PHYSICAL REVIEW B VOLUME 25, NUMBER 11 1 JUNE 1982

Mössbauer study of magnetic properties in low-stage $FeCl_3$ intercalated graphite

S. E. Millman, M. R. Corson,* and G. R. Hoy†
Department of Physics, Boston University, Boston, Massachusetts 02215

(Received 17 August 1981)

Using relaxation theory, we have completed the first fits to the broadened Mössbauer spectra observed about the magnetic transition temperature in stage-1 and -2 ferric chloride intercalated graphite compounds. We conclude that the major Fe^{3+} site undergoes a magnetic phase transition at 4.2 ±0.5 K for the stage-1 compound and 2.0 ±1.5 K for the stage-2 compound. These results are significant in showing that the magnetic phase transition, at least in the stage-1 compound, is strongly influenced by three-dimensional interactions. In agreement with Hohlwein *et al.* but in disagreement with others, we find that thermally activated electrons, donated by the graphite lattice, are frozen onto 20 ±3% of the Fe^{3+} sites to create Fe^{2+} sites at low temperature.

I. INTRODUCTION

Intercalated graphite compounds in general, and ferric chloride intercalated graphite compounds in particular, are usually thought of, at least to first approximation, as two-dimensional systems.[1-3] In this work, we show that the stage-1 compound undergoes a magnetic phase transition at about 4.2 K while the stage-2 compound orders at about 2.0 K. We further show that the magnetic transition, at least in the stage-1 compound, is influenced by three-dimensional interactions. Recent neutron-diffraction and magnetic-susceptibility studies[4-6] have failed to confirm or deny the magnetic phase transition previously reported by both magnetic susceptibility and Mössbauer studies.[1-3,7] Even among those who have cited a magnetic phase transition, there is a wide discrepancy in both the magnetic transition temperature and the electronic-spin alignment.[1-3,7] There is also wide disagreement as to the formation of Fe^{2+} sites in these compounds.[1,2,8,9] In this paper, we show that a large number of iron sites, about 20%, become Fe^{2+} ions at low temperatures.

The amount of Fe^{2+} present in a given sample and whether the compound undergoes a magnetic phase transition is strongly influenced by the amount of intercalant vacancies. In fact, if a sufficient amount, about 20%, of sites next to vacancies is found in the spectrum of a sample, there will be no Fe^{2+} sites found in its spectrum at low temperatures. The samples reported here have been carefully scrutinized both for staging fidelity using $00l$ x-ray diffraction and for intercalent vacancies by employing Mössbauer spectroscopy. Only samples containing no perceptible amount, i.e., less than 2%, of iron vacancies, chlorine vacancies, $FeCl_3$ vacancies, and $FeCl_2$ impurities were considered for this work. Given all of these sample dependent parameters, it is not surprising to observe the wide discrepancies found in the literature.

The spectra of the low-stage compounds undergo major changes in the rather broad temperature region between 10.0 K and 65 mK due to the dynamic effects of the onset of both magnetic order and ionic-spin relaxation. Since these effects also begin at different temperatures, there are two different temperatures of interest for these samples. We have quantitatively analyzed our spectra using the "nonadiabatic" stochastic theory of line shape in the mean-field approximation developed by Blume.[10] Previous Mössbauer studies of low-stage ferric chloride intercalated graphite compounds have made little attempt to quantitatively or qualitatively analyze these spectra. The proper analysis of these spectra is important both in showing that there is a magnetic phase transition in these compounds and in finding the transition temperature as a function of the separation between magnetic planes.

II. EXPERIMENTAL

The samples studied were prepared by intercalating anhydrous $FeCl_3$ into highly ordered pyrolytic graphite using the two-zone vapor transport method. Employing this growth process, the graphite temperature was maintained at 350 °C while the temperature of the ferric chloride was varied to achieve the different stages. An overpressure of about 250 Torr of chlorine gas was used to encourage staging. The intercalated compounds were charaterized for identity and uniformity of staging using $00l$ x-ray diffraction both before and after our Mössbauer measurements. Both samples were essentially single staged, since they showed only minute secondary diffraction peaks of other stages. The stage-1 sample exhibited some regions of pristine graphite. The inclusion of regions of pristine graphite was minimized by using a relatively thin stage-1 sample.

The samples were further checked for fidelity of in-plane density by taking their Mössbauer spectra at room temperature and liquid-nitrogen temperature as shown in Fig. 1. At these temperatures, both stages can be fit quite well with a single Lorentzian line whose linewidth (0.38 mm/sec) and isomer shift (0.48 and 0.56 mm/sec at room temperature and liquid-nitrogen temperature, respectively) are essentially the same as that of pristine anhydrous $FeCl_3$.[11] This indicates that there is neither a change in site symmetry at the iron ions nor is there any appreciable formation of either iron vacancies, chlorine vacancies, $FeCl_3$ vacancies, or $FeCl_2$ impurities in these samples. For comparison, Fig. 2 exhibits a sample in which about 20% of the iron sites are located next to vacancies, as can be deduced from the large quadrupole split site seen on the wings of the majority site. This identification of vacancies will be discussed in more detail elsewhere.[12] Notice that even the majority site can no longer be fitted with a single Lorentzian line. It is also interesting to note that this sample contains only about 3% Fe^{2+} sites at low temperatures. Thus, the amount of Fe^{2+} found at low temperatures is strongly influenced by the in-plane density of the given sample.

The molecular structure of graphite $FeCl_3$ has been determined by x-ray and electron-diffraction studies[13] and by electron microscopy studies.[14] These studies have concluded that the molecular structure of graphite $FeCl_3$ is essentially unchanged from that of its two constituents in agreement with that deduced from the room temperature and liquid-nitrogen temperature Mössbauer spectra. As in pristine anhydrous $FeCl_3$, the iron ions form hexagonal planes where each iron atom is surrounded by an octahedron of chlorine ions. There is some evidence of slight distortions of this octahedron due to the binding of the chlorine ions with the carbon atoms.[13]

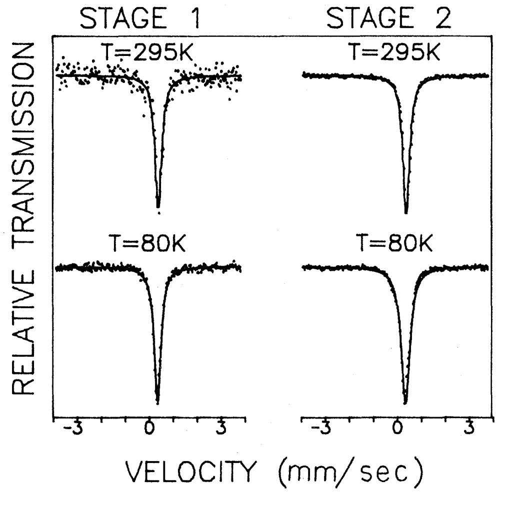

FIG. 1. This figure shows our experimental results along with the theoretical fits of the low-stage spectra at 295 and 80 K. Zero velocity corresponds to the center of gravity of an iron foil spectrum at room temperature.

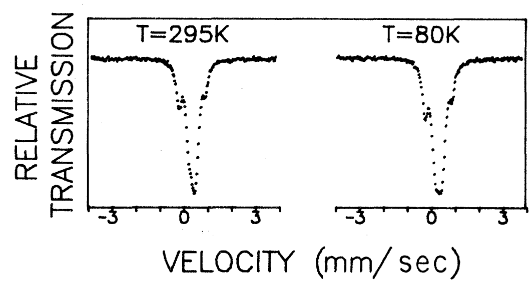

FIG. 2. This figure exhibits a sample at 295 and 80 K in which about 20% of the iron sites are located next to vacancies. These sites are located on the wings of the majority site.

Our Mössbauer spectra were taken in transmission geometry with the γ-ray direction parallel to the graphite c axis using our $^3He/^4He$ dilution refrigerator Mössbauer spectrometer. At 4.2 K and below the temperature was controlled to within 0.01 K. The maximum nonlinearity of the velocity drive was calculated and measured to be within 0.1%.

III. RELAXATION THEORY

We have applied the "nonadiabatic" stochastic theory of line shape in the mean-field approximation developed by Blume[10] to quantitatively analyze our Mössbauer spectra. We have used the Hamiltonian

$$\mathcal{H} = g\beta\vec{I}\cdot\vec{H}(\theta)f(t) + (e^2qQ/2)[3I_z^2 - I(I+1)] \ ,$$

where I is the nuclear spin, θ is the angle between the effective magnetic field and the electric-field-gradient symmetry axis, and the function $f(t)$ is a stationary, Markovian chain which is restricted to taking on the values ± 1. The effect of $f(t)$ jumping between its two values as time evolves is to cause the effective magnetic field to jump between "up" and "down" along the easy axis of magnetization. This theory is useful in describing magnetic order, since the probability of finding the effective magnetic field "up" does not have to equal that of finding it "down." In this model, the shape of the Mössbauer spectra are determined by both the amount of magnetic order present in the system and the flipping rate of the electronic spins.

IV. ANALYSIS

Figure 3 shows our experimental spectra of the stage-1 and -2 compounds at 10.0 K, 4.2 K, 3.00 K, 2.50 K, and 65 mK, together with our theoretical fits and composite subspectra. Although the spectra of the stage-1 and -2 compounds are very similar at 10.0 K and 65 mK, there are pronounced differences in the intermediate temperature region.

An examination of the 65-mK spectra of the stage-1 and -2 compounds clearly indicates the existence of three distinct composite subspectra in each compound. A comparison of the spectra of these compounds indicates that not only are the three composite subspectra identical for both stages, but also the relative ratio of subspectra are the same at this temperature. The major component of these spectra, labeled site *A* in Fig. 3, exhibits the full six-line hyperfine pattern having line intensities close to the ratio 3:4:1:1:4:3. These intensity ratios indicate that the easy axis of Fe^{3+} ionic spins lies in the basal plane. This is quite different from the complicated magnetic spiral structure found in pristine anhydrous $FeCl_3$.[15] We will later present evidence which clearly indicates that this site magnetically orders. Site *B* also exhibits the full six-line hyperfine pattern, but it has line intensities close to the ratio of 3:2:1:1:2:3 indicating a three-dimensional random orientation of the iron ionic spins. The presence of the six-line hyperfine pattern will later be shown to be due to an Fe^{3+} spin-relaxation time which is long compared with the nuclear Larmor period, rather than to magnetic order. As seen from Table I, the values of the large quadrupole splitting and the large isomer shift relative to both site *A* and site *B* clearly indicate that site *C* is due to Fe^{2+} ions. In contrast to site *A*, the electronic spins are pointing parallel to the *c* axis of the graphite. All of the other spectra shown in Fig. 3 were

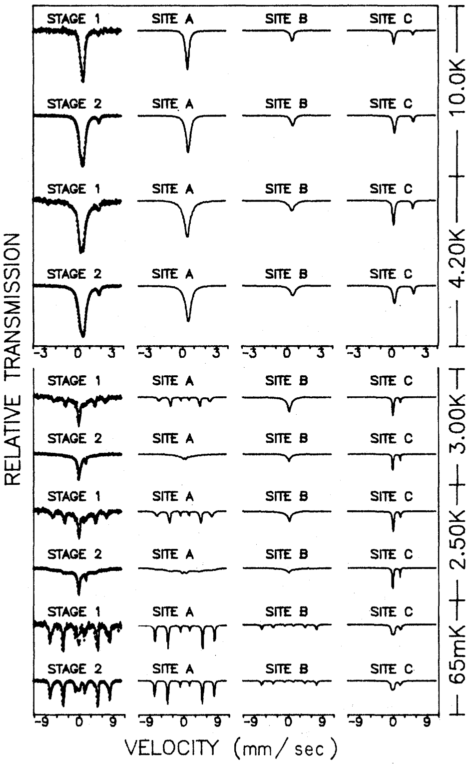

FIG. 3. The first column shows our experimental results together with the theoretical fits. In each row the remaining columns show the decomposition of the theoretical fits into their individual subspectra. The characteristics and relative ratios of the individual subspectra are tabulated in Table I. At 4.20 K and above, sites *A* and *B* are indistinguishable since magnetic order has not yet set into site *A*. Therefore, for these temperatures we have depicted the relative ratios of these sites found at 65 mK. The extra structure near zero velocity in the thin stage-1 sample is due to iron in our beryllium windows. Zero velocity corresponds to the center of gravity of an iron foil spectrum at room temperature.

TABLE I. This table lists the characteristics of the subspectra shown in Fig. 1.

