ESR   STUDY OF AlCl₃ GRAPHITE INTERCALATED COMPOUNDS

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INTRODUCTION

Conduction Carrier spin resonance (CCSR)
is an excelent tool for the study of
graphite intercalation compounds (1)
(GICs) and highly oriented pyrolitic
graphite (HOPG) (2). Drastic changes in
the resonance parameters have been re-
ported when HOPG is intercalated with
either donor alkali-metal atoms (3,4)
or acceptor halide molecules (5,6).Thus
the study of these effects can give val-
uable contribution to a better understan
ding of the transport properties, band
structure, phase transition, etc., in
these highly anisotropic materials .

In this work we report CCSR experi
ments in the acceptor AlCl₃-GICs, stage
2,4 and 7 from low (≈10K) to room tem-
peratures.

We show that for thin samples of
AlCl₃-GICs the temperature dependence of
the in-plane $\rho_a(T)$ and the c-axis $\rho_c(T)$
resistivities, can be   obtained
from the temperature dependence of the
intensity and lineshape of the CCSR. The
results indicate that the main contribu-
tion to ρ_a and ρ_c comes from the elec-
tron phonon scattering and thermally ac
tivated hopping mechanisms respectively.

In a recent report (7), experi-
ments in AlCl₃-GICs stage 7, revealed a
striking phase transition at Tc=170K.We
have attributed this to a quasi-two-di-
mensional (2D) "order-disorder" first
order phase transition experienced by
the intercalant AlCl₃ molecules. The ob
servation of a well defined hysteresis
cycle in the resonance parameters(line-
width, intensity and diffusion time)
induced us to admit the existence of a
metastable phase below the transition
temperature .

EXPERIMENTS

Single stage n=2, 4 and 7 samples
of AlCl₃-GICs were prepared using a
conventional two zone vapor growth tech
nique (8). Quartz tube of 4 mm inner
diameter and 0,5 mm wall appropriated
for the CCSR experiments were used for
sample preparation. The stage of the
samples were determined by X-ray in   a
conventional θ - 2θ scan. CCSR experi-
ments were carried out in a conventio-
nal Varian E-15 X-band reflection
spectrometer. Samples of 7x3x0,1 mm³
were placed inside the cavity such that
the microwave magnetic field (H1)
remained always perpendicular to the
c-axis. This guarantees that for thin
samples the wave penetrates mainly along
the c-axis direction and therefore the
skin depth will be governed by ρ_a. The
external magnetic field was perpendicu-
lar to the c-axis to prevent magnetic
field frequency modulation effects on
the lineshape (9).

RESULTS

All samples showed a single "me-
tallic" resonance with an asymetry
parameter A/B ratio greater than 2.55
which can be analised in terms of
Dyson's theory (10) for the limit of
thick samples, i.e. when the skin
depth is much smaller than the
thickness of the sample (11).

Figure 1 shows the experimental
temperature dependence of the square of
the relative intensity and diffusion
time obtained from the resonances of
the stage 2 and 4 samples.Within the
experimental accuracy no temperature
and stage dependence was observed in

the g-value (g=2.0035±0.0006).Small
increase of the linewidth., from about
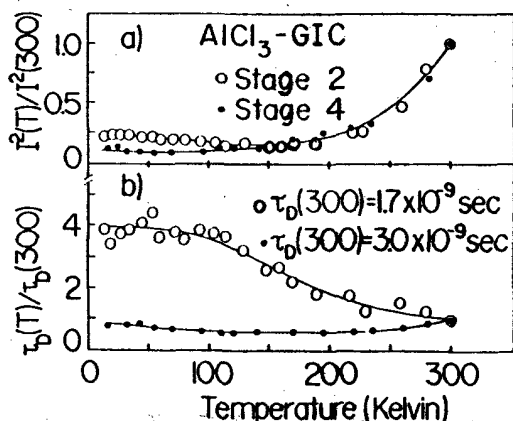4 to 5 Gauss,toward low temperature was
observed.

Fig.1. CCSR parameters in $AlCl_3$-GICs
stage 2 and 4, (a) square of the rela-
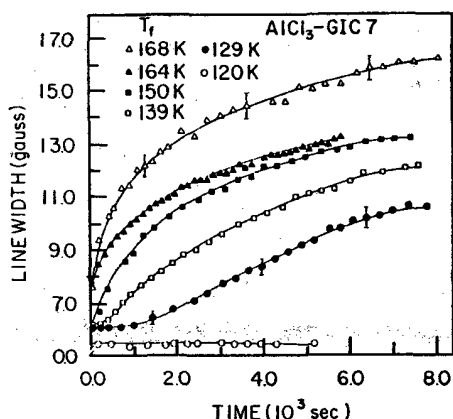tive intensity and (b) diffusion time.

