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Low-temperature ESR and magnetic behavior of $CrCl_3$- and $NiCl_2$-based intercalation and bi-intercalation compounds

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Electron-spin-resonance (ESR) investigations have been carried out on $CrCl_3$-based graphite intercalated (GIC) and bi-intercalated (GBIC) compounds as well as on a stage-2 $NiCl_2$ graphite intercalation compound. The measurements have been performed at the *X*-band frequency and over the temperature range 4.2–294 K. In each case, the ESR spectrum displays a single line down to a temperature $T_s \sim T_{\rm pr}$, the magnetic ordering temperature of the relevant intercalant pristine form. Below T_s, the ESR spectrum becomes complex and consists of several resonance lines. The evolution of the ESR spectrum with changing temperature and angular orientation of the applied field is presented. In the single-line regime, with decreasing temperature, the resonance line always narrows at first, and then broadens rapidly as T approaches T_s. The resonance field (H_r) exhibits an anisotropic shift; however, its mean value ($Hrm = [(Hr_\parallel)(Hr_\perp)^2]^{1/3}$) does not remain temperature independent throughout the temperature range, as has been predicted for uniaxially anisotropic low-dimensional systems in the paramagnetic phase, but shows a downward trend as T gets closer to T_s. The observed ESR characteristics, and hence the magnetic behavior, are discussed in connection to the well-established islandic nature of the intercalate layer for this class of transition-metal chloride GIC's and GBIC's. The role of intraisland magnetic short-range-order and of interisland frustrated magnetic interactions is stressed.

I. INTRODUCTION

In the quest to understand low-dimensional magnetism, graphite intercalation compounds (GIC's) with magnetic species as intercalants provide an excellent system of compounds for studying the relationship between dimensionality, magnetism, and related phase-transition behavior.[1-4] The advantage that this class of materials presents is the possibility of controlling the magnetic dimensionality by varying the number of carbon layers, i.e., the stage number, which separate the consecutive magnetic planes.

Layered transition-metal chlorides, namely, $CoCl_2$, $NiCl_2$, and $MnCl_2$, have proved to be very useful as magnetic intercalants[3-5] for the in-plane crystallographic structure and magnetic interaction remain almost unchanged after intercalation, while the interplanar repeat distance is greatly increased by the presence of the intervening graphite layers, leading to a dramatic weakening of the interlayer magnetic interaction. Another important feature that this class of GIC's has is an in-plane islandic morphology, where each intercalant layer does not extend infinitely, but is divided into many islandlike two-dimensional (2D) clusters of finite size ($\sim$100–200 Å).[6,7] This unusual set of characteristics and thus the unusual interplay between them seem to be the source of the complicated nature of the magnetic phase transitions exhibited by these compounds at low temperature.[8-10]

Recently, doubly intercalated systems of graphite have been more and more the focus of attention.[11-13] These systems contain a regular sequence of two kinds of intercalant layers, and consequently they are known as graphite bi-intercalation compounds (GBIC's). In the latter the interplanar repeat distance is even greater than in the simpler GIC's, which certainly leads to an enhanced bidimensionality, the effect of which on the magnetic behavior can be explored.

Pristine transition-metal chloride $CrCl_3$ has a hexagonal layered-type crystal structure. It undergoes a magnetic phase transition below $T = 16.8$ K to an antiferromagnetic state, and similarly to $CoCl_2$ and $NiCl_2$, with the spins lying in the basal planes and forming ferromagnetic layers which alternate in direction along the c axis.[14-16] [Both $CoCl_2$ and $NiCl_2$ have also a layered crystal structure, but with a triangular planar arrangement rather than a hexagonal one (as in the case of $CrCl_3$) because of the different metal-to-chlorine ratio between the two cases.] The interplanar magnetic coupling is considerably weaker than the intraplanar one, with a ratio of $\approx \frac{1}{425}$, which is an order of magnitude smaller than in the cases of $NiCl_2$ ($\approx \frac{1}{20}$) and $CoCl_2$ ($\approx \frac{1}{13}$).[17,18] However, very little work relating to $CrCl_3$ GIC's is found in the literature, very likely because of the difficulty with which the intercalation process of $CrCl_3$ in graphite occurs.[19]

Members of our group have recently synthesized and characterized new compounds of stage-1, -2, and -3 $CrCl_3$ GIC's, as well as $CrCl_3$ $CdCl_2$, and $CrCl_3$-$MnCl_2$ GBIC's. Preliminary investigations of their magnetic properties by ac susceptibility and magnetization measurements have revealed a transition temperature T_c around 11 K.[20,21] Below T_c a large hysteresis behavior is exhibited between the zero-field-cooled and field-cooled magnetizations, as in the case of $CoCl_2$ and $NiCl_2$ GIC's.[5,22] To investigate further the magnetic behavior of these compounds, we have used the electron-spin-resonance (ESR) technique. Details of the angular and temperature dependences of

TABLE I. Estimated compositions and filling factors of intercalated layers for the compounds of the present study. T_s is the temperature below which a multiple-line regime appears in the ESR spectrum.

Compound	Composition	Filling factor (±0.05)	T_s (K)
$CrCl_3$·GIC, stage 1	$C_8CrCl_{3.3}$	0.75	18±1
$CrCl_3$ GIC, stage 2	$C_{16}CrCl_{3.3}$	0.75	18±1
$CrCl_3$ GIC, stage 3	$C_{23}CrCl_{3.3}$	0.75	17±1
$CrCl_3$-$CdCl_2$ GBIC	$C_{23}CrCl_{3.3}(CdCl_{2.2})_{2.2}$	0.75($CrCl_3$), 0.63($CdCl_2$)	18±1
$CrCl_3$-$MnCl_2$ GBIC	$C_{23}CrCl_{3.3}(MnCl_{2.2})_{2.1}$	0.75($CrCl_3$), 0.60($MnCl_2$)	19±1
$NiCl_2$ GIC, stage 2	$C_{11}NiCl_{2.1}$	0.71	42±2

the linewidth and resonance field, between room temperature and 18 K, were presented in our most recent publication,[23] where the anisotropic 2D character of these systems was clearly demonstrated. The present paper deals with the ESR behavior of these compounds principally in the low-temperature region (below 18 K). The results of this work plus reexamined ESR data from an earlier published work on stage-2 $NiCl_2$ GIC (Ref. 24) by two of the authors (S.F.) and (J.A.) suggest that the in-plane intraisland spin-spin correlation effect becomes very important far above T_c but below T_{pr}, the magnetic ordering temperature of the pristine chloride. This appears to lend support for the Rancourt model of 2D superferromagnetism, proposed to explain the magnetism of this class of chloride GIC's.[3,9,25] Furthermore, a glasslike nature of "frustrated" interisland magnetic interactions has also been conveyed.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The intercalation process of graphite to synthesize stage-1, -2, and -3 $CrCl_3$ GIC's was carried out by vapor reaction of $CrCl_3$ in a chlorine atmosphere ($T=800\,^{\circ}C$, $P_{Cl}=4$ atm). While stage-3 samples were prepared with single crystals of Madagascar natural graphite, the preparation of stage-1 and -2 samples was possible only with Kish graphite ($\phi=3$ mm). For the synthesis of the bi-intercalation compounds $CrCl_3$-$CdCl_2$ and $CrCl_3$-$MnCl_2$ GBIC's, the synthesized stage-3 $CrCl_3$ GIC (in which two graphite interlayer galleries out of three remain unoccupied) was used as a precursor and, hence, was subsequently fully intercalated with $CdCl_2$ or $MnCl_2$. All the synthesized samples were structurally characterized by $(00L)$ and precession x-ray-diffraction techniques. Further details on materials synthesis and characterization are reported elsewhere.[26] The estimated compositions and filling factors of intercalated layers are given in Table I.

The ESR measurements were performed at the X-band frequency (~ 9.3 GHz) using a field-modulated spectrometer in the temperature range between 4.2 K and room temperature. The magnetic field could be rotated (i) in a plane containing the c axis and perpendicular to the c plane, as well as (ii) in the c plane itself.

For all the investigated systems, a single Dysonian ESR line is observed down to a temperature T_s around 18 K in the case of $CrCl_3$-based compounds and around 42 K in the $NiCl_2$ GIC (Table I). The asymmetry ratio A/B is found to lie approximately between 2 and 4, lower than for pure graphite ($A/B \approx 6$). Below T_s the ESR spec-

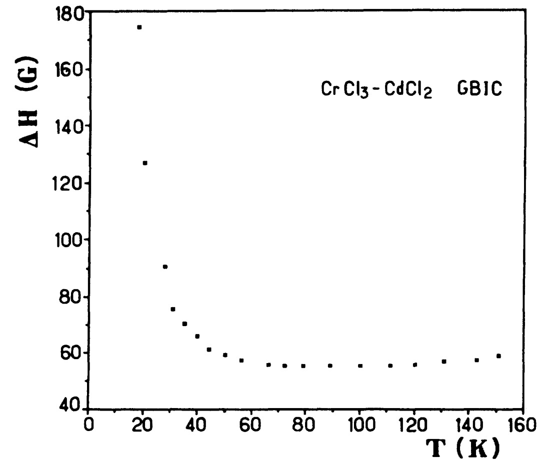

FIG. 1. Variation of the ESR linewidth with temperature in the single-line regime for the case of the $CrCl_3$-$CdCl_2$ GBIC. $H_{ap} \perp c$ ($\theta=90°$), $\nu=9.38$ GHz.

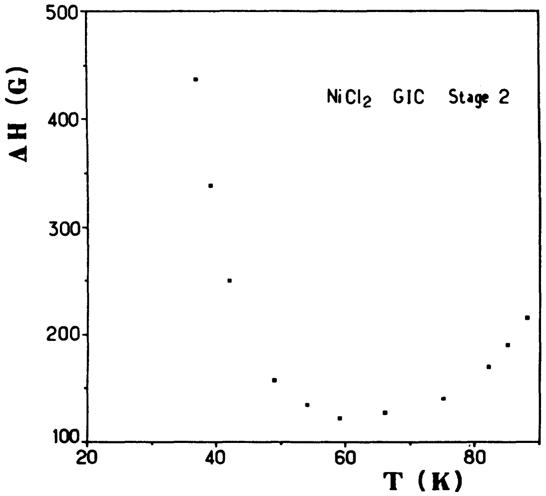

FIG. 2. Variation of the ESR linewith with temperature in the single-line regime for the case of the stage-2 $NiCl_2$ GIC. $H_{ap} \perp c$ ($\theta=90°$), $\nu=9.35$ GHz.

trum becomes complex and consists of at least two, and up to five, resonance lines, depending on the crystal considered and on its orientation with respect to the applied magnetic field. As T is lowered from room temperature, the linewidth decreases continuously, and after reaching a minimum, it increases, displaying a divergentlike behavior (Figs. 1 and 2). At the same time, the resonance field exhibits an anisotropic shift with falling temperature (Figs. 3 and 4). Fuller details and analyses of the linewidth and resonance-field dependence on temperature and orientation in the single-line regime, i.e., above T_s, have been described in earlier reports.[23,24] Our principal concern here is the behavior of the ESR spectrum below T_s.

Figures 5 and 6 illustrate the evolution of the ESR spectrum with decreasing temperature for both orientations $\theta=0°$ ($\mathbf{H}_{\rm ap}\|\mathbf{c}$) and $\theta=90°$ ($\mathbf{H}_{\rm ap}\perp\mathbf{c}$), respectively, for the case of the $CrCl_3$-$CdCl_2$ GBIC. Here θ denotes the angle formed between the c axis and the applied magnetic field ($\mathbf{H}_{\rm ap}$). Similarly, Fig. 7 illustrates the case of the $NiCl_2$ GIC for $\theta=90°$. In Fig. 8 curves (a), (b), and (c) denote the ESR spectra at 4.2 K for the $CrCl_3$-$CdCl_2$ GBIC, $CrCl_3$-$MnCl_2$ GBIC, and stage-1 $CrCl_3$ GIC, respectively, with $\mathbf{H}_{\rm ap}\|\mathbf{c}$; curve (d) is that of the $NiCl_2$ GIC at 15 K. The corresponding spectra for the case of $\mathbf{H}_{\rm ap}\perp\mathbf{c}$ are shown in Fig. 9. Figure 10 illustrates the progressive evolution of the ESR spectrum at 4.2 K as θ varies between 0° and 90° for the case of the $CrCl_3$-$CdCl_2$ GBIC. The effect of rotating $H_{\rm ap}$ in the c plane on the ESR spectrum is shown in Figs. 11 and 12 for the stage-3 $CrCl_3$ GIC, where α represents the angle formed between an arbitrary axis and $H_{\rm ap}$, all in the basal c plane.

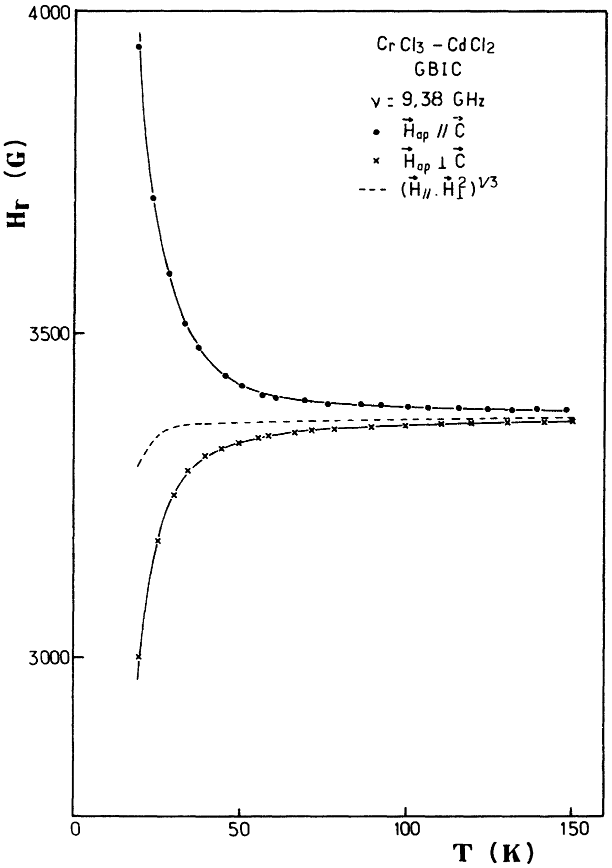

FIG. 3. Temperature dependence of the resonance field for the case of the $CrCl_3$-$CdCl_2$ GBIC. $\mathbf{H}_{\rm ap}\|\mathbf{c}$ ($\theta=0°$) (●), $\mathbf{H}_{\rm ap}\perp\mathbf{c}$ ($\theta=90°$) (×), guide to the eye (solid curve), and $H_{\rm rm}=(\mathbf{H}_{r\|}\cdot\mathbf{H}_{r\perp}^2)^{1/3}$ (dashed curve); $\mathbf{H}_{r\|}$ and $\mathbf{H}_{r\perp}$ indicate the resonance fields for applied field ($\mathbf{H}_{\rm ap}$) parallel and perpendicular to the c axis, respectively. $\nu=9.38$ GHz.

III. DISCUSSION

From the ESR results in Figs. 1–9, combined with the data presented earlier in Refs. 23 and 24, we find the low-temperature ESR behavior of this class of compounds to be characterized by the following: (i) a single resonance line which exhibits a divergentlike broadening when T approaches a certain characteristic temperature T_s from above, (ii) the appearance of several (two to five) resonance lines below T_s, which individually continue to broaden while drifting apart from one another, and (iii) T_s is dependent on the transition-metal-chloride intercalant, in such a way that T_s is always of the same order as $T_{\rm pr}$, the magnetic ordering temperature of the pristine chloride concerned. This can readily be seen by comparing Fig. 5 or 6 ($CrCl_3$-$CdCl_2$ GBIC) with Fig. 7 ($NiCl_2$ GIC). In the case of $CrCl_3$ based intercalation compounds, where $T_{\rm pr}(CrCl_3)\approx17$ K, T_s lies somewhere between 16 and 18 K, while for the $NiCl_2$ GIC, where $T_{\rm pr}(NiCl_2)\approx50$ K, T_s is somewhere in the vicinity of 42

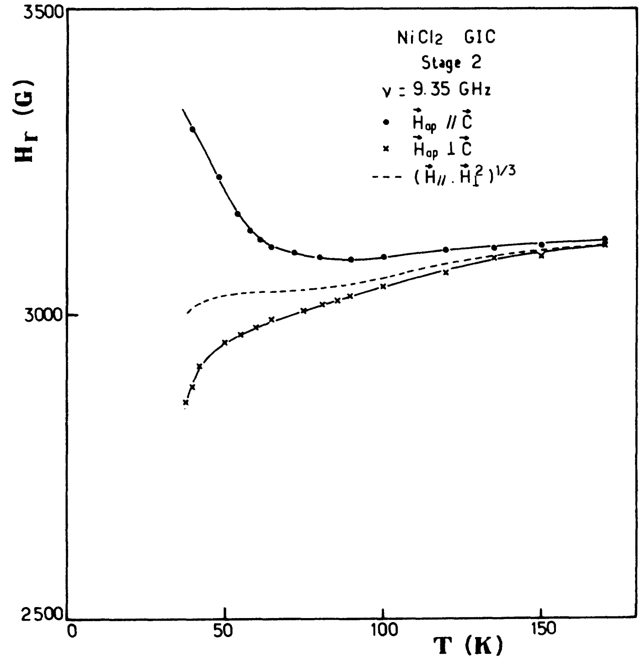

FIG. 4. Temperature dependence of the resonance field for the case of the stage-2 $NiCl_2$ GIC. $\mathbf{H}_{\rm ap}\|\mathbf{c}$ ($\theta=0°$) (●), $\mathbf{H}_{\rm ap}\perp\mathbf{c}$ ($\theta=90°$) (×), guide to the eye (solid curve), and $H_{\rm rm}=(\mathbf{H}_{r\|}\cdot\mathbf{H}_{r\perp}^2)^{1/3}$ (dashed curve). $\nu=9.35$ GHz.

K. Note that the magnetic transition temperature T_c, observed from low-field magnetic-susceptibility measurements, is around 11 K (Refs. 20, 21, and 26) for the $CrCl_3$-intercalated systems and around 18–20 K for the stage-2 $NiCl_2$ GIC.[5,27]

A. Single-line regime ($T > T_s$) versus multiple-line regime ($T < T_s$)

A divergentlike increase in the resonance linewidth generally reflects the increase in the range of static correlations between spins, as well as the thermodynamic slowing down of spin fluctuations.[28] Also, the presence of more than one resonance line in the ESR spectrum below T_s signals that the system is no longer in the usual or simple paramagnetic state. In other words, below T_s the observed ESR is not a pure, simple paramagnetic resonance, but is rather an ESR of strongly coupled or correlated spins subject to easy-plane anisotropy (xy-like spin symmetry with the basal c plane being the easy plane).[29]

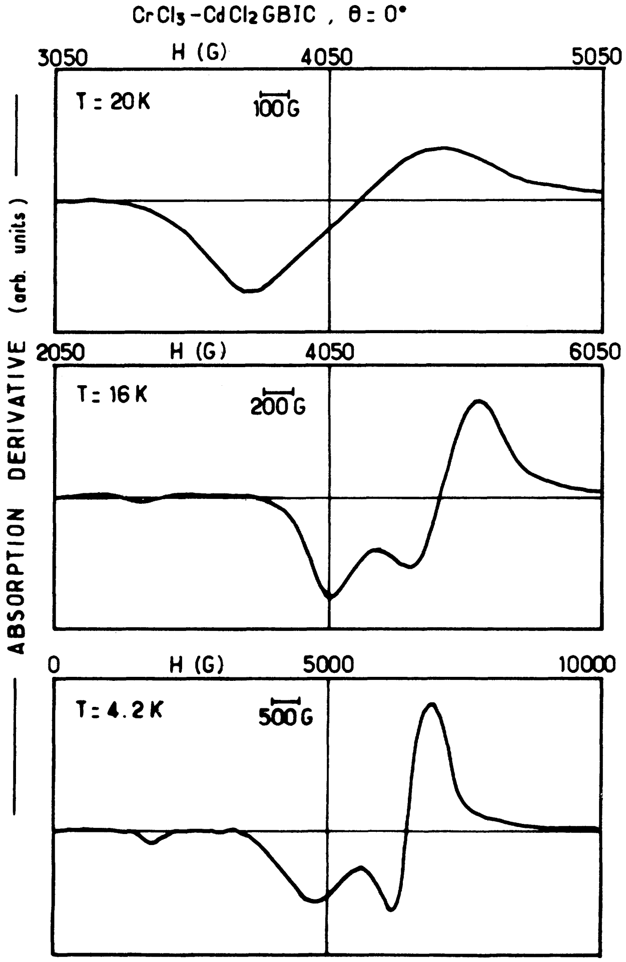

FIG. 5. ESR spectra of the $CrCl_3$-$CdCl_2$ GBIC for $\mathbf{H}_{ap} \| c$ ($\theta = 0°$) and at various temperatures, showing the passage from the single-line regime to the complex "polyline" regime below $T_s \sim 18$ K. $\nu = 9.38$ GHz.

Indeed, as Rancourt, Hun, and Flandrois have pointed out,[3,9,25] given the fact that the in-plane exchange forces in this class of intercalated-graphite systems are the same as those in the pristine materials and given the islandic structure of the intercalant layer (with an average island size ~ 150 Å), one can expect the intraisland spins to be strongly correlated at temperatures at or below T_{pr} and thus the formation of large supermoments at temperatures higher than T_c. It follows that each supermoment can be regarded as a magnetically short-range-ordered 2D cluster of spins. In fact, specific-heat data obtained by Onn *et al.* for the stage-2 $NiCl_2$ GIC (Ref. 30) have indicated that magnetic short-range order is predominant above the magnetic transition temperature T_c in this system.

In this connection we will also recall here in some detail an early but very pertinent nuclear-magnetic-resonance (NMR) study carried out by Bragin, Novikov, and Ryabchinko on the stage-2 $NiCl_2$ GIC.[31] These authors performed extensive investigations of chlorine NMR behavior in this GIC system and made the following observations.

(i) As the temperature is increased from 1.75 K, the NMR line broadens and the resonance frequency (ν_{NMR})

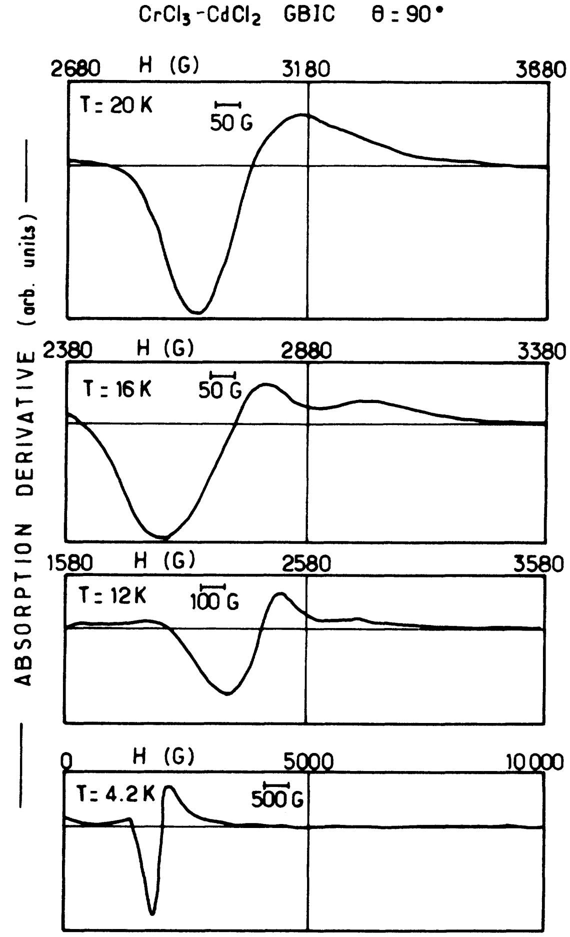

FIG. 6. Same as Fig. 5, but $\mathbf{H}_{ap} \perp c$ ($\theta = 90°$).

decreases linearly, but does not vanish, as $T \rightarrow T_c$ (~ 18 K). Above 17 K, however, the NMR line becomes too broad to be observed.

(ii) The temperature dependence of the resonance frequency, $\nu_{\mathrm{NMR}}(T)$ (reproduced here in Fig. 13), extrapolates to zero at $T \approx 50$ K, coinciding with the magnetic ordering temperature T_{pr} of pure $\mathrm{NiCl_2}$.

(iii) The existence of two nonequivalent sites for the Cl ions in the intercalated $\mathrm{NiCl_2}$ layers, which is manifested by the presence of a doublet in the NMR spectrum, is related to the existence of two slightly different values for the transferred hyperfine field (H_{TF}) acting on the chlorine nuclei, with one H_{TF} value similar to that of pure $\mathrm{NiCl_2}$ and the other somehow slightly higher.

Since ν_{NMR} in zero external magnetic field is deter-

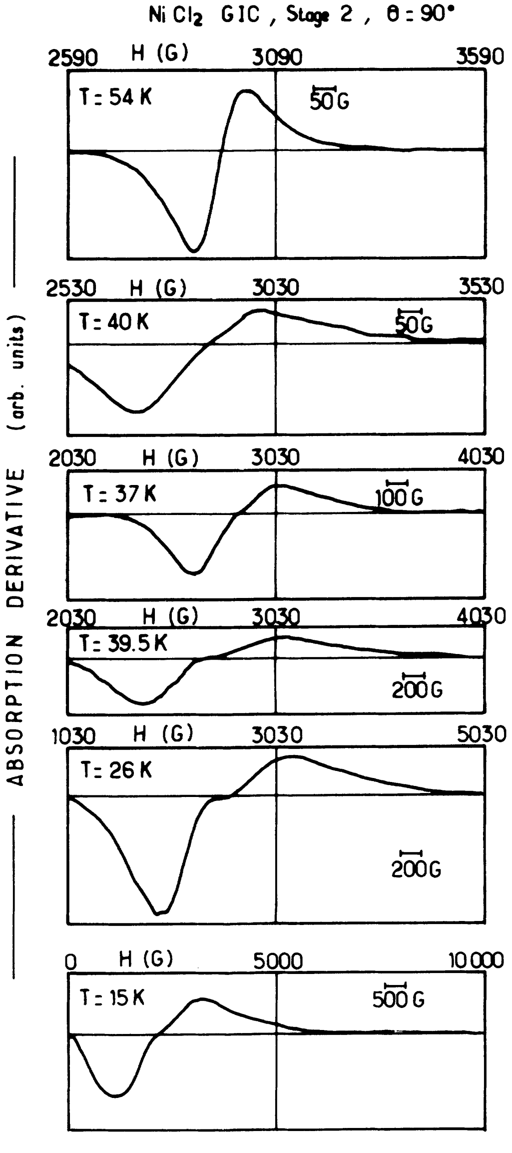

FIG. 7. ESR spectra of the stage-2 $\mathrm{NiCl_2}$ GIC for $\mathbf{H}_{\mathrm{ap}} \perp \mathbf{c}$ ($\theta = 90^\circ$) and at various temperatures, showing the passage from the single-line regime to the complex "polyline" regime below $T_s \sim 42$ K. $\nu = 9.35$ GHz.

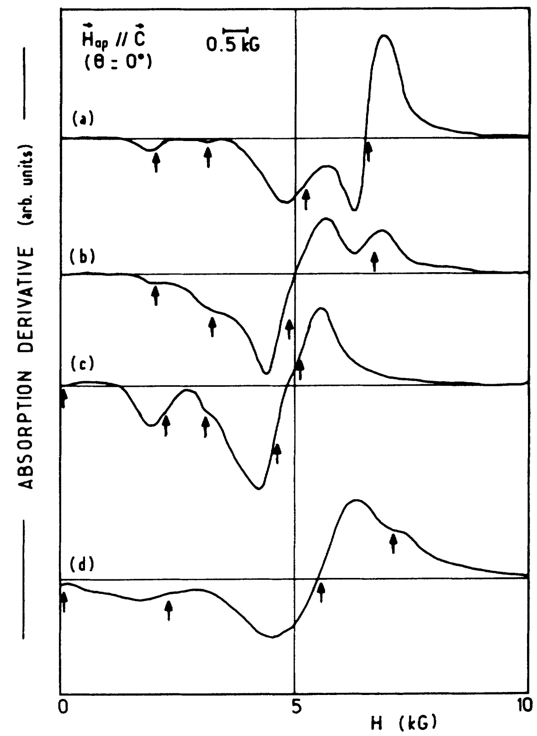

FIG. 8. ESR spectra for different investigated systems with $\mathbf{H}_{\mathrm{ap}} \parallel \mathbf{c}$ ($\theta = 0^\circ$): (a) $\mathrm{CrCl_3}$-$\mathrm{CdCl_2}$ GBIC, (b) $\mathrm{CrCl_3}$-$\mathrm{MnCl_2}$ GBIC, and (c) stage-1 $\mathrm{CrCl_3}$ GIC, all at $T = 4.2$ K; (d) stage-2 $\mathrm{NiCl_2}$ GIC at $T = 15$ K. The arrows indicate the approximate positions of the resonance fields.

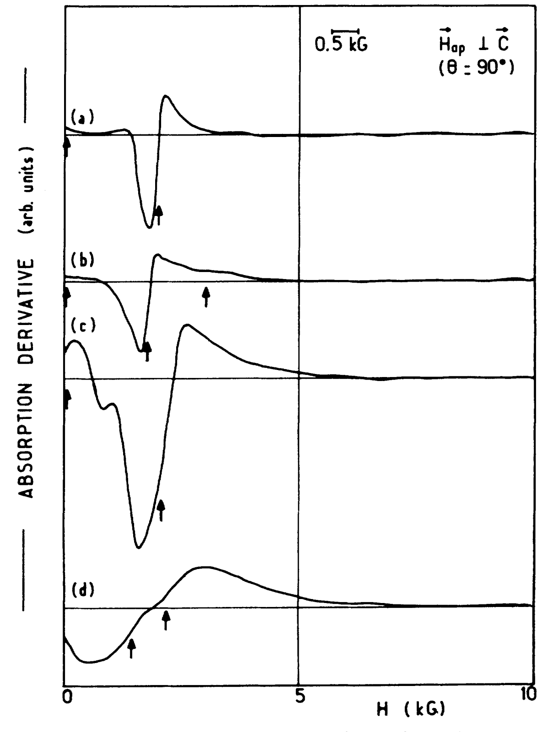

FIG. 9. ESR spectra for different investigated systems with $\mathbf{H}_{\mathrm{ap}} \perp \mathbf{c}$ ($\theta = 90^\circ$): (a) $\mathrm{CrCl_3}$-$\mathrm{CdCl_2}$ GBIC, (b) $\mathrm{CrCl_3}$-$\mathrm{MnCl_2}$ GBIC, and (c) stage-1 $\mathrm{CrCl_3}$ GIC, all at $T = 4.2$ K; (d) stage-2 $\mathrm{NiCl_2}$ GIC at $T = 11$ K. The arrows indicate the approximate positions of the resonance fields.

mined by "microscopic" spontaneous magnetization, Bragin, Novikov, and Ryabchinko have concluded that in this 2D system of the $NiCl_2$ GIC the "macroscopic" magnetization, which was measured earlier by Karimov[32] and whose appearance requires the establishment of a long-range magnetic order in the system (in this case it occurs at $T \leq 18$ K), does not correspond to the "microscopic" magnetization of the Ni^{2+} layers, which is responsible for the NMR frequency. It follows that in the "macroscopically" paramagnetic (i.e., "superparamagneticlike") region, between 18 and 50 K, there is some kind of short-range order, and thus ν_{NMR} for Cl^- will differ from zero, but the NMR line will be greatly broadened by short-range-order fluctuations and can therefore no longer be observed. (In this connection a recent Cl NMR study of the stage-1 $CoCl_2$ GIC by Tsuda, Yasuoka, and Suzuki[33] revealed a broad NMR signal at 1.4 K, which also became unobservable above 4.2 K). As far as the two nonequivalent sites observed for chlorine in this system is concerned, no satisfactory explanation for its origin has been reached by Bragin, Novikov, and Ryabchinko.

The inability of these authors to give a full account of their interesting observations stemmed from their unawareness (at the time) of the islandic nature of the intercalant layer in this class of GIC's, an intrinsic characteristic of major importance in determining these compounds' behavior.[3,4,9] Hence the short-range order observed by Bragin, Novikov, and Ryabchinko between T_c and T_{pr} is due to the island supermoments which form, independently of one another, below T_{pr} but well above T_c (the critical temperature at which the intersupermoment interactions become important enough for long-range order to take place) and which then complicate the ESR behavior as discussed above. With respect to the two different Cl sites observed in their NMR study, the fact that one site (S_1) is subjected to a H_{TF} identical to that in pristine $NiCl_2$ while the other site (S_2) is subjected to a little higher H_{TF} can also be understood in the context of the in-plane island morphology of the intercalate layer. It is believed that the S_2 site is that of those excess Cl ions which are located at the islands' periphery and which are responsible for the charge transfer from the host graphite layers. The S_1 site, on the other hand, is that of all the remaining stoichometric Cl ions located inside the islands.

In view of the picture that the spins inside the islandic 2D clusters are magnetically—or more precisely ferromagnetically—ordered at $T \leq T_{pr}$, the question which may be raised concerning the possibility of such a

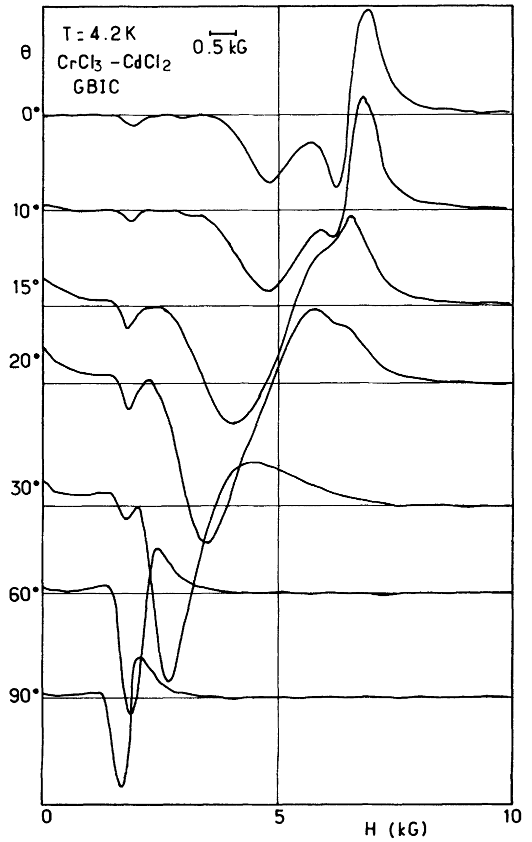

FIG. 10. Representative example of the ESR spectrum evolution when θ, the angle between the applied field (H_{ap}) and c axis, is varied between 0° and 90°. This represents the case of the $CrCl_3$-$CdCl_2$ GBIC at 4.2 K.

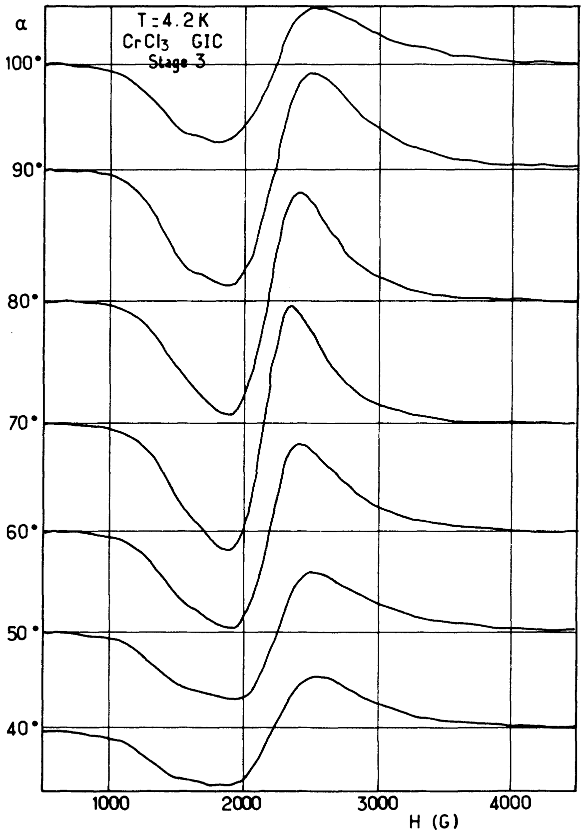

FIG. 11. ESR spectrum variation when the applied field is rotated in basal c plane. α represents the angle formed between H_{ap} and an arbitrary axis in the basal c plane. α is varied for a 60° span with steps of 10°. This represents the case of the stage-3 $CrCl_3$ GIC at 4.2 K.

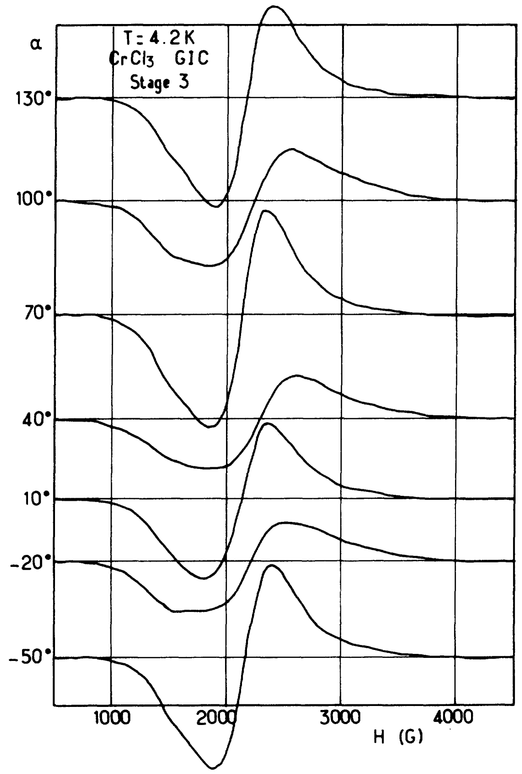

FIG. 12. Same as Fig. 11, but α is varied for a 180° span with steps of 30°. Note the 60° periodicity.

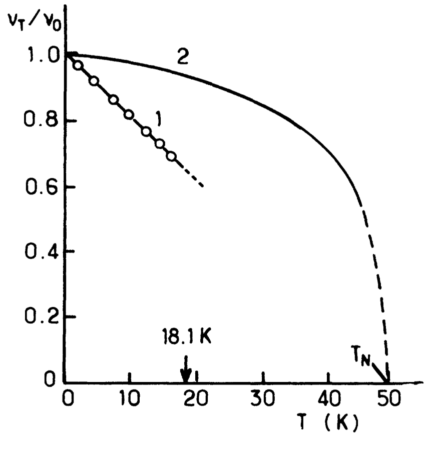

FIG. 13. Temperature dependence of chlorine NMR resonance frequency [from Bragin, Novikov, and Ryabchinko (Ref. 31)]: (1) stage-2 $NiCl_2$ GIC, 18.1 K$=T_c$; (2) pristine $NiCl_2$, $T_N=T_{pr}\approx 50$ K.

2D order taking place in the present systems is pertinent. To answer this question we will refer to a relevant work carried out by Kuhlow on pristine $CrCl_3$.[15] This author performed detailed investigations of magnetic ordering in single-crystal $CrCl_3$ at the phase transition temperature zone by measuring the specific Faraday rotation (β) (which is directly related to magnetization) as a function of temperature (T) and applied magnetic field (H) and made the following observations.

(i) Each of the $(\beta \text{ vs } T)_H$ curves exhibits two characteristic temperatures T_1 and T_2 ($T_1 > T_2$), the former corresponding to an inflection point and the latter to a maximum.

(ii) Between T_1 and T_2 these curves display a temperature and field dependence typical of ferromagnetic materials, while below T_2 the curves show a decline typical of antiferromagnetic materials.

(iii) Being field independent, T_1 is found to have the same value of 16.8 K for all the $(\beta \text{ vs } T)_H$ curves. On the other hand, extrapolating T_2 to the zero-applied-field limit yields a value for T_2 of 15.5 K.

(iv) $T_1=16.8$ K coincides with the specific-heat anomaly temperature observed earlier by Kostryokova and Lukyanova.[34] $T_2=15.5$ K, on the other hand, coincides with the temperature of the magnetic susceptibility maximum measured by Bizette, Terrier, and Adam.[35]

These and other observations led Kuhlow to the conclusion that, below the transition temperature $T_1=16.8$ K, the $CrCl_3$ layers in the pristine crystal first reach a *two-dimensional* ferromagnetic ordering, with the "ferromagnetic single-layer domains" having a random distribution along the c axis, as a result of the thermal agitation which overcomes the weak interlayer magnetic interaction. Then, with decreasing temperature, the magnetization in the layers increases, until $T_2=15.5$ K is reached, i.e., the temperature at which the antiferromagnetic (AF) coupling between the layers becomes strong enough and a 3D AF order appears; hence the net magnetization decreases. In this connection it should be noted that, in the case of pristine $NiCl_2$, two characteristic or critical temperatures have also been reported at the magnetic phase-transition zone, $T_1=52.4$ K, associated with the specific-heat anomaly,[36] and a lower temperature $T_2=49.6$ K associated with the magnetic-susceptibility maximum[37] (also with the ESR linewidth maximum[38]). Consequently, some authors refer to T_1 as the Néel temperature for $NiCl_2$,[39] while others refer to T_2.[40] In view of the above observation and of the similarity between the physical properties exhibited by these two transition-metal chlorides $NiCl_2$ and $CrCl_3$, we believe that the magnetic ordering in pristine $NiCl_2$ occurs in the same sequence as described above for $CrCl_3$.

B. Multiple-line regime ($T < T_s$) ESR behavior

Returning now to the ESR behavior for temperatures far below T_s (or T_{pr}), we find in Figs. 8 and 9 (orientations $\theta=0°$ and 90°, respectively) that there exists a general similarity in various features of the ESR spectra belonging to the different compounds, notably in the number, sequencing, and width of the resonance lines, as well as, in many instances, in the position of the lines (i.e., the resonance field). Note that spectra (a), (b), and (c) in both Figs. 8 and 9 are for different $CrCl_3$-based intercalation compounds, while spectra (d) are for the $NiCl_2$ GIC. The latter, in turn, are very similar to the spectra obtained by Suzuki, Murata, and Suematsu,[41] which are shown here in Fig. 14 for the sake of comparison. Figure 10 illustrates how the "polyline" ESR spectrum evolves when θ

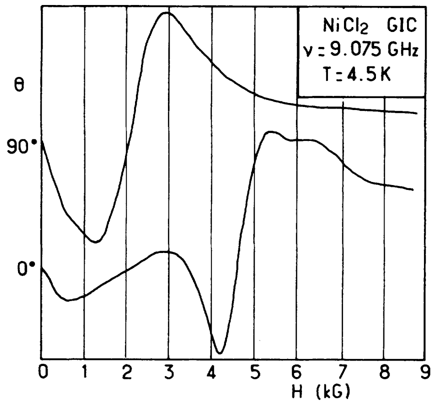

FIG. 14. ESR spectra of the stage-2 $NiCl_2$ GIC, obtained by Suzuki, Murata, and Suematsu (Ref. 41), at $T = 4.5$ K, for both angular orientations $\theta = 0°$ and 90°. Compare with our results in Figs. 7–9.

is varied from 0° to 90°. As can be seen, most of the change and shift (toward lower fields) occurs in the range between 0° and 30°; above the latter all the lines collapse into one or sometimes two lines. At the same time, a resonance or absorption behavior appears in the zero- or near-zero-field region, as soon as θ becomes different from zero. In the configuration $\theta = 90°$ (i.e., the applied field parallel to the basal c plane), the ESR behavior exhibits a small, but clearly seen, 60° periodic angular dependence when H_{ap} is rotated in the basal c plane. This periodicity, illustrated in Figs. 11 and 12, reflects the system's in-plane hexagonal symmetry. A 60° periodic angular dependence has also been reported for the pristine chlorides $NiCl_2$ (Ref. 42) and $MnCl_2$ (Ref. 43) at temperatures below their respective magnetic ordering temperature. This probability means that the latter behavior is characteristic of the chloride planes themselves, regardless of whether they are in the pristine or intercalated form. Furthermore, it confirms earlier observations on $NiCl_2$, $MnCl_2$ (Ref. 6), and $CrCl_3$ GIC's (Refs. 5, 19–21, and 23–26) that, although there is a translational disorder between the intercalant metal-chloride 2D lattice and that of the graphite host (as a result of the uncommensurability of the two lattices), the relative orientation of both lattices (one with respect to the other) is fixed.

C. Frustration and spin-glass-like behavior

The behavior of the resonance field (H_r) vs temperature (T) in the single-line regime (Fig. 3) is, as shown in our previous report,[23] typical for all the $CrCl_3$-based intercalated compounds. With falling T, this behavior is characterized by a continuous increase or decrease in H_r depending on whether the applied field (H_{ap}) is parallel or perpendicular to the c axis, respectively. Meanwhile, the resonance-field mean value, defined by $H_{rm} = [(H_{r\parallel})(H_{r\perp})^2]^{1/3}$, remains temperature independent (starting from the high-T limit) for most of the temperature range, but then it displays a downward deviation as T starts to approach T_s. The temperature-independent behavior of H_{rm} is well understood for low-dimensional and uniaxially anisotropic Heisenberg systems in the paramagnetic state.[44] The downward deviation, on the other hand, has been interpreted as resulting from a crossover of the spin symmetry (in the 2D intercalate islands) from 2D Heisenberg-like to 2D XY-like behavior.[23,45,46] This amounts to an intraislandic effect. However, one cannot ignore or disregard other effects and mechanisms which can cause or contribute to such a downward shift of H_{rm}. In fact, it has been shown theoretically by Nagata[47] that magnetic randomness or disorder and associated frustration (i.e., spin-glass-like effects) do lead to a downward shift of H_{rm}. The main element of Nagata's theory is the nonuniform internal field which exist in such system. Experimentally, this type of ESR behavior has been observed earlier in canonical spin glasses[48] and, more recently, in the (more relevant to us) randomly mixed two-dimensional Heisenberg system $K_2Cu_xMn_{1-x}F_4$ by Yamada, Nagano, and Shimoda.[49] The latter system contains competing in-plane ferromagnetic and antiferromagnetic exchange interactions, and hence there arises frustration. Their H_r-vs-T results for relatively high x values, e.g., $x = 0.84$, reproduced here in Fig. 15, show trends similar to our results for the $CrCl_3$-based intercalated compounds (Fig. 3). Yamada, Nagano, and Shimoda have interpreted the H_{rm} downward shift observed in their case as due to the inhomogeneous internal field caused by frustration, in accordance with Nagata's theory. For lower x values, $x = 0.62$, for instance, $H_{r\parallel}$ shows a little different behavior: It slightly decreases at first with T and then it increases with further lowering of temperature (see Fig. 16), while $H_{r\perp}$ shifts downward all the time. The resulting stronger downward trend of H_{rm}, observed in this case, can be attributed to increased frustration effect arising from the higher degree of disorder associated with lower x (i.e., higher degree of random mixing between Cu and Mn). The behavior of our H_r-vs-T results for the $NiCl_2$ GIC (shown in Fig. 4) carries a remarkable resemblance

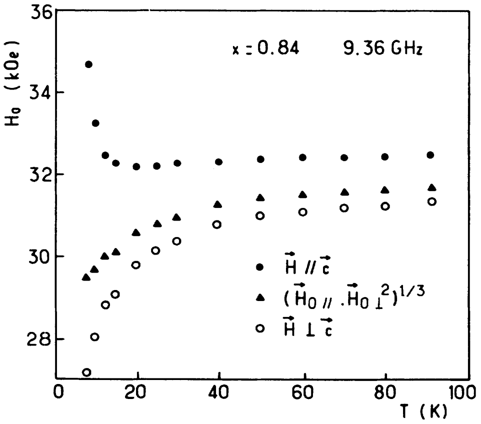

FIG. 15. ESR resonance fields $H_{0\parallel}, H_{0\perp}$ and their mean value $(H_{0\parallel} \cdot H_{0\perp}^2)^{1/3}$ vs temperature for $K_2Cu_xMn_{1-x}F_4$ with $x = 0.84$ [results of Yamada, Nagano, and Shimada (Ref. 49)]. Compare with Fig. 3.

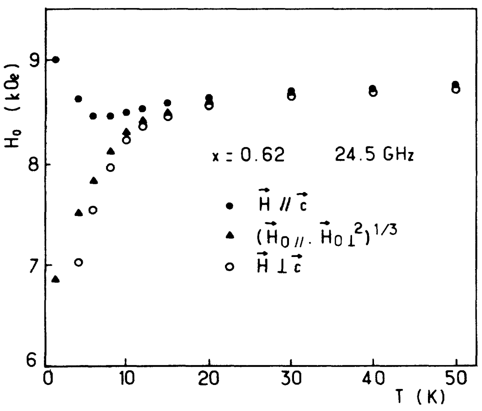

FIG. 16. ESR resonance fields $\mathbf{H}_{0\parallel}, \mathbf{H}_{0\perp}$ and their mean value $(\mathbf{H}_{0\parallel} \cdot \mathbf{H}_{0\perp}^2)^{1/3}$ vs temperature for $K_2Cu_xMn_{1-x}F_4$ with $x = 0.62$ [results of Yamada, Nagano, and Shimoda (Ref. 49)]. Compare with Fig. 4.

to that of the $K_2Cu_xMn_{1-x}F_4$ of Yamada, Nagano, and Shimoda with $x = 0.62$, reproduced in Fig. 16.

In view of these observations, our ESR H_r-vs-T results point toward the existence of a nonuniform internal field and associated magnetic frustration in the present class of graphite intercalation and bi-intercalation compounds. The presence of such frustration effect may be explained by considering the following facts and arguments.

(i) There exists intrinsic in-plane structural randomness which originates from the intercalate's islandic (as well as Daumas-Herold domain) morphology and which can lead to magnetically weak zones in the interface regions between the individual spin islands in the plane.[3,4,9]

(ii) In pristine $NiCl_2$, while the in-plane nearest-neighbor exchange constant J_{1n} is ferromagnetic with a value of $\approx +22$ K, the in-plane next-nearest-neighbor exchange constant J_{2n} is antiferromagnetic and non-negligible with respect to $J_{1n}, J_{2n} \approx -5$ K.[17] Furthermore, Regnault *et al.*[50] have shown that in pristine $NiBr_2$, an isomorph of $NiCl_2$, the in-plane third-nearest-neighbor exchange constant J_{3n} is ≈ -5 K with the ratio $J_{3n}/J_{1n} \approx -0.3$, and hence the effect of J_{3n} must be taken into consideration. On the grounds of the "isomorphicity" between the two halides $NiBr_2$ and $NiCl_2$, Regnault *et al.* have argued that further spin-wave investigations are needed to verify whether the general assumption that J_{3n} in $NiCl_2$ is negligible with respect to J_{1n} is indeed valid or not. No detailed information concerning J_{2n} and J_{3n} are available to us for pristine $CrCl_3$; however, on the basis of the preceding arguments and observations, it would not be unexpected if J_{2n} and/or J_{3n} are found to be antiferromagnetic and non-negligible vis-à-vis J_{1n} [ferromagnetic, $\approx +5$ K (Refs. 14 and 15)]. In the intercalated system, broken exchange bonds or pathways are certainly present at the periphery of, and at the interface between, the intercalate islands, that is to say, in the magnetically weak or magnetically-diluted-like regions. (Matsuura *et al.*[51] have evoked a similar notion of an interisland "interface effect." This, according to them, results from an indirect interaction through the intermediary fragments of islands of much smaller size scattered among the main islands. A computer-simulation study on intercalation and stage transformation kinetics by Kirczenow[52] appears in support of such a speculation.) This, coupled with the fact that $J_{1n} > 0$ (F) and J_{2n} and/or $J_{3n} < 0$ (AF), can lead to a competition of positive and negative interactions and thus to *interisland* magnetic frustration. It is useful here to evoke an analogy to the insulating dilute magnetic spin-glass system $Eu_xSr_{1-x}S$, where the frustration effect arises similarly from the competition between the nearest-neighbor ferromagnetic ($J_1 > 0$) exchange interaction and the next-nearest-neighbor antiferromagnetic ($J_2 < 0$) exchange interaction, with $J_2/J_1 \approx -0.5$.[53–55] Moreover, the spin-glass phase in the latter system is seen as a collection of mostly ferromagnetic spin clusters which interact via frustrated antiferromagnetic exchange bonds and also, possibly, magnetic dipolar forces.

(iii) There is an absence of interplanar structural correlation between the finite-size intercalate islands[6,56] and increasing evidence that the small interplanar magnetic interaction is principally classical dipolar in nature.[13,57,58] In fact, Rancourt *et al.* have recently discussed the role of the interplanar (as well as the intraplanar) classical dipole-dipole forces as a possible source of magnetic frustration and spin-glass behavior in this class of graphite intercalation systems.[57]

It is important to note that our ESR results are not the only observations which suggest spin-glass-like behavior in this type of GIC's and GBIC's; through various experimental observations, other spin-glass-like effects have been exhibited by this class of $CoCl_2$-, $NiCl_2$-, and $CrCl_3$-based graphite intercalated and bi-intercalated compounds, at temperatures near and below their respective transition temperature T_c. These are as follows.

(i) A hysteretic spin-glass-like cusp in the temperature dependence of the low-field dc magnetic susceptibility.[13,57,59]

(ii) A logarithmic time dependence of the magnetization relaxation behavior.[4,12,60] Spin-glass systems are well known to exhibit such a behavior.[54,61]

(iii) Characteristic memory phenomena of the magnetization,[4,12,60] which appear during a series of heating and cooling runs, a behavior inherent in a spin-glass system below its "freezing" temperature T_g.[62]

(iv) The complex ac susceptibility $\chi^*(\omega)$ behavior at very low frequencies: Below T_c, the dispersion part χ' starts to depend on ω, and the absorption part χ'' appears but remains nearly frequency independent throughout all its temperature variation.[4,51,60] This latter feature of χ'' (i.e., its ω independency) indicates, according to the fluctuation-dissipation theorem, the nonlinear slow $1/\omega$ nature of the magnetic fluctuations.[51,63,64] This behavior is generally observed in random or disordered systems, namely, spin glasses,[63,64] and has been predicted to be related to the logarithmic-with-time relaxation of the magnetization, mentioned above. Matsuura *et al.*[51] have discussed the origin of this $1/\omega$-type fluctuation behavior of the intercalated compounds, indicating that it is due to a complicated distribution of the interisland interactions.

(v) Recent and detailed neutron-diffraction investigations on stage-2 $CoCl_2$ and $NiCl_2$ (GIC's) (Ref. 65) have revealed evidence of spin disorder. Furthermore, very recent neutron-diffraction experiments on the stage-3 $CrCl_3$ GIC) (Ref. 26) have shown no reflection lines due to magnetic order, down to ≈ 2 K.

(vi) Last, specific-heat measurements on the $NiCl_2$ GIC (Ref. 30) have shown the magnetic contribution to be linearly temperature dependent, a behavior usually expected of spin-glass or cluster-glass-like systems.[54,55]

IV. CONCLUSION

This ESR study on $CrCl_3$-based graphite intercalation and bi-intercalation compounds, as well as on the stage-2 $NiCl_2$ graphite intercalation compound, has revealed very useful and complementary information on the magnetic behavior of this class of materials. The observed behavior of the ESR spectrum which becomes complex below a temperature $T_s \approx T_{\rm pr}$—the magnetic ordering temperature of the intercalant's pristine form—in conjunction with earlier obtained NMR (Ref. 31) and specific-heat[30] data, indicate that the in-plane intraislandic spins become very strongly correlated (there is magnetic short-range ordering and resulting supermoment formation) and subject to easy-plane anisotropy (XY-like spin symmetry), far above T_c—the magnetic transition temperature of the intercalated system—but below $T_{\rm pr}$. The similarity in the general conduct of the low-temperature ESR observed for the various investigated compounds may very well mean that the same physical mechanisms are at the origin of the magnetic behavior of all these systems. The main features of this behavior show very little dependence (i) on the intercalant identity $CrCl_3$ or $NiCl_2$ and (ii) on the interplanar spacing between the magnetic layers; hence they seem to be determined principally by the in-plane characteristics and interactions. This observation is in agreement with the outcome of a recent magnetic-susceptibility study on the bi-intercalation system $CrCl_3$-$NiCl_2$ GBIC.[13] The downward shift of the resonance-field mean value $H_{\rm rm}$ observed as T approaches T_s, with decreasing temperature, is thought to arise from two contributions: (1) an intraisland effect where there is a crossover of the spin symmetry from 2D Heisenberg-like to 2D XY-like and (2) an interisland effect associated with frustrated magnetic interactions in the magnetically weak regions at the islands' peripheries and in the interface zones between them.

Thus the emerging picture is that, below $T_{\rm pr}$, in this class of acceptor graphite-intercalated compounds, there are a strong intraislandic interspin interaction with an XY-type anisotropy and a complicated interisland interaction of a glasslike nature. Finally, given the close similarity in behavior between the $NiCl_2$ and $CoCl_2$ GIC, the physical picture resulting from this study is believed also to apply to the $CoCl_2$-based graphite intercalated systems.

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