		Isomer shift (mm/sec)[a]			Quadrupole interaction (mm/sec)[b]			Percent contribution		
T	Stage	Site *A*	Site *B*	Site *C*	Site *A*	Site *B*	Site *C*	Site *A*	Site *B*	Site *C*
10.0 K	1	0.56 ±0.02	c	1.21 ±0.03	≤0.26	c	−1.89 ±0.02	80 ±5	c	20 ±5
4.20 K	1	0.56 ±0.02	c	1.21 ±0.03	≤0.26	c	−1.92 ±0.02	80 ±5	c	20 ±5
3.00 K	1	0.64 ±0.02	0.56 ±0.02	1.25 ±0.04	≤0.26	≤0.26	−1.94 ±0.02	42 ±5	38 ±5	20 ±5
2.50 K	1	0.64 ±0.02	0.56 ±0.02	1.25 ±0.04	≤0.26	≤0.26	−1.95 ±0.02	51 ±5	29 ±5	20 ±5
65 mK	1	0.64 ±0.02	0.56 ±0.02	1.25 ±0.04	≤0.26	≤0.26	−2.00 ±0.02	62 ±5	18 ±5	20 ±5
10.0 K	2	0.58 ±0.02	c	1.21 ±0.03	≤0.26	c	−1.89 ±0.02	77 ±3	c	23 ±3
4.20 K	2	0.58 ±0.02	c	1.21 ±0.03	≤0.26	c	−1.92 ±0.02	77 ±3	c	23 ±3
3.00 K	2	0.66 ±0.02	0.58 ±0.02	1.25 ±0.04	≤0.26	≤0.26	−1.94 ±0.02	50 ±3	27 ±3	23 ±3
2.50 K	2	0.66 ±0.02	0.58 ±0.02	1.25 ±0.04	≤0.26	≤0.26	−1.95 ±0.02	60 ±5	22 ±5	18 ±5
65 mk	2	0.66 ±0.02	0.58 ±0.02	1.25 ±0.04	≤0.26	≤0.26	−2.00 ±0.02	62 ±3	18 ±3	20 ±3

[a] The isomer shift is measured relative to an iron foil absorber at room temperature.

[b] The quadrupole interaction is $\Delta E_Q = e^2qQ/2$.

[c] At 4.20 K and above one cannot distinguish between site *A* and site *B* since magnetic order has not, as yet, set in.

also fit assuming these three sites. The relative ratios of these three sites used in all the composite subspectra shown in Fig. 3 are also tabulated in Table I.

Due to its 3:4:1:1:4:3 ratio of peak heights observed in the 65-mK spectrum, site *A* was fitted at intermediate temperatures assuming an effective magnetic field which was constrained to flip stochastically in the basal plane. That this spin orientation is due to a magnetic phase transition can be further seen from the following evidence. The left column of Fig. 4 shows the theoretical subspectra of site *A* used to fit the spectra of the stage-1 sample at 3.00 K, 2.50 K, and 65 mK. The magnetic field, which can be measured as the spacing between outer peaks, is clearly decreasing as the temperature is raised. Quantitatively, the reduced magnetization, normalized to 493 kOe is 0.85 ±0.015, 0.90 ±0.015, and 1.00 ±0.015, at 3.00 K, 2.50 K, and 65 mK, respectively. Had this site not undergone a magnetic phase transition but had only experienced a decrease in the electronic spin flipping rate, its spectra would follow the sequence depicted in the right column of Fig. 4. Notice that the position of the peaks does not change as the flipping rate is increased, but that increasing the rate has only the effect of broadening the linewidths of the peaks. In fact, it has been shown rigorously that to first order in the relaxation rate the linewidths will increase but the line positions will remain the same.[16] The shift in peak positions coupled with the narrow lines shown in Fig. 4 clearly indicates the existence of a magnetic phase transition. We note, that recent preliminary results of magnetic susceptibility and neutron-diffraction studies[4–6] have failed to confirm this magnetic phase transition. However, despite the many sample dependent parameters cited previously, both of these measurements are macroscopic in nature. We, however, note that a very recent magnetic susceptibility experiment on well-staged and well-characterized stage-1 and -2 samples has revealed an antiferromagnetic susceptibility peak whose transition temperature occurs at about 4.3 and 1.3 K for the stage-1 and -2 compounds, respectively.[17] This result agrees quite well with the transition temperature found here by Mössbauer spectroscopy and again underscores the need for characterization in addition to the standard 00*l* x-ray diffractograms.

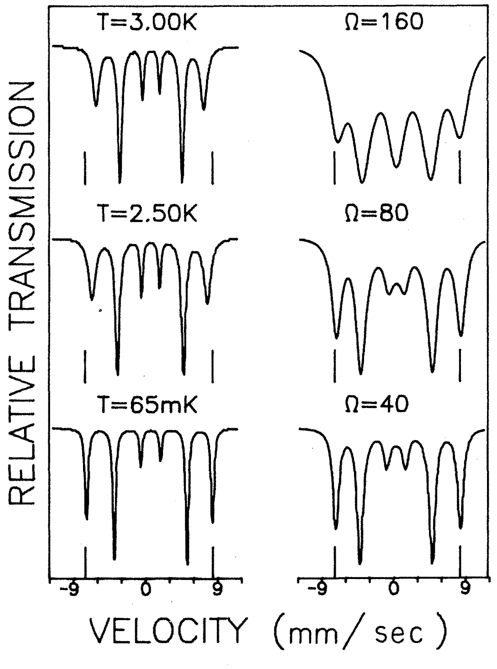

FIG. 4. The first column reproduces the site *A* subspectra for the stage-1 sample shown in Fig. 3. The second column depicts a typical spin-relaxation set of spectra with no magnetic order.

If we examine the isomer shift of site *A* tabulated in Table I, we notice for both stages that between 3.00 and 4.2 K there is a change in isomer shift of −0.08 ±0.02 mm/sec. A similar change in isomer shift has been reported for pristine anhydrous $FeCl_3$ upon magnetically ordering.[18] Furthermore, the saturation values of the hyperfine magnetic field at site *A* is 493 ±8 kOe for stage-1, and 493 ±4 kOe for stage-2. These values agree quite well with the saturation magnetic field of 495 kOe reported for pristine anhydrous $FeCl_3$ which is known to magnetically order.[19]

The magnetic transition temperature of site *A* in the stage-1 compound is found to be 4.2 ±0.5 K, in agreement with previous results.[1–3,7] Although the identity of the magnetic transition temperature of this site in the stage-2 compound is made difficult due to spin-relaxation broadening, it seems to fall within the range of 2.0 ±1.5 K. This is in rough agreement with the value of 3.6 ±0.3 K quoted by Ohhashi and Tsujikawa[1] but in disagreement with the value of 8.5 K quoted by Karimov *et al.*[7] It seems rather difficult to understand that the sequence of magnetic transition temperatures quoted by Karimov *et al.*,[7] i.e., 3.6 K for stage-1 and 8.6 K for stage-2, can be physically reasonable. Diluting a sample by adding another diamagnetic graphite plane should either decrease the magnetic transition temperature or have it remain the same. Rather, it seems that much unintercalated $FeCl_3$, which is known to magnetically order at 8.8 K,[19] or perhaps much $FeCl_2$, was present in their sample. We also note that the large similarity in both Mössbauer spectra and magnetic transition temperatures between our stage-1 spectra and both the stage-1 and -2 spectra shown by Ohhashi and Tsujikawa[1] suggests that their stage-2 sample contained some stage-1 regions. As shown in Fig. 3 there is quite a difference in Mössbauer spectra between stages 1 and 2 in the temperature interval of 4.2 to 2.5 K. In fact, a comparison of both the 3.00-

and 2.50-K spectra of the stage-1 and -2 compounds shown in Fig. 3 clearly indicates that the magnetic transition temperature in the stage-2 compound is markedly lower than that of the stage-1 compound. Since both of these samples contain the same sites and relative ratio of sites at both 10.0 K and 65 mK, we can conclude that the magnetic order found in the stage-1 sample is clearly influenced by three-dimensional interactions. The presence of three-dimensional interactions would also explain the downward trend in magnetic transition temperatures, i.e., 8.8, 4.2, and 2.0 K for pristine anhydrous $FeCl_3$, stages 1 and 2, respectively, when one adds planes of diamagnetic carbon atoms between the magnetic layers.

Although a six-line hyperfine pattern is observed at 65 mK for site *B*, it is not due to long-range magnetic order. It is rather due to a Fe^{3+} spin-relaxation time which is long compared to 10^{-9} sec which can produce a well-defined hyperfine magnetic field.[20] As opposed to site *A*, the ratio of peak heights is quite close to 3:2:1:1:2:3 indicating a three-dimensional random orientation of the iron ionic spins. Also, as opposed to site *A*, no quardrupole splitting can be measured at 65 mK but the lines have broadened. Both of these observations can be quantitatively explained as a consequence of the random orientation of the Fe^{3+} spins relative to the crystallographically fixed electric-field-gradient tensor in these layered compounds. No evidence of a change in isomer shift was observed between the 10.0 K and 65 mK spectra suggesting that a magnetically ordered phase has not yet appeared. Consistent with the absence of a magnetic phase transition, we find that the saturation hyperfine magnetic fields of 452 ±8 kOe in stage-1 and 452 ±4 kOe in stage-2 compounds are smaller than those of site *A* and pristine anhydrous $FeCl_3$.[19]