Fig.2. Time dependence of the CCSR
linewidth in the stage 7 $AlCl_3$-GIC at
various temperature below the critical
temperature Tc=170K

    Figure 2 shows for stage 7, the
time dependence of the CCSR linewidth
for various temperatures Tf between
120K and 170K. After a quenching of
approximately 400K/min.from room to low
temperature (T≈100K), the temperature
was quickly raised up to a final value
Tf (120K<Tf<170K), where the time
evolution of the resonance was moni-
tored during approximately two hours.

In order to emphasize the different
kinetics observed when this temperature
is reached after cooling or heating the
sample, we shown in fig.3 the time
broadening of the linewidth at Tf=160K
when the temperature Tf is approached
from the high temperature side and from
the low temperature side of the transi-
tion. From these results it is evident
that the system is "memorizing" its
previous thermal history, suggesting a
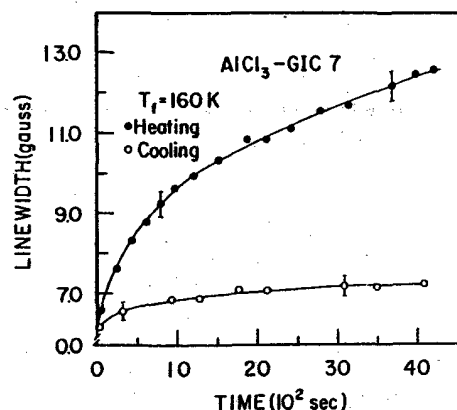first-order character for this
order-disorder phase transformation.

Fig.3 Time dependence of the CCSR
linewidth in the stage 7 $AlCl_3$-GIC at
Tf=160 K. Open circles correspond   to
data taken when the temperature Tf was
obtained by quenching from the room
temperature, and closed circles   corres
pond to data taken when the temperature
Tf was obtained by heating from a low
temperature T≈100K, wich was previously
obtained by quenching from room tempe-
rature.

ANALYSIS AND DISCUSSION

    All our $AlCl_3$-GICs show, at
room temperature, a single isotropic
resonance and an intensity approximately
five times larger than that correspon-
ding to a comparable sample size of HOPC
We can therefore argue that the observed
resonance comes mainly from a system of
unpaired spins associated to the conduc-
tion carriers (holes in our case)
created during the intercalation   pro-
cess.

Figure 1a shows the temperature dependence of the square of the relative resonance intensity for stage 2 and 4 samples. As we mentioned above, the experimental results indicate that the thickness of the samples were always much larger than the skin depth. Therefore, the intensity of the resonance will be proportional to the skin depth and, consequently, the square of the resonance intensity should scale with the in-plane resistivity. For GICs the carrier's density of states at the Fermi level can be taken to be temperature independent. Thus the temperature dependence of ρ_a will be determined by the temperature dependence of the square of the relative resonance intensity only

$$\rho_a(T)/\rho_a(300) = I^2(T)/I^2(300) \qquad (1)$$

The experimental points in figure 1a actually follow the typical temperature dependence of ρ_a usually measured in acceptor GICs(12,13), and also predicted theoretically by Pietronero and Strassler (14) for the scattering of the conduction carriers by both the phonons of the graphite layers and the modes of the charged intercalating molecules. The shape of the observed resonances in all our experiments are typically Dysonian-like with an asymmetry parameter, A/B ratio, larger than the diffusionless limit A/B=2.55. According to Dyson's theory(10) this indicates that the resonance spins are diffusing across a skin depth which is smaller than the thickness of the sample. For this limit and using the analysis given by Feher and Kip (11) we can obtain the diffusion time from the lineshape of the resonance.

As we mentioned above for the geometry adopted in our experiments, the skin depth is governed by ρ_a, then, according to Khanna (5) the diffusion time will be determined by ρ_a and ρ_c:

$$\tau_D(T)=\{N(E_F)e^2c^2/2\;\hbar\omega\}\rho_a(T)\rho_c(T) \qquad (2)$$

where $N(E_F)$ is the carrier's density of states at the Fermi level and ω the microwave frequency.

For GICs the density of states at the Fermi level can be considered temperature independent (15). Therefore, the temperature dependence of the diffusion time will be mainly determined by $\rho_a(T)$ and $\rho_c(T)$. Figure 1b shows the temperature dependence of the diffusion time for the stage 2 and 4 samples. The evaluation of the diffusion time already includes the small temperature dependence of the linewidth.

