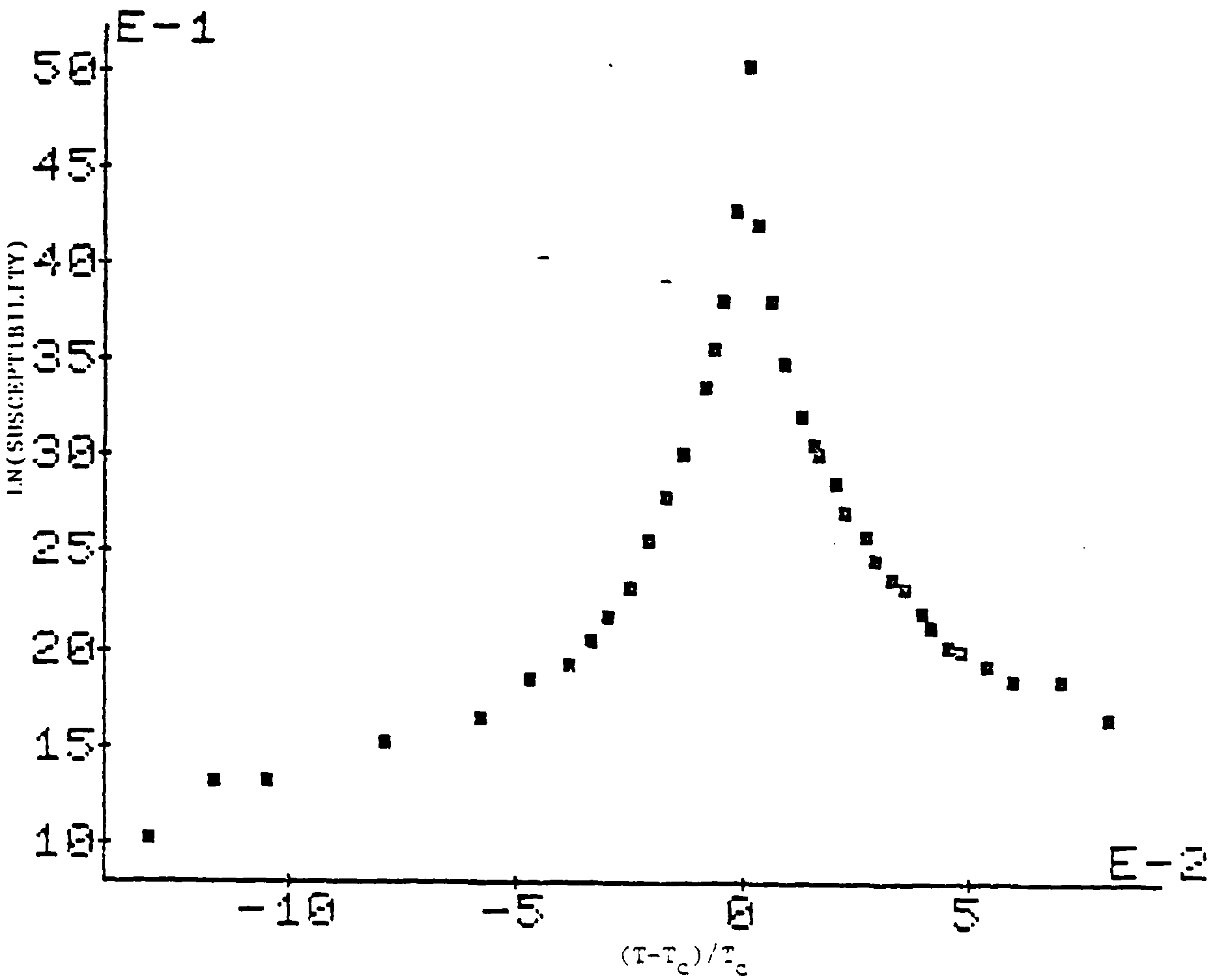

FIGURE 7

Figure 7

Data of Fig. 4 corrected for the shape of the sample. The logarithm of the susceptibility is plotted against the reduced temperature (T-Tc)/Tc.