The coexistence of sites *A* and *B* was also noted by Ohhashi and Tsujikawa[1] who attributed their presence to superparamagnetism, with a distribution of spin-flopping times, for the individual clusters, which are near the Larmor period of the nucleus. However, such a distribution could not explain the two distinct six-line Fe^{3+} hyperfine patterns which we observe at 65 mK. Hohlwein *et al.*[2] also found that only a fraction of the Fe^{3+} ions are in the magnetically split pattern. In fact, an extrapolation of their fraction of the total Mössbauer absorption in the magnetically split pattern does not seem to approach unity as the temperature goes to zero in agreement with our data. No explanation was offered for this phenomenon. A possible explanation might be that site *B* is due to an admixture of high-stage or unstaged region in the primarily low-stage samples. However, a recent neutron-diffraction study[21] of an even much thicker sample grown under the same growth conditions as our samples, indicates that less than 2% of their stage-2 sample was a mixture of other stages. Also, x-ray diffractograms performed on our samples failed to find any significant amount of staging infidelity. It therefore seems unlikely that site *B* is due to an admixture of high-stage or unstaged regions. Rather, since sites *A* and *B* are identical above the magnetic transition temeprature, we believe that site *B* may be due to peripheries of magnetic domains or domain walls. This identification would also explain the temperature dependence of the relative ratio of site *A* to site *B* below the magnetic transition temperature. We, however, can offer no explanation as to why the electronic spins at site *B* would lie randomly in three dimensions while those at site *A* lie only in the basal plane.

As shown in Fig. 1, at liquid-nitrogen temperature and above there is no evidence of the Fe^{2+} component, site *C*. This is true regardless of the temperature cycling of the sample. Similar to Hohlwein *et al.*,[2] but in disagreement with others,[1,8,9] we attribute the presence of Fe^{2+} ions to electrons donated by the graphite which become trapped on about 20% of the Fe^{3+} sites at low temperatures. The isomer shift of site *C* at 10.0 K and below is the same as that reported for both anhydrous $FeCl_2$ (Ref. 22) and for graphite $FeCl_2$.[23] We find no evidence of the two different Fe^{2+} sites reported for graphite $FeCl_2$ (Ref. 23); however, our values of quadrupole splitting are considerably higher than that of anhydrous $FeCl_2$ (Ref. 22) and fall between those of the two different Fe^{2+} sites observed in graphite $FeCl_2$.[23] This suggests that the environment of site *C* is different than that of anhydrous $FeCl_2$ and graphite $FeCl_2$. This is not unreasonable considering the large amount of regular Fe^{3+} sites, about 80%, and the chemical changes brought about by the trapping process. The 3:1 ratio of peak heights in the spectra of site *C* indicates that although the direction of the major axis of the electric-field-gradient tensor is found to be parallel to the *c* axis, similar to anhydrous $FeCl_2$, its negative sign is opposite that of anhydrous $FeCl_2$.[22,24] The absence of iron sites with chlorine vacancies at both room tempeature and liquid-nitrogen temperature along with the direction of the major axis of the electric-field-gradient tensor indicates that there is formation of ($FeCl_3^-$), and not $FeCl_2$, when these Fe^{2+} sites are formed. The saturation magnetic field at site *C* is 25 ±5 kOe for both stages, and as opposed to the ionic spins of site *A*, site *C* at 65 mK can only fit by assuming that the ionic spins are pointing parallel to the *c* axis. The value of the saturation magnetic field and direction of the electronic spins are quite similar to that reported for anhydrous $FeCl_2$ (Refs. 22 and 24) and graphite $FeCl_2$.[23] The temperature dependence of these Fe^{2+} sites and their stage-dependent ratio to Fe^{3+} sites will be discussed more fully elsewhere.[12]

As stated before and shown in Fig. 1, at room temperature and liquid-nitrogen temperature the spectra can be fit quite well assuming only one Lorentzian line. This implies that little or no quadrupole splitting is experienced at the nucleus. However, at 65 mK for both stages a displacement of lines 1 and 6 relative to the inner lines by − 0.13 mm/sec is observed. The value of the quadrupole splitting is related to this displacement for small quadrupole splittings, by

$$\Delta E_Q = \frac{-(0.13)(2)}{3\cos^2\theta - 1} ,$$

where θ is the angle between the major axis of the electric-field-gradient tensor and the electronic spins. The minimum value for ΔE_Q is obtained when the major axis of the electric-field-gradient tensor is pointing along the direction of the electronic spins. If the major axis of the electric-field-gradient tensor would have been pointing perpendicular to the electronic spins, the obtained value of $\Delta E_Q = 0.26$ mm/sec would likely be discernible at higher temperatures. This quadrupole splitting, which is not observed in anhydrous $FeCl_3$ is probably induced by the Fe^{2+} ions present in the compound at low temperatures. The presence of this anisotropy field creates an easy axis of magnetization in the basal plane along which the spins at site A may point. As mentioned previously, the Fe^{2+} spins also point parallel to the major axis of the electric field gradient at the Fe^{2+} site.