It is interesting to note that from eq. 2 $\rho_c(T)$ can be determined from $\tau_D(T)$ and $\rho_a(T)$ which are obtained from the lineshape and intensity of the resonance, respectively i.e.

$$\frac{\rho_c(T)}{\rho_c(300)} = \frac{\tau_D(T)/\tau_D(300)}{\rho_a(T)/\rho_a(300)}$$

$$= \frac{\tau_D(T)/\tau_D(300)}{I^2(T)/I^2(300)} \qquad (3)$$

Figure 4 shows $\rho_c(T)$ obtained for stage 2 and 4. At high temperature this results suggest a thermally activated process for the c-axis conductivity, probably a hopping-like mechanism

$$\rho_h = \rho_{oh}\exp\{E/KT\}$$

and at low temperature a metallic-like behaviour with a stage dependent residual resistivity, which might have its origin in narrow highly conducting channels (16) existing along the c-axis.

$$\rho_m = \rho_{om} + \beta T^n$$

We found that $\rho_c(T)$ shown in figure 4, can be closely reproduced by this phenomenological approach with a set of parameters

$$\rho_{om}/\rho_{oh} = (800 \pm 100), \quad \beta/\rho_{oh} = 6$$

$$n=1, \quad E= (1250\pm 50)K \text{ for stage 2}$$

and

$$\rho_{om}/\rho_{oh} = (45 \pm 5), \quad \beta/\rho_{oh} = 0,5$$

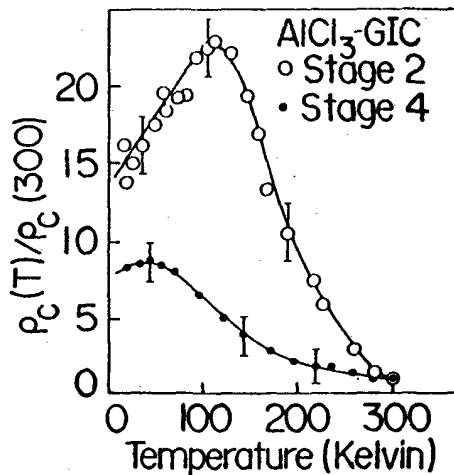$$n=1, \quad E= (560 \pm 20)K \text{ for stage } 4$$

Fig. 4 Temperature dependence of the relative c-axis resistivity.

Figure 5 shows that for temperatu res just below Tc the time broadening of the linewidth shows a scaling behaviour

$$\{\Delta H(t) - \Delta H(0)\} \, \alpha \, t^n \qquad (4)$$

The best fit of the experimental data at 164K and 168K gives $n=0.42\pm0.06$.

According to Elliot's theory (17) the main contribution to the CCSR linewidth is given by the spin lattice relaxation through phonon scattering via conduction carrier spin-orbit coupling. Elliot's calculation leads to a linewidth which is proportional to the inverse of the conduction carrier's mean free path ($\Delta H \alpha \lambda^{-1}$). In our previous work (7,9) we attributed the observed hysteresis cycle in the CCSR linewidth to an order-disorder first-order phase transition, experienced by the $AlCl_3$ mol elcules in the intercalant layers, which in turn affects the in-plane conduction carrier mobility.

Recent in-plane diffuse x-ray sca ttering experiments in $SbCl_5$-GICs by Homma and Clarke (18) revealed that one of the coexisting intercalated molecular specie, $SbCl_3$, experiences an order dis order phase transition at Tc=230K. They

identified the low temperature solidli ke phase as an almost commensurate (2% off) ($\sqrt{39} \times \sqrt{39}$) R ($\pm16.1^0$) super lattice. Ultrasonic experiments (19) and ac calorimetry (20) in $SbCl_5$-GICs, have also attributed the observed transition at 230K to a disorder-liquid to incommensurated-solid phase experienced by the intercalant $SbCl_3$ molecular spe cie.
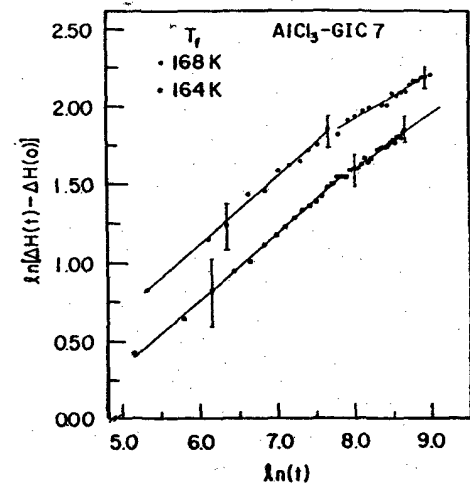

Fig.5 - Time evolution of the CCSR linewidth in the stage 7 $AlCl_3$-GIC at 164K (squares) and 168K (circles). The solid lines are fits to scaling behavior (see text).

Following these ideas we suggest that in our stage 7 $AlCl_3$-GIC, upon cooling through the first-order phase transition at Tc=170K the supercooled--liquid-like phase may freeze in many small domains or islands of a weakly incommensurate structure of $AlCl_3$ mole-cules . If the linear sizes of the do-mains are much smaller than (1 + Δ1) (1 +Δ1)/Δ1$\approx$1^2/Δ1 (19,21), which corresponds to a characteristic domain with the molecules occupying all the positions between the botton and the top of the graphite potential , most of the intercalant molecules will be registered near the botton of the graphite potential wells, yielding an almost unperturbed potential on the graphite layers and consequently an almost unchanged CCSR linewidth at the transition. Now, when the temperature is raised we claim that near Tc but

before that the superheated-solid-to
-liquidlike phase transformation takes
place, the intercalant molecules   may
have enough thermal energy to migrate
and the domains grow in time.   When
their size becomes comparable   to
$1^2/\Delta 1$ most of the molecules will   be
shifted from the botton of the graphite
potential wells. This will probably mod
ify the charge density distribution   on
the carbon layers, which in turn may
shorten the conduction carrier   mean
free path, leading to the observed time
broadening of the linewidth.   Alterna-
tively, it is possible that the growth
of these microdomains may allow the
formation of regions, within   the
Daumas-Herold domains (14), with higher
aluminium to carbon concentration which,
via spin-orbit coupling (17), causes
the shortening of the conduction
carriers mean free path, leading   in
turn, to the observed time broadening
of the CCSR linewidth. In both cases
the CCSR linewidth would be directly
measuring the time growing of the
average linear domains size (L),

$$\{\Delta H(t) - \Delta H(0)\} \; \alpha \; \lambda^{-1} \; \alpha \; L \quad (5)$$

This is supported by the observed
power-law evolution of the experimental
time broadening of the linewidth   shown
in figure 5.

Monte Carlo simulations, perfomed
by Sahni et al (21) of the kinetics   of
domain growth in 2D systems quenched
from high temperature (T>>Tc) to low tem
perature (0.5Tc<T<Tc), for both small and
large Q degenerecies,   show an universal
or lattice-independent   power-law behav-
ior for all   values   of Q but with expo
nents falling gradually from the classi-
cal value 1/2 (Q=2 Ising limit)   predic-
ted by Lifshitz (22) and Allen and   Cahn
(23)   for antiphase domain coarsening to
a constant value of 0.41 for large
Q (Q>30). Since no simulations of
incommensurate structure have been done
yet,   our thermal broadening of the
linewidth near Tc agrees, in terms of
scaling, only qualitatively with Monte
Carlo simulations for either triangular
square,   or   even honeycomb lattices

with large Q values. At temperatures
below Tc, however,   our results show
that the kinetics becomes slower, and
at even lower temperatures (T<140K) the
domain configuration seems to be ini-
tially frozen (see fig.2). Although Mon
te Carlo simulations (21)   for square
or honeycomb lattices show strong
pinning effects at low temperatures,
and although Lifshitiz (22) and Safran
(24)   have discussed the difficulty
in equilibrating systems with high
degeneracy, we cannot associate one of
these structures with our low-temperatu
re phase. First, as we said before, the
re are no Monte Carlo simulations of
the kinetics of domain growth for weak-
ly incommensurate phases, and   second,
the structure for T<Tc is unknown expe
rimentally for $AlCl_3$-GICs. Therefore we
suggest that the time evolution of the
CCSR linewidth observed near Tc can be
attributed to the time growing of   the
average linear domain size of unknown
yet, probably a weak incommensurate
triangular superlattice with high Q
degeneracy, Q>10, (21). At lower temper
atures (T<140K) the observation of   a
slower ordering kinetics could be due
either to a configuration of frozen-in
microdomains forming a quasi-2D
glasslike state, or (unlikely)   to
pinning effects due to square or   hon-
eycomb superlattices.

The sluggish kinetics observed
after an elapsed time of 40 minutes
near the   transition temperature,
n=0.32±0.06) (see fig.5), can be attibu-
ted to a pinning of the domain bounde-
ries on the Daumas-Herold domain walls.
Our data does not reveal any effect of
critical fluctuations near the transi-
tion temperature (25)

CONCLUSIONS

In this work we showed that CCSR
can give valuable information about the
charge transport properties in GICs.
Also we believe that the observed time
broadening of the CCSR linewidth could
be attributed to the time growing of the
average domain size of, probably, a weak
incommensurate superlattice. Then,   we
showed that CCSR experiment can be a
very helpful technique for studying the

kinetics of quasi-2D domain ordering in GICs.

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