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Kinetics of ordering in graphite-$SbCl_5$ studied by ESR

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Spin-resonance experiments allowed us to study the kinetics of ordering in the quasi-two-dimensional order-disorder phase transition observed at $T_c = 210 \pm 2$ K in stage-4 $SbCl_5$-intercalated graphite. Quenching from the disordered phase ($T \gg T_c$) reveals a time broadening of the linewidth with a scaling behavior ($\sim t^n$), which we attribute to the time growth of the average linear domain size of a weakly incommensurate superlattice. Fittings of the experimental data give $n \simeq 0.48$ for $T < T_c$ and $n \simeq 0.55$ for $T > T_c$, which are close to the exponents obtained in Monte Carlo simulations for domain growth of degenerate superlattices. For $T \simeq T_c$ a much faster kinetics is observed, which may indicate the presence of critical phenomena. A more sluggish kinetics is observed after an elapsed time of approximately 50 min, and at low temperatures ($T \ll T_c$), the results indicate that the system is in a metastable frozen-in state.

Antimony pentachloride–graphite intercalated compounds ($SbCl_5$-GIC's) have recently been the subject of many experimental studies[1–8] as a consequence of the interesting properties originating from their quasi-two-dimensional (2D) phase transitions experienced by the intercalant molecules at various temperatures. In a recent Communication[8] we reported conduction-carrier spin-resonance (CCSR) experiments in stage-2, -3, and -4 $SbCl_5$-GIC's. In agreement with the trend observed with other experimental techniques for high-stage $SbCl_5$-GIC's,[4,5] our stage-4 sample showed, as far as the CCSR linewidth is concerned the largest hysteretic behavior around the transition temperature. $SbCl_5$-GIC's are particularly suitable for studying the kinetics of ordering in these quasi-2D transformations, because the intercalant molecular species and their in-plane phase structures are rather well known for this system. We hope that this information will help us to obtain a better understanding of our experimental results for $SbCl_5$-GIC's and $AlCl_3$-GIC's.[9]

In this work we have studied the kinetics of ordