

Phase transition in AlCl_3 -graphite as seen by the thermal hysteresis in the conduction-carrier spin resonance

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A phase transition at 168 K has been recognized from the thermal hysteresis of the conduction-carrier spin-resonance parameters in the stage-7 acceptor AlCl_3 -graphite intercalated compound (GIC). Below the transition temperature, the final low-temperature in-plane residual resistivity of the sample was found to be dependent on its previous thermal history. Paradoxically, quenching effects, contrary to previous reports on low-stage acceptor GIC's, leave the system in an "orderedlike" state of higher in-plane conductivity.

We report the first observation of a thermal hysteresis in the linewidth and intensity of the conduction-carrier spin resonance (CCSR) which reveals a phase transition at 168 K in the stage-7 acceptor AlCl_3 -graphite intercalated compound (AlCl_3 -GIC7). To the best of our knowledge this is the first report on a high-stage acceptor GIC with a phase transition where the in-plane residual resistivity can be changed by an appropriate thermal treatment of the sample below the transition temperature. In particular, a quenching (~ 400 K/min) from room temperature to $T < T_c$ leaves the system in a state of higher in-plane conductivity, contrary with what is normally observed in low-stage acceptor GIC's, where quenching effects leave the system in states of lower in-plane conductivity.¹

Pure-stage AlCl_3 -GIC7 was obtained from highly oriented pyrolytic graphites (HOPG) (typical dimensions $3 \times 8 \times 0.1$ mm³) by the conventional zone-growth technique.² In order to avoid any sample deterioration during the CCSR and x-ray measurements, the sample was kept in the same sealed tube where intercalation was processed. The stage of the sample was determined by measuring the (001) x-ray diffraction pattern obtained from a θ - 2θ scan using molybdenum $K\alpha$ radiation.

CCSR experiments were carried out in a conventional X-band reflection spectrometer: A standard TE_{102} (100 kHz) room-temperature cavity was adapted to a cold nitrogen gas flux system allowing measurements between 100 and 280 K. The sample was placed into the cavity with the microwave magnetic field parallel to the a plane. For this geometry the microwaves propagate in the c -axis direction and the skin depth is governed by the in-plane resistivity $\rho_a(T)$. In order to minimize contributions from magnetoresistance effects to the in-plane resistivity and to the diffusion time which can mask the temperature dependence of the latter two parameters,³ we shall be mainly concerned with the data obtained for the external magnetic field perpendicular to the c axis, where these contributions are expected to be negligible.³

Figure 1(a) shows a typical room-temperature CCSR spectrum which was found to be isotropic as far as the linewidth and field at resonance are concerned. Therefore, Dyson's line-shape analysis⁴ for motionally narrowed CCSR can be applied to our experimental CCSR spectra in order to determine the resonance parameters. The isotropic g value (2.0040 ± 0.0005) was found to be temperature independent between 100 and 280 K.

Figure 2 shows the temperature dependence of the linewidth. Above 180 K the measured linewidth is totally reversible during the process of cooling and heating of the sample. Below 170 K small differences in the final low-temperature linewidth are obtained, which depend upon the

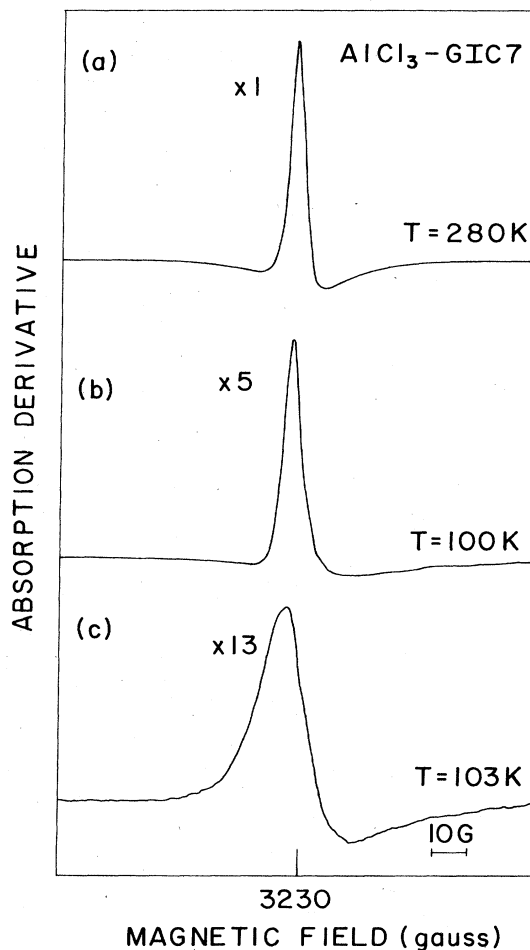


FIG. 1. CCSR spectra of AlCl_3 -GIC7 at (a) room temperature, (b) $T = 100$ K after a fast cooling corresponding to curve a in Fig. 2, and (c) $T = 103$ K after the low-temperature thermal treatment corresponding to curve d in Fig. 2.

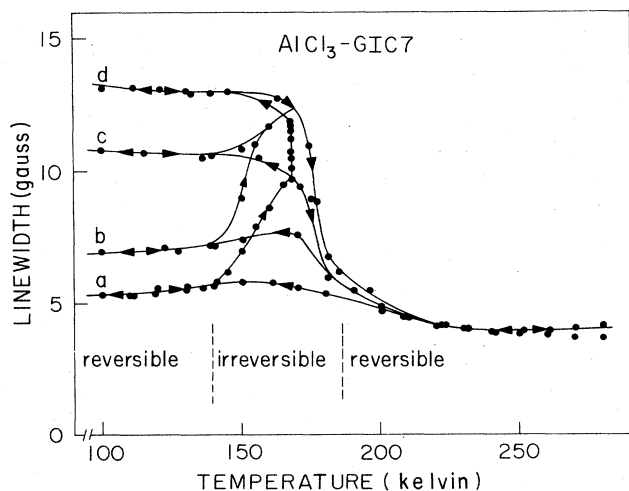


FIG. 2. Temperature dependence of the CCSR linewidth in $\text{AlCl}_3\text{-GIC7}$. Curves *a*, *b*, *c*, and *d* correspond to different thermal treatments of the sample (see text).

cooling rate. Curves *a* and *b* in Fig. 2 correspond to fast (5 min per data point, ~ 3 K/min) and slow (30 min per data point, ~ 0.3 K/min) cooling rates, respectively. If during the process of slow cooling we stop at any temperature between 150 and 170 K, no appreciable increase of the linewidth is observed after a few hours. Also, if we stop during the fast cooling, or even after a quenching, at any temperature within this interval, the linewidth grows slowly from values on curve *a* to those on curve *b*, in about half an hour, without any further detectable increase after a few hours. The linewidths obtained after quenching are about 10% lower than those values shown by curve *a*. Both curves *a* and *b* are reversible between 100 and 140 K, but on heating the sample beyond 140 K the linewidth broadens much faster than during the cooling process, evidencing the irreversibility of this parameter in the region between 140 and 175 K. Heating the sample at the same rate as in the cooling process produces a linewidth maximum at 168 K. Smaller and larger maxima are found for the fast and slow heating rates, respectively. Also, if during the fast heating process we stop at the temperature of 168 K it is observed that in at most half an hour the linewidth grows until it reaches the same maximum value obtained during the slow heating process, revealing a much faster kinetics for the heating than for the cooling process below the transition temperature; i.e., the system is "memorizing" its previous thermal history. In both cases, as soon as the temperature increases above 175 K one observes a very fast narrowing of the linewidth which results in the reversible high-temperature region described above. This thermal hysteresis cycle can be repeated indefinitely without any appreciable difference from cycle to cycle.

In the irreversible region between 140 and 175 K the following striking behavior is observed: If during the heating process, independently of the heating rate (curves *a* or *b*), the process is interrupted and the sample starts to be cooled down from any temperature within this interval, the resonance linewidth will still show a small broadening until the temperature gets close to 140 K, where the linewidth then remains constant down to 100 K (see curve *c*). Now if the

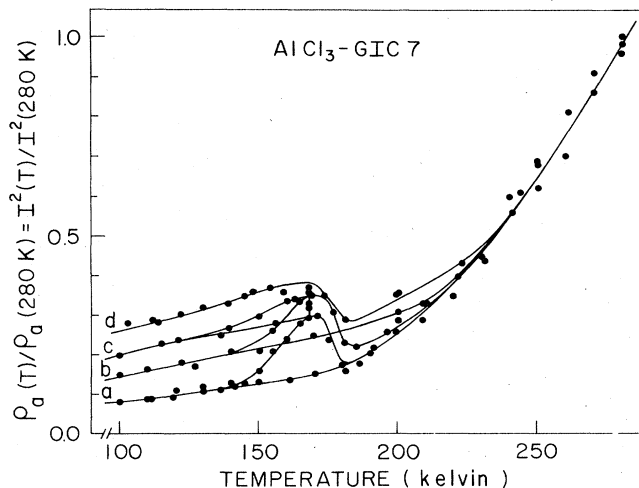


FIG. 3. Temperature dependence of the relative in-plane resistivity obtained from the temperature dependence of the square of the relative CCSR intensity in $\text{AlCl}_3\text{-GIC7}$.

temperature is raised, a reversible region is again observed up to 140 K. Above this temperature the irreversible region, where the linewidth broadens quickly, is once more observed. If enough time (no more than half an hour) elapses at any temperature within the irreversible region approached from the low-temperature side, the linewidth will always reach its final maximum value of about 13.5 G. Once this value is reached the linewidth does not show any appreciable temperature dependence (curve *d*) unless the temperature is raised above 175 K, where the linewidth will experience the narrowing transformation into the reversible high-temperature region.

Figures 3 and 4 show, respectively, the measured temperature dependence of the square of the relative resonance intensity and the diffusion time corresponding to the experimental points in Fig. 2. Features similar to those found for the linewidth are also observed for the temperature depen-

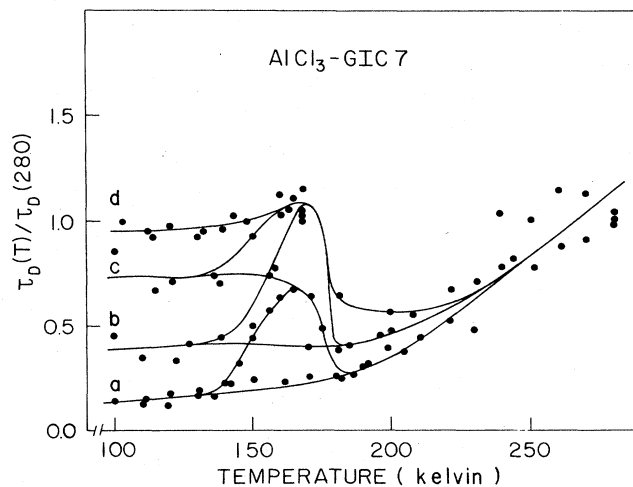


FIG. 4. Temperature dependence of the conduction carrier diffusion time τ_D in $\text{AlCl}_3\text{-GIC7}$.

dence of these two parameters as far as reversibility, irreversibility, and hysteresis are concerned. Figures 1(a), 1(b), and 1(c) show, respectively, the observed CCSR spectra at room temperature and at 100 K before and after the thermal treatment corresponding to curves *a* and *d* in Fig. 2.

Assuming that the linewidth of the CCSR spectra is mainly due to spin-lattice relaxation through a phonon scattering via conduction-carrier spin-orbit coupling, Elliot's theory⁵ shows that for temperatures below the Debye temperature ($200 \text{ K} < \theta_D < 400 \text{ K}$ for GIC's) the CCSR linewidth can be written as³

$$\Delta H = \frac{(\Delta g)^2 \theta_D^3}{\gamma m^* \mu(T) T^2}, \quad (1)$$

where Δg is the *g*-shifting relative to the free-electron *g* value ($g_e = 2.0023$), θ_D the Debye temperature, γ the electronic gyromagnetic ratio, m^* the carrier's effective mass, and $\mu(T)$ the in-plane carrier mobility.

In the light of Eq. (1) we claim that the transition observed in the resonance linewidth at 168 K is caused by a sudden change in the in-plane carrier mobility at the transition. Consequently, an increase in the in-plane resistivity should also be observed at the transition. Figure 3 actually shows this by an increase in the relative intensity of the resonance which for GIC's, through the skin depth,³ should be proportional to the temperature dependence of the in-plane resistivity *only*, since no temperature dependence of the carrier density is expected in GIC's:

$$\frac{\rho_a(T)}{\rho_a(280 \text{ K})} = \frac{I^2(T)}{I^2(280 \text{ K})}. \quad (2)$$

Following Khanna, Falardeau, Heeger, and Fischer⁶ the diffusion time τ_D , i.e., the time for a conduction carrier to travel across the skin depth, can be written as

$$\tau_D = \frac{e^2 c^2 N(E_F) \rho_c(T) \rho_a(T)}{2\pi\omega}, \quad (3)$$

where $N(E_F)$ is the carrier density of states at the Fermi level, ω the microwave frequency, and $\rho_c(T)$ and $\rho_a(T)$ the *c*-axis and in-plane resistivities, respectively. Therefore, assuming that the *c*-axis resistivity does not change significantly at the transition temperature (see below) an increase in the in-plane resistivity should also cause an increase in the diffusion time. Although the scattering of the data is relatively large, due to inherent difficulties associated with the determination of the diffusion time from the asymmetry of the resonance (*A/B* ratio⁴), Fig. 4 shows a clear increase in the diffusion time at the transition temperature.

It is interesting to note that Eqs. (1)–(3) not only predict that if a transition occurs in the carrier mobility it should be observed independently in the linewidth, intensity, and asymmetry of the resonance, but also that the size of the relative change in ΔH , I^2 , and τ_D at the transition should scale one to each other as follows:

$$\frac{\Delta H(T_+) - \Delta H(T_-)}{\Delta H(T_-)} = \frac{I^2(T_+) - I^2(T_-)}{I^2(T_-)} = \frac{\tau_D(T_+) - \tau_D(T_-)}{\tau_D(T_-)}, \quad (4)$$

where T_+ and T_- are the temperatures right below and above the transition, respectively. From Figs. 2–4 we actually observe that the relative change of all of these param-

eters at the transition is close to 1.5 ± 0.3 . This confirms our earlier assumptions that the *c*-axis resistivity and the carrier density do not experience a significant change at the transition.

We think that the discussion given above demonstrates unambiguously that the transition at 168 K, observed independently in three parameters of the resonance, is caused by a transition in the conduction-carrier in-plane mobility.

It is interesting to note in Fig. 3 that, for the case of fast cooling, the temperature dependence of the in-plane resistivity obtained from the intensity of the resonance shows the typical temperature dependence usually found for acceptor GIC's⁷ and also predicted by Pietronero and Strassler⁸ for the scattering of the conduction carriers by both the phonons of the graphite layers and the modes of the charged intercalate molecules. It is also interesting to note that below the transition temperature, depending upon the thermal treatment, the system can be frozen in various states corresponding to different in-plane mobilities or residual resistivities (curves *a*, *b*, *c*, and *d* in Figs. 2 and 3). In particular, a quenching from room temperature to temperatures below the transition leaves the system in its highest in-plane conductivity condition.

Finally, we argue that the transition observed in the conduction-carrier in-plane mobility at 168 K, during the cooling process, is caused by an in-plane "order-disorder-like" first-order phase transition of the intercalant molecules, which in turn affects the conduction-carrier in-plane mobility via a pinning of the charged intercalate molecules to the carbon atoms. We suggest that, at high temperatures, the intercalate molecule layers are in a "liquidlike" phase which undergoes a transition to a low-temperature "ordered-solid-like" phase with an associated in-plane mobility for the conduction carriers which is slightly greater for the higher cooling rates (see curves *a* and *b* in Figs. 2 and 3). We think that these small differences in the in-plane mobility could be accounted for by the combined effects of supercooling and thermal fluctuations present in a first-order phase transition. In the case of slow cooling and right below the transition the system will be in a supercooled liquid phase and thermal fluctuations will allow the nucleation of small amounts of solid in the liquid phase before the transformation takes place. Now, if the temperature is further lowered, the liquid-to-solid transformation finally occurs, and an ordered-solid phase with "frozen-in defects" may be obtained, and consequently a lower in-plane mobility should be expected for this slow cooling process (curve *b*). On the other hand, if the cooling proceeds quickly, fluctuation effects are minimized and the final ordered-solid phase could be considered "free of defects," leading to a higher in-plane mobility (curve *a*). For our experimental conditions we believe that our highest quenching rates are still not fast enough to freeze a disordered-solid (amorphous or glassy) phase at low temperature, because if this had been the case a broader line would be observed instead of a narrower one.

Furthermore, below the transition temperature, by heating the sample as described above, we claim that it is possible to take the system from the low-temperature "ordered-solid-like" phase into various "disordered-solid-like" phases corresponding to lower in-plane mobilities for the conduction carriers (curves *c* and *d* in Figs. 2 and 3). This last transformation, which originates the hysteresis cycle, could be caused by either a thermally activated disorder

within the intercalate molecule layers or also by a stage change which could drive the system into a lower stage with a lower in-plane mobility.^{9,10} Although we have shown that no change in the *c*-axis resistivity is actually observed at the transition, we cannot disregard the possibility of a stage change, which for low-stage samples in general involves a change in the *c*-axis resistivity,^{11,12} because for high-stage GIC's the *c*-axis resistivity does not depend much on the sample stage.^{13,14} On the other hand, a thermally activated process, as a mechanism responsible for the increase of the resistivity below the transition during the heating process, is in qualitative agreement with the work of Markiewicz,¹⁵ where Frenkel-type defects can be created in an ordered phase via a thermally activated process. Below the transition, following Markiewicz's ideas, we argue that during the sample heating the low-temperature "ordered-solid-like" phase (curves *a* and *b*) is being thermally disordered via an activated process. The different kinetics for the heating and cooling processes are responsible for the different thermal behavior of the linewidth during these processes. Also, when the temperature is reversed at any time during the process of heating, the disorder obtained at that time will be "frozen in," evidencing the irreversibility of this part of the cycle (see curves *c* and *d*). A further increase of the temperature will produce a superheating of this "disordered-solid-like" phase, that together with the thermal fluctuations will induce its transformation to the "liquidlike" phase at around 168 K, where the motional narrowing is once more reestablished. Careful experiments to determine quantitatively the time and temperature dependence of this thermally activated process, within the irreversible region, are in progress at the moment in our group. We would like

to mention that the unusual kinetics observed during the heating process, giving rise to an intermediate "disordered-solid-like" phase, resembles the melting of two-dimensional solid systems where an intermediate "liquid-crystal-like" phase is expected.^{16,17} It is evident that low-temperature x-ray experiments are needed in order to characterize more precisely these phase transformations and the nature of their associated phases, because transformations between high-temperature commensurate and low-temperature incommensurate phases could in principle yield the observed behavior of the conduction-carrier in-plane mobility. Evidence of phase transitions has been observed in resistivity experiments on AlCl_3 ,¹⁸ AsF_5 ,⁷ SbCl_5 -GIC,¹⁹ and in specific-heat experiments on stage-1 AlCl_3 -GIC.²⁰

In summary, we have shown that CCSR is a powerful technique which can be used to study the transport properties of acceptor GIC's. Although complementary experiments are necessary to determine the nature of the low-temperature "ordered- and disordered-like" phases in stage 7 AlCl_3 -GIC, we believe that we have found the first high-stage acceptor GIC showing an in-plane order-disorder first-order phase transition with the striking kinetics that, due to its "thermal memory" (hysteresis cycle), the residual resistivity can be increased continuously, within certain limits, by an appropriate thermal treatment of the sample below its transition temperature.

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