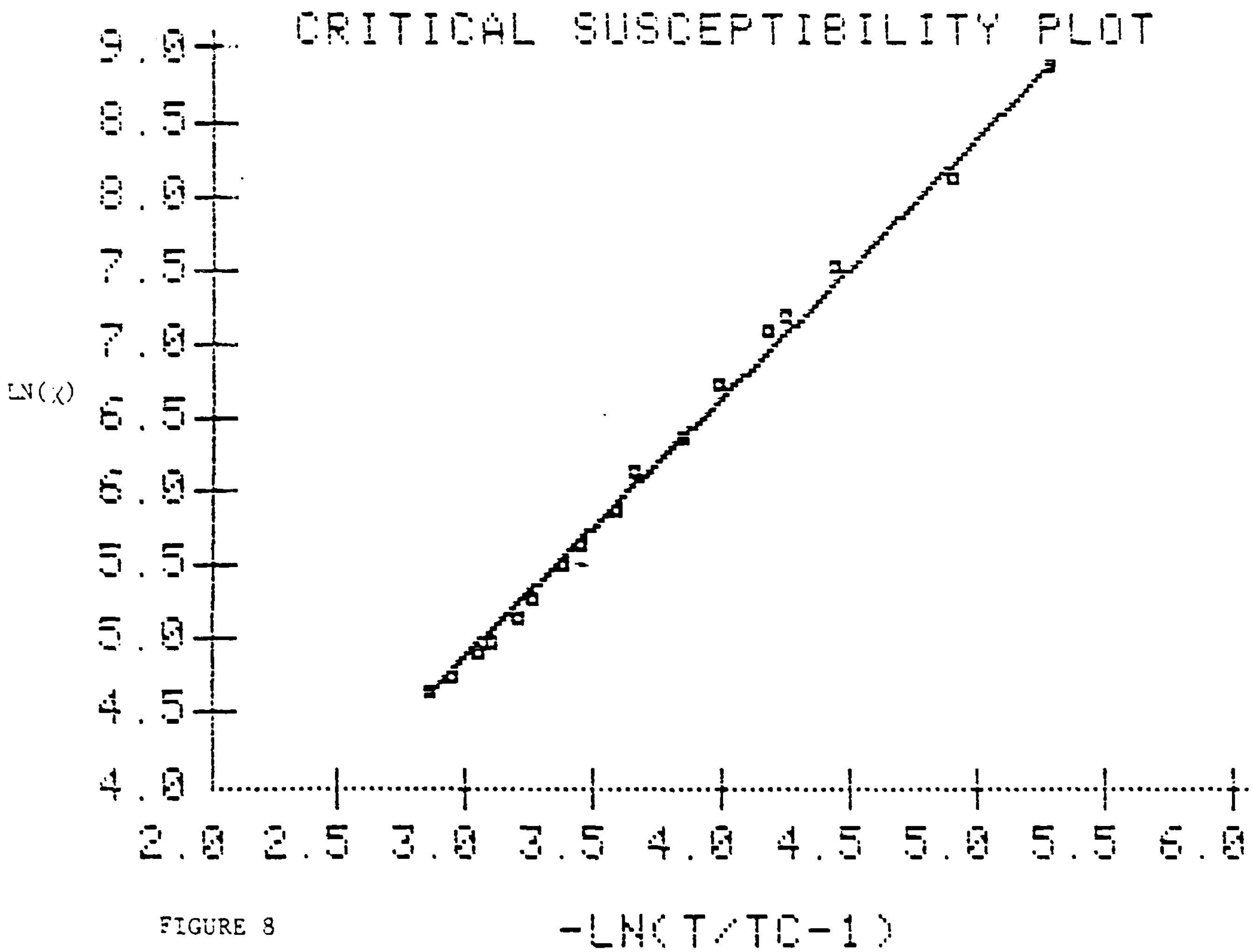

FIGURE 8

Figure 8

The natural logarithm of the susceptibility plotted against the logarithm of the reduced temperature, showing that the transition obeys a power law

$\chi \propto \left(\frac{T-Tc}{Tc}\right)^{-\gamma}$ with $\gamma = 1.75$.

Figs. 9a and b show the logarithm of the maximum susceptibility as a function of the applied field in gauss along the c and a axes respectively, while Figures 10a and b show the temperature of the susceptibility maxima as a function of the applied field along the c and a axes respectively.

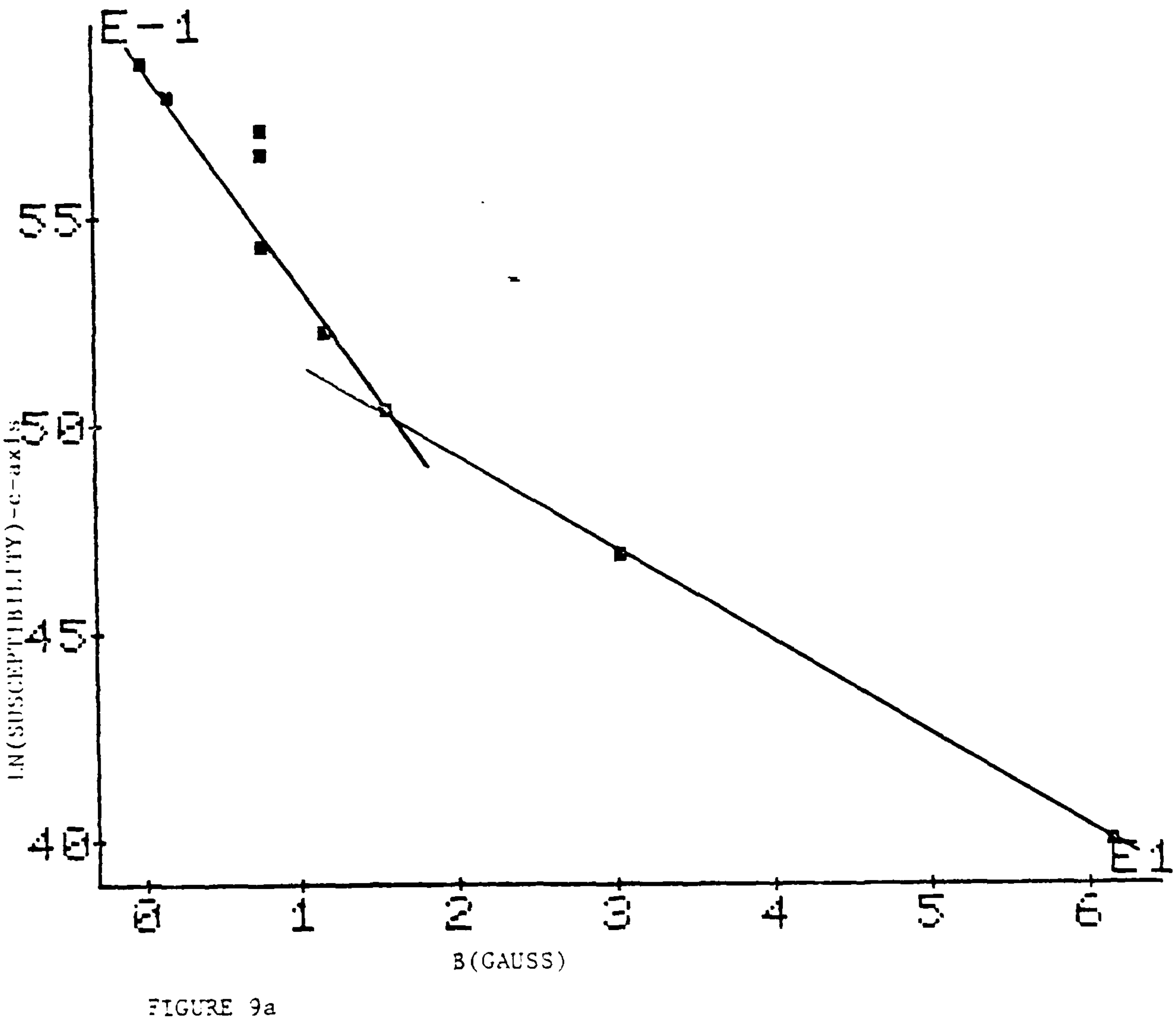

FIGURE 9a

Figure 9a

The logarithm of the size of the susceptibility maxima shown in Fig. 5 as a function of the applied magnetic field along the c-axis.

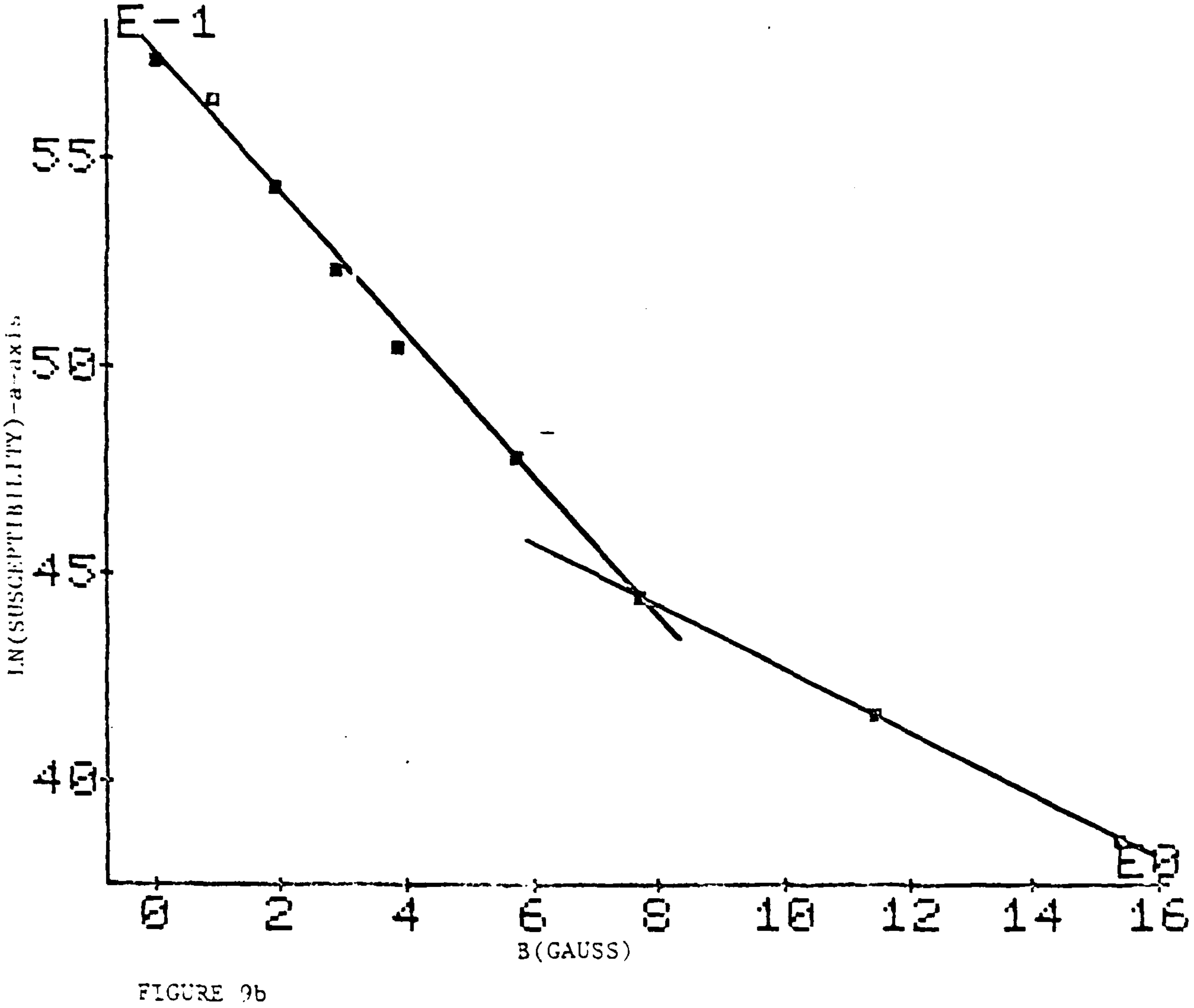

Figure 9b

The logarithm of the size of the susceptibility maxima shown in Fig. 6 as a function of the applied magnetic field along the b-axis.

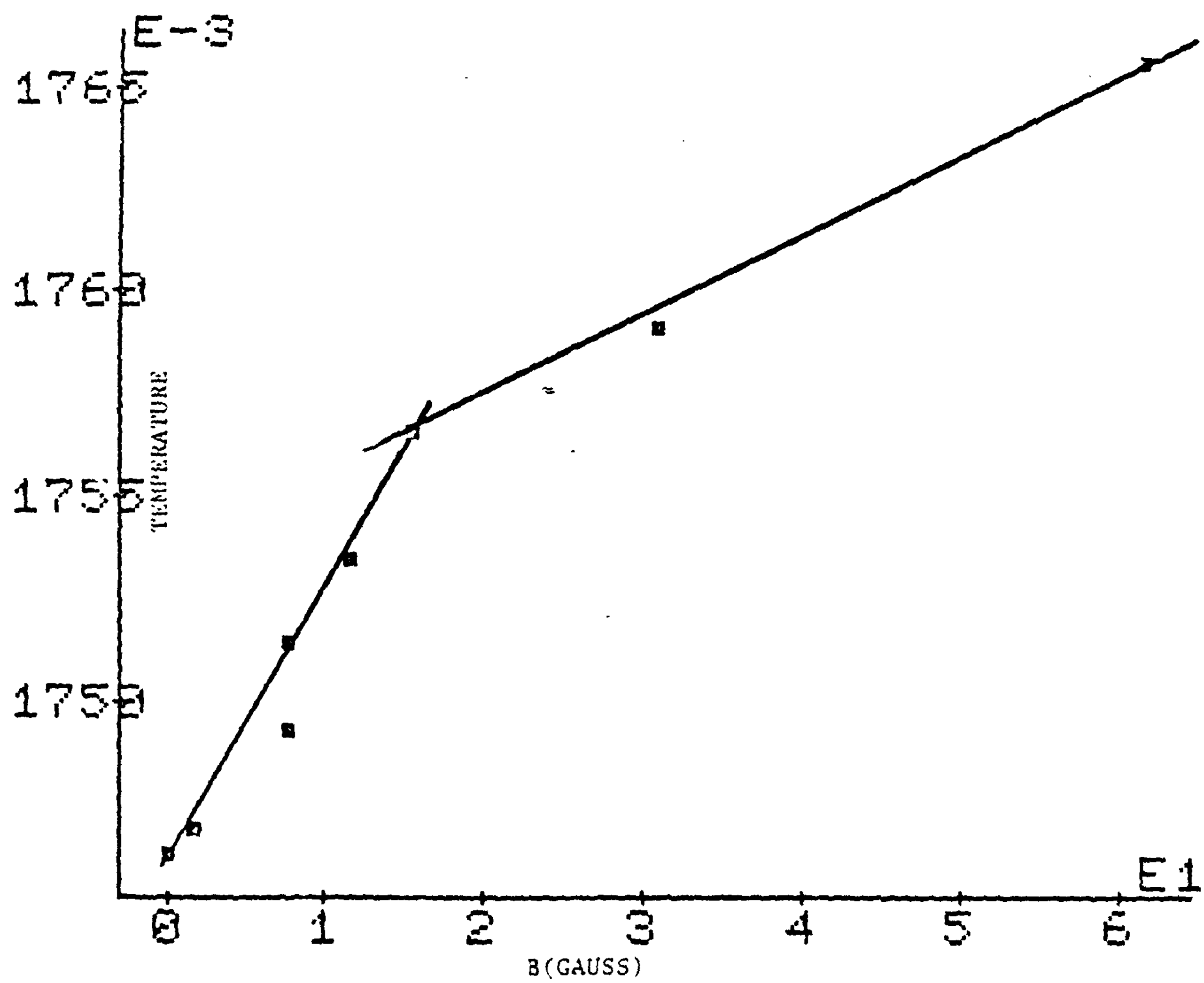

FIGURE 10a

Figure 10a

The temperature of the susceptibility peak shown in Fig. 5 as a function of the applied magnetic field along the c-axis.

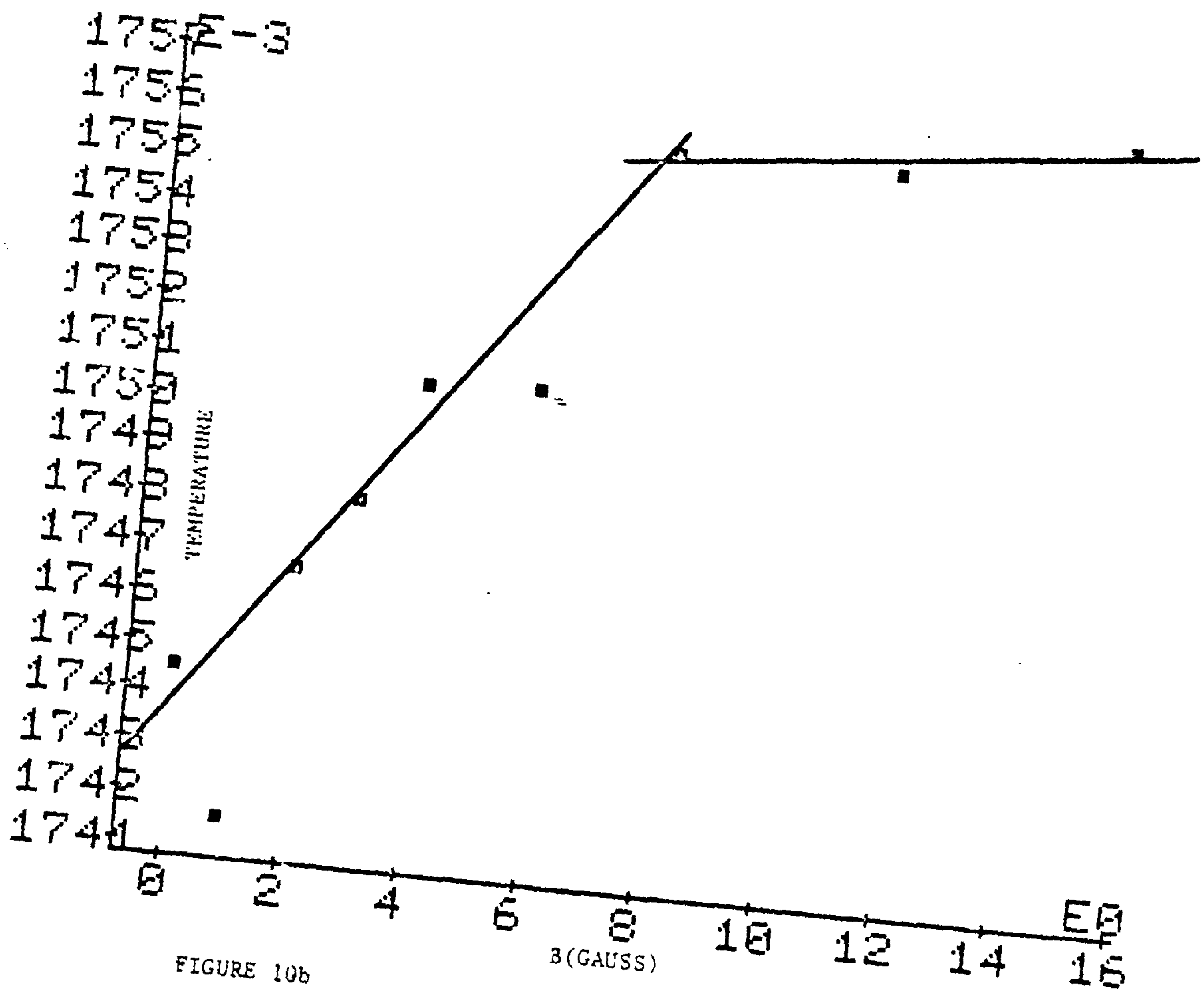

Figure 10b

The temperature of the susceptibility peak shown in Fig. 6 as a function of the applied magnetic field along the b-axis.

One notes that there is a distinct change in the behavior of the maxima from the low to a high field. This change takes place at 17 gauss if the field is applied along the c-axis while the crossover point is 7.5 gauss if the field is applied along the a-axis. The lines denote the least squares fit to the low and high temperature behavior respectively. Similar phenomena were found in $NiCl_2$ and $CoCl_2$ intercalated graphite. By measuring the in-phase and out-of-phase components of the susceptibility, one can infer that there is a resistivity maximum at the maximum in susceptibility. The in and out of phase (quad) susceptibilities of stage 6 are shown in Figure 11 while Figure 12 shows the conductivity as deduced from the phase shift.

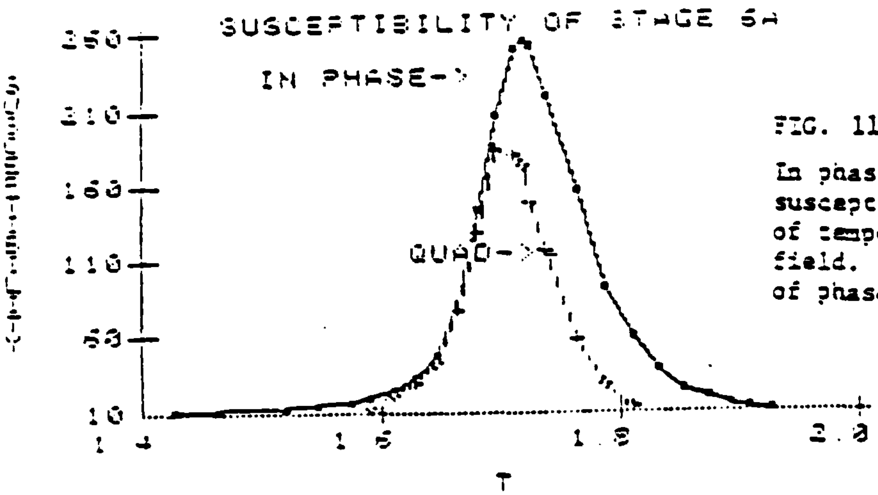

FIG. 11

In phase and out of phase susceptibility as a function of temperature in zero magnetic field. Quad denoting the out of phase component

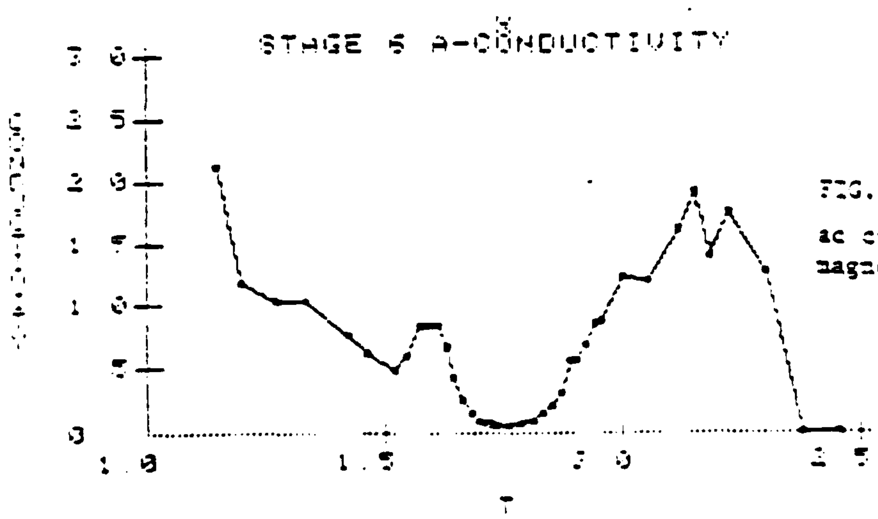

FIG. 12

ac conductivity in zero magnetic field

It was also shown that the size of the susceptibility maximum can be correlated. within a stage 2 sample, with the number of vacancies in that sample as measured by the Mössbauer effect. This was shown for samples which have 7% of iron sites neighbors to vacancies, 9% and 11%. The susceptibilities as well as the Mössbauer spectra are shown in Figures 13 and 14. This, along with

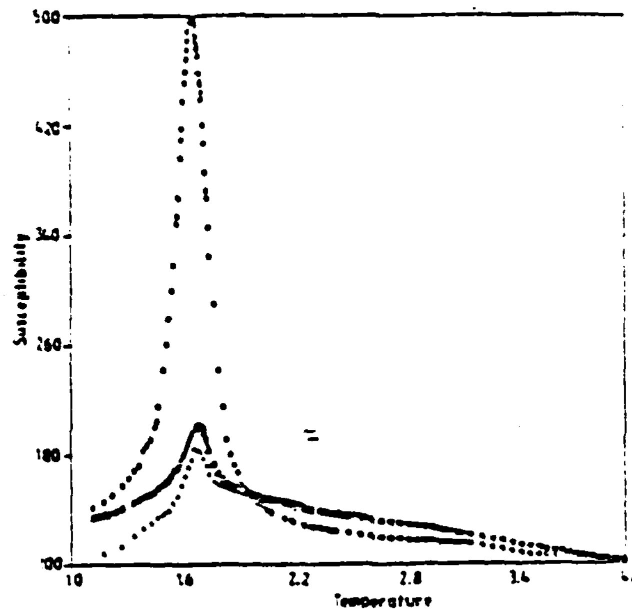

FIG. 13 Susceptibility versus temperature for three different stage 2 graphite-$FeCl_3$ compounds. The susceptibility is plotted in arbitrary units but each sample has been normalised for the relative amount of iron it contains. Δ, sample 1; □, sample 2; ○, sample 3.

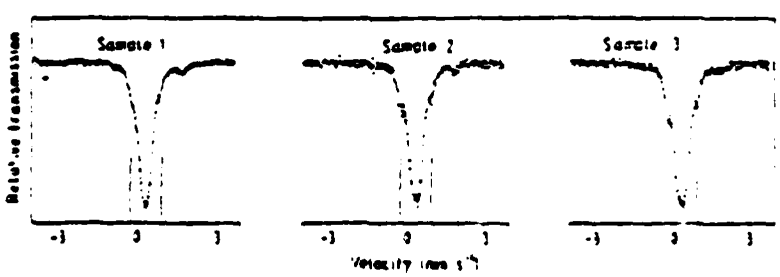

FIG. 14 Corresponding Mössbauer spectra for the three samples whose susceptibility curves are shown in figure 1. The position of the two peaks which comprise the iron sites nearest neighbour to iron vacancies are indicated by the straight lines. Zero velocity is measured relative to the centre of gravity of an iron foil spectrum at room temperature.

the power dependence of the susceptibility peak, corrected for the shape factor, at temperatures above the maximum, argues strongly that the maximum is an indication of a spin glass transition.

We have recently investigated stage 3 $FeCl_3$ graphite and find that its characteristics are similar to those of stage 2. Also, in an attempt to see a temperature hysteretic behavior of the 1.7 K transition we cooled the sample in a magnetic field. A different susceptibility should have been observed for a spin-glass but none was found.

Working on this grant during the grant period were:

G. O. Zimmerman - P.I.

Dr. C. Nicolini - Research Associate

Dr. A. Ibrahim - Research Associate

K. Galuszeewski - Graduate Student

A. Kaplan - Undergraduate Student

A. Papaconstantino - Graduate Student

Appendix I

Publication in Extended Abstracts

'84 M.R.S. Meeting, Boston Nov. 26-30

CRITICAL EXPONENT γ OF THE MAGNETIC ANOMALY OF STAGE-6 $FeCl_3$ INTERCALATED GRAPHITE+

G.O. Zimmerman, C.Nicolini, D. Solenberger, D. Gata, B. Holmes
Physics Department
Boston, MA 02215

We have discovered a susceptibility maximum in all stages of $FeCl_3$ intercalated graphite which occurs at about 1.700K.[1,2] The size of the maximum varies by a factor of 30, being smallest in stage 1 and greatest in stage 6. This phenomenon appears to be two dimensional in origin. The temperature of the maximum does not vary from stage to stage. In stage 2, we have correlated the size of the maximum with the number of iron vacancies[3]. The measurements shown here are for stage-6 $FeCl_3$ intercalated graphite where the maximum is most pronounced.

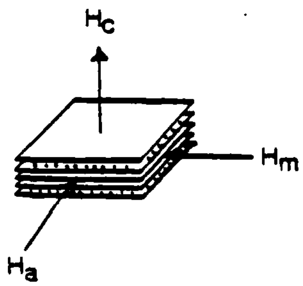

Figure 1

Intercalated Graphite
H_m is the measuring field
H_a and H_c are externally applied fields

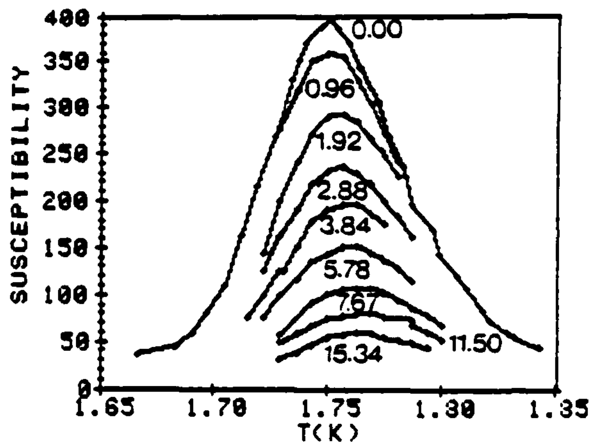

Figure 2

Susceptibility as a function of temperature in an applied magnetic field (numbers denote field in Gauss)

Fig. 1 shows the geometry of our arrangement. The susceptibility was measured by a standard A.C.[4] technique at 40Hz with the measuring field H_m parallel to the graphite planes. The measuring field was always smaller than 0.1 G.

Fig. 2 shows the magnetic susceptibility as a function of temperature. The highest peak is zero magnetic field, while the consecutively lower peaks are in fields of 0.96, 1.92, 2.88, 3.84, 5.75, 7.67, 11.50 and 15.34 G respectively along the a-direction (Fig. 1). One observes that in addition to attenuating the maximum, an applied field shifts the temperature of the maximum to a higher temperature.

Because of the high susceptibility at the maximum the external measuring field which each individual magnetic spin sees is shielded by the neighboring spins and that shielding depends on the shape of the sample. We measure χ_{ext} and would like to measure χ_{int}, where χ denotes the magnetic susceptibility. χ_{int} is the response of the magnetic spin to the field it experiences while χ_{ext} is the response to an external field. The relation between χ_{int} and χ_{ext} is[5]

$$\chi_{int} = \frac{\chi_{ext}}{1 - z\chi_{ext}}$$

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

$$\epsilon = \frac{1}{\chi_{\epsilon \Delta T}}$$

When this correction is applied to the susceptibility at zero applied magnetic field one obtains the points in Fig. 3.

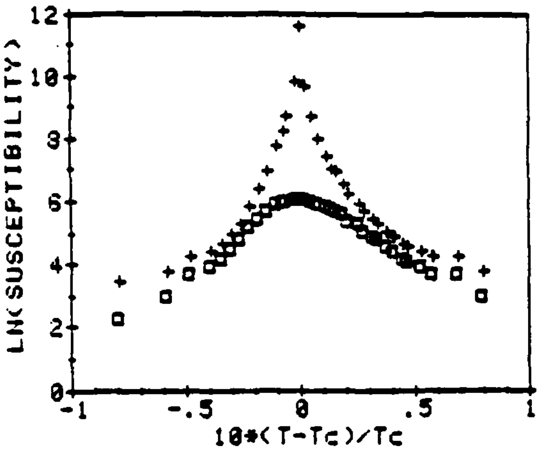

Figure 3

Natural logarithm of the susceptibility at 0 field as a function of the reduced temperature

+ is shape-corrected susceptibility

□ is uncorrected susceptibility

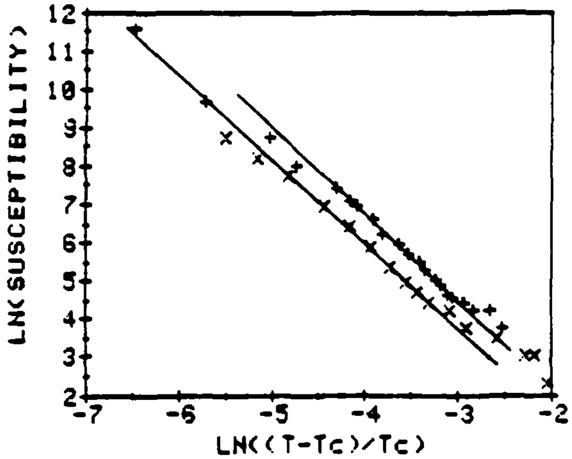

Figure 4

Logarithm of the susceptibility at 0 field as a function of the reduced temperature showing the universal power law behavior

$+ : T > T_c$

$x : T < T_c$

Fig. 3 shows the natural Logarithm of the susceptibility plotted against the reduced temperature (T - Tc)/Tc where Tc is the temperature of the maximum. The + are the corrected susceptibilities while the □ are the uncorrected values. The reduced temperature was expanded by a factor of 10.

Fig. 4 shows the natural logarithm of the susceptibility as a function of the reduced temperature. The + are for T > Tc while X denotes points for T < Tc. This plot suggests that the susceptibility χ goes as

$$\chi \propto \left| \frac{T - T_c}{T_c} \right|^{-\gamma}$$

with $\gamma = 1.97 \pm .1$ for T > Tc and $\gamma = 1.85 \pm .1$ for T < Tc. The slopes of the drawn lines denote the values of γ. Although similar functional behavior of the susceptibility has been observed in many other systems and is a consequence of the universality of the characteristics of second order phase transitions, the value of γ is between 1 and 1.25 in three dimensional transitions, while it is predicted to be 1.75 for a two dimensional Ising model. Our values appear to be higher than that. We are thus dealing with a new phenomenon.

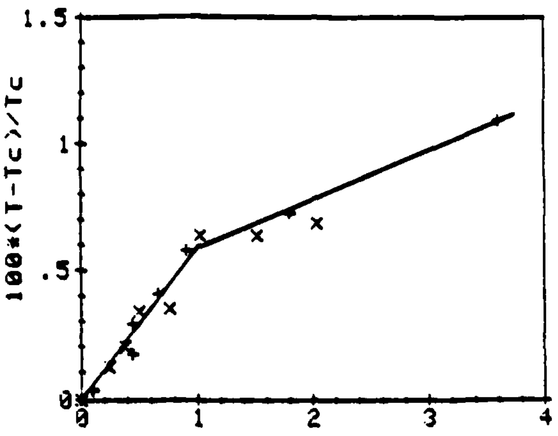

Figure 5

Temperature dependence of the maximum as a function of the applied magnetic field

+ : H_c
x = H_a

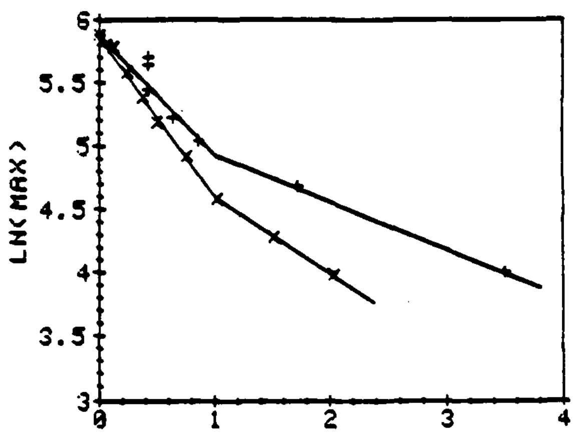

Figure 6

Logarithm of the maximum susceptibility as a function of the applied magnetic field

+ = H_c
x = H_a

Fig. 5 shows the magnetic field dependence of the temperature at the susceptibility maximum + denotes the points for the field applied along a direction normal to the planes while x denotes the field applied parallel to the planes. The temperature is the reduced temperature multiplied by 100 where Tc is the temperature of the maximum at zero field. The field is the field in units of Ho where Ho is 17 G for the Hc direction and 7.5 G for the Ha direction, and denotes the transition from low field to high field behavior. A field applied along Ha is more than a factor of 2 more effective than that applied along Hc. The slope of (T - Tc)/Tc at low field is a factor of 3 greater than that at high field.

Fig. 6 shows the size of maximum, plotted on a logarithms scale as a function of the scaled field H/Ho with + along Hc and x along Ha as shown in Fig. 1, with the same values of Ho as in Fig. 5 again and observes a low and a high field behavior

$$\chi_{MAX}(H) = \chi_{MAX}(0)\, exp\left(-\frac{\phi H}{H_o}\right)$$

with ϕlow - 1.3, ϕhigh = 0.6 for Ha and ϕlow = 1, ϕhigh = 0.4 for Hc. Similar behavior was observed in other magnetic intercalation compounds.[2]

1) G.O. Zimmerman, B.W. Holmes and G. Dresselhaus, Extended Abstracts of the 15th Biennial Conference on Carbon, University of Pennsylvania p. 42, (1981).
2) M. Elahy, C. Nicolini, G. Dresselhaus and G.O. Zimmerman, Solid State Communications 41, 289 (1982).
3) S.E. Millman and G.O. Zimmerman, Journal of Physics C16, 189 (1983).
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Appendix II

Publication in Extended Abstracts

'84 M.R.S. Meeting

Boston Nov. 26-30

Electrical Conductivity of $FeCl_3$ Intercalated Graphite*

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Introduction

The electrical conductivity of stage-6 $FeCl_3$ intercalated graphite was measured in the vacinity of the 1.75K susceptibility anomaly[1,2] by measuring the out of phase a.c. susceptibility. The measurements were made at frequencies between 40 and 1000 Hz and as a function of the magnetic field. The electrical conductivity is one of the properties most drastically changed by intercalation both in acceptor and donor graphite intercalation compounds,[3] (GIC), and special attention has been paid to their in-plane conductivity[4,5] which can be a factor of 10^6 greater than that along the c-axis (perpendicular to the plane). Our measurements were stimulated by the fact that we observed a maximum in the out-of-phase magnetic susceptibility, χ, accompanying an in-phase susceptibility, χ', maximum when the measuring field was parallel to the plane. No such maximum was observed with the field along the c-axis which would have measured the in-plane conductivity. χ'' is proportional to the conductivity, and with the measuring magnetic field parallel to the plane we are mainly sampling the changes in the conductivity along the c-axis. The maximum in χ'' comes at a temperature typically down by 2×10^{-2}K lower than that of χ' as shown in Fig. (1).

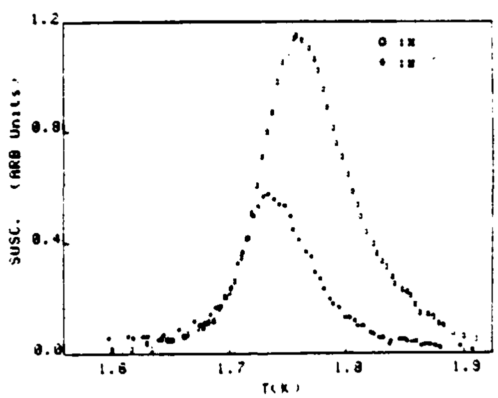

FIGURE 1
In-phase and out-of-phase components of the susceptibility as a function of temperature in zero field

Experimental

The samples were prepared by a standard technique and analyzed for staging fidelity by x-ray analysis. Mössbauer analysis verified the $FeCl_3$ content and number of vacancies. Preparation of the sample and more details about the experimental technique can be found in ref [4]. The conductivity measurements were made by a standard ac bridge method operating at frequency in the range of 40-1000 Hz. By using a phase sensitive detector we were able to observe both the in-phase (related to the susceptibility) and the out-of-phase (proportional to the conductivity) signals. The orientation of the magnetic field at the sample was perpendicular to the c-axis, therefore the magnetic moments in the basal-plane and the conductivities σ in the a-c plane were measured with the variation coming from the conductivity along the c-axis.

Results and Discussion

The most striking result in this work is the temperature dependence of the c-axis conductivity which exhibits an anomaly in the form of a sharp peak at temperatures near 1.73K in zero magnetic field. This conductivity behavior is indeed correlated with the same anomaly which we have seen in the in-plane magnetic susceptibility (χ) and reported in this volume[2]. As shown in Fig.(2) the peak is very sensitive to any external applied magnetic field, it disappears in a field $H \approx 5G$ and at frequency $f = 39.7$ Hz. The field dependence of the conductivity may relate this ano- to the mechanism which causes the peak in χ. An enhancement in σ is expected when the system has a magnetic anomaly.

As shown in Fig.(3), the conductivity at the peak monotonically decreases as the applied magnetic field increases. This reflects the fact that there is a microscopic process which depends on the magnetic phase of the system and causes the peak in σ. Fig. (4) shows the shift in temperature of the peaks for different values of the applied field. This shift indicates that the magnetic contribution is the dominant mechanism to the peak in σ.

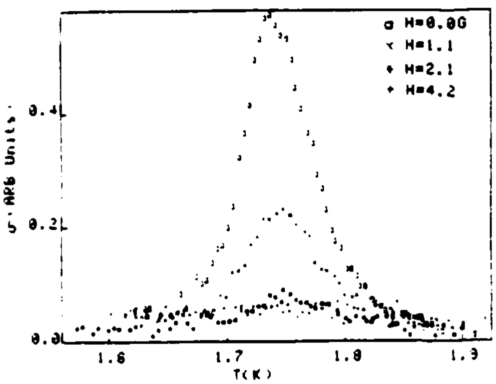

FIGURE 2
The in-plane conductivity as a function of temperature in an applied magnetic field

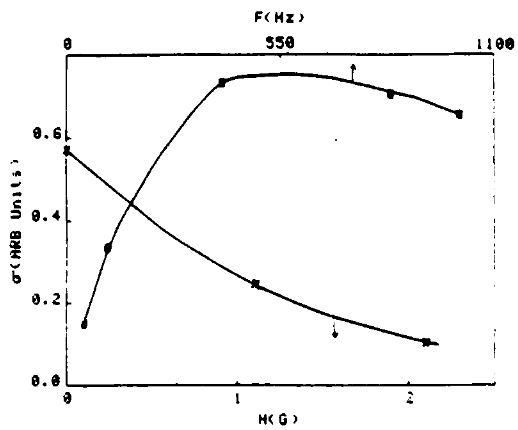

FIGURE 3
The conductivity at the peaks as a function of the applied magnetic field and the frequency

There are other effects which might interfere with these measurements, for example, skin effect or size effect. For materials of a metallic-like conductivity, the skin effects can be eliminated if the frequency is in the range of $f \lesssim 2 \times 10^6\rho^2$ (f in KHz, ρ in μΩcm). Within the limits of the resistivity of our sample, a typical value of f should be less than 2MHz which is much higher than the maximum frequency which has been used ($f \lesssim 1$ KHz). The size effect would be a major factor only if the mean free path is comparable with the sample size. Therefore, we do not expect any contribution to our data from these effects.

We also have measured σ at different frequencies and Fig.(5) shows the frequency dependence of σ at the peak. As shown by Fig.(4) and Fig.(5), the anomaly in σ persists at all frequencies but we have observed a variation in the magnitude of the peaks, also they are shifted to different temperatures. This frequency behavior was compared with reported data between the out-of-phase component and 1/fσ for a similar bridge [6]; they were very consistent as far as the peak size is concerned although the temperture variation is real. Therefore, no frequency effects interfere with the data and the observed peak size variation is just a frequency dependence in the bridge itself.

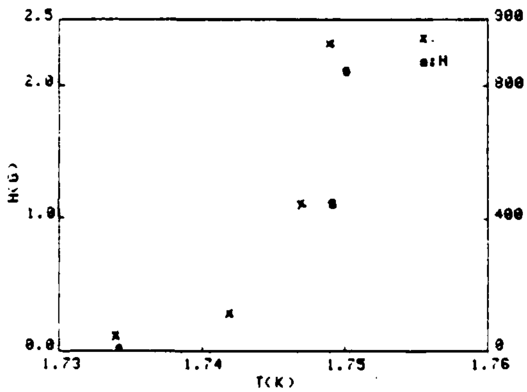

FIGURE 4
The temperature of the peaks as a function of the applied magnetic field and the frequency

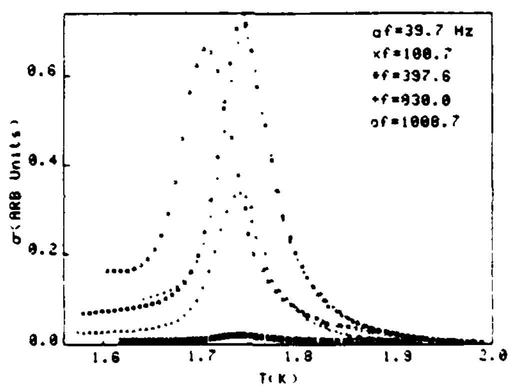

FIGURE 5
The in-plane conductivity as a function of temperature in a zero field and at different frequencies

In conclusion, low temperature phase transition of c-axis conductivity has been seen in stage-6 GIC and is related to the same phenomena which causes the peak in the magnetic susceptibility. The above anomaly is reminiscent of spin-glass behavior where at a certain temperature the magnetic spins are frozen.

*Supported by the Air Force Office of Scientific Research AFOSR Grant 82-0286.

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