V. DISCUSSION OF THE RELAXATION CALCULATION

In Table II we have listed the values of the magnetic ordering parameters and relaxation rates which were used to fit sites A and B in Fig. 3. The small saturation magnetic field observed at site C makes it impossible to do a reliable relaxation analysis of this site. The relaxation rate Ω is defined as the bare rate, i.e., the rate obtained after the Boltzmann population factors have been divided out. There is no evidence of a critical slowing down process for Ω as magnetic order sets in. We do find considerable relaxation broadening *before* the onset of magnetic order in both stages as can be seen from Table II.

The effects of the relaxation process also begin at a higher temperature in the stage-1 compound than in the stage-2 compouund. This can be clearly seen by the great similarity in the spectra of the stage-1 compound at 4.2 K and that of the stage-2 compound at 3.50 K shown in Fig. 5. Since the relaxation rate of the Fe^{3+} ions begins affecting the shape of the Mössbauer spectra above 4.2 K for both stages, the onset of relaxation precedes that of the magnetic ordering of site A for both stages. However, at both 3.00 and 2.50 K we find that although the relaxation rates are essentially stage independent, the ordering parameter is markedly lower in the stage-2 compounds, as can be seen from Fig. 3. The relaxation rates of sites A and B in the spectra of both the stage-1 and -2 compounds show a strong temperature dependence. This is surprising since spin-spin relaxation processes, which are temperature independent, usually dominate at such low temperatures. Also, the electronic configuration of the high spin Fe^{3+} ion at both sites A and B is such that the orbital angular momentum is practically absent. This would also tend to minimize any spin-lattice relaxation processes. The scarcity of data points makes any reliable estimate of the exact temperature dependence of Ω impossible. It is, however, possible that the relaxation rate is somewhat influenced by the mean-field approximation made in the relaxation model used.

TABLE II. This table lists the magnetic characteristics of the subspectra.

T	Stage	Magnetic order parameter[a] Site A	Site B	Bare flipping rate Site A	Site B
4.20 K	1	0+0.1	0	10 000 ±200	10 000 ±200
3.00 K	1	0.85 ±0.015	0	4 000 ±40	2 400 ±60
2.50 K	1	0.90 ±0.015	0	2 000 ±40	1 700 ±60
65 mK	1	1.00 ±0.015	0	b	≤20
4.20 K	2	0	0	30 000 ±200	30 000 ±200
3.00 K	2	0.25 ±0.10	0	1 067 ±40	2 400 ±60
2.50 K	2	0.40 ±0.050	0	400 ±40	800 ±60
65 mK	2	1.00 ±0.015	0	b	≤20

[a] The magnetic order parameter is defined as the ratio of the hyperfine field to the saturation hyperfine field.

[b] The flipping rate when the magnetic order parameter is unity cannot be measured using the Mössbauer effect.

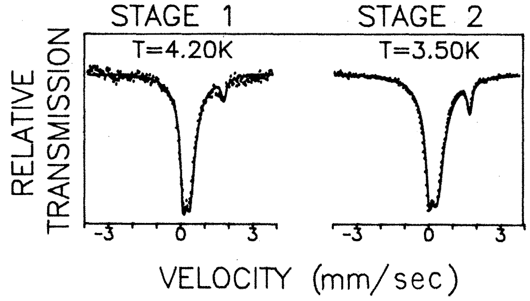

FIG. 5. The stage-1 and -2 spectra at 4.20 and 3.50 K, respectively. Notice the similarity of these spectra. Zero velocity corresponds to the center of gravity of an iron foil spectrum at room temperature.

VI. CONCLUSION

By using a stochastic mean-field relaxation model, we have completed the first fits to the broadened spectra observed about the magnetic transition temperature in low-stage ferric chloride intercalated graphite compounds. Through this analysis we have concluded that the major Fe^{3+} site in these samples undergoes a magnetic phase transition at 4.2 ±0.5 K for the stage-1 compound and 2.0 ±1.5 K for the stage-2 compound. In agreement with Hohlwein *et al.*, but in disagreement with others, we have found that thermally activated electrons, donated by the graphite lattice, are frozen onto 20 ±3% of the Fe^{3+} sites to create Fe^{2+} sites at low temperatures. These sites may also exhibit a magnetic phase transition, but the smallness of the saturation hyperfine magnetic field makes the positive identification of this transition, with Mössbauer spectroscopy alone, impossible. The electronic spins of the majority Fe^{3+} site point parallel to the basal plane while those of the Fe^{2+} site point perpendicular to the basal plane. At both sites the spins point parallel to the major axis of the electric-field-gradient tensor. We also fine a minority Fe^{3+} site which does not undergo a magnetic phase transition to as low as 65 mK. We think that this site is due to the periphery of small magnetic domains or domain walls. We also show that the magnetic order, at least in the stage-1 compound is strongly influenced by three-dimensional interactions.

ACKNOWLEDGMENTS

We are happy to acknowledge many helpful discussions with Professor George Kirczenow, Professor Gene Dresselhaus, Professor George Zimmerman, and Dr. Laurence Passell. Our deep gratitude is expressed to Dr. C. Underhill and Dr. H. Mazurek for preparing and characterizing our samples. This work was partially supported by the National Science Foundation under Grant No. DMR 77-19017.

---

[*] Present address: Physics Department, Bowdoin College, Brunswick, Me. 04011.

[†] Present address: Physics Department, Old Dominion University, Norfolk, Va. 23508.

[1] K. Ohhashi and I. Tsujikawa, J. Phys. Soc. Jpn. 36, 422 (1974).

[2] D. Hohlwein, P. W. Readman, A. Chamberod, and J. M. D. Coey, Phys. Status Solidi B 64, 305 (1974).

[3] K. Ohhashi and I. Tsujikawa, J. Phys. Soc. Jpn. 36, 980 (1974).

[4] G. O. Zimmerman, B. W. Holmes, and G. Dresselhaus, in Extended Abstracts of the 15th Biennial Conference on Carbon, University of Pennsylvania, 1981 (unpublished), p. 42.

[5] D. G. Onn, M. G. Alexander, J. J. Ritsko, and S. Flandrois, in Ref. 4, p. 44

[6] J. D. Axe, C. F. Majkrzak, L. Passell, S. K. Satija, G. Dresselhaus, and H. Mazurek in Ref. 4, p. 52.

[7] Yu. S. Karimov, A. V. Zvarykina, and Yu. N. Novikov, Fiz. Tverd. Tela (Leningrad) 13, 2836 (1971) [Sov. Phys. Solid State 13, 2388 (1972)].

[8] M. L. Dzurus and G. R. Hennig, J. Am. Chem. Soc. 79, 1051 (1957).

[9] G. K. Wertheim, P. M. Th. M. von Attekum, H. J. Guggenheim, and K. E. Clements, Solid State Commun. 33, 809 (1980).

[10] M. Blume, Phys. Rev. 174, 351 (1968).

[11] J. G. Hooley, M. W. Bartlett, B. V. Liengme, and J. R. Sams, Carbon 6, 681 (1968).

[12] S. E. Millman and G. Kirczenow (unpublished).

[13] J. M. Cowley and J. A. Ibers Acta Crystallogr. 9, 421 (1956).

[14] E. L. Evans and J. M. Thomas, J. Solid State Chem. 14, 99 (1975).

[15] J. W. Cable, M. K. Wilkinson, E. O. Woolan, and W. C. Koehler, Phys. Rev. 127, 714 (1962).

[16] M. J. Clauser, Phys. Rev. B 3, 3748 (1971).

[17] S. E. Millman, B. W. Holmes, and G. O. Zimmerman (unpublished).

[18] C. W. Kocher, Phys. Lett. 24A, 93 (1967).

[19] J. P. Stampfel, W. T. Oosterhuis, B. Window, and F. de S. Barros, Phys. Rev. B 8, 4371 (1973).

[20] F. van der Woude and A. J. Dekker, Phys. Status Solidi 9, 775 (1965).

[21] L. Passell (private communications).

[22] K. Ono, A. Ito, and T. Fujita, J. Phys. Soc. Jpn. 19, 2119 (1964).

[23] K. Ohhashi and I. Tsujikawa, J. Phys. Soc. Jpn. 37, 63 (1974).

[24] D. J. Simkin, Phys. Rev. 177, 1008 (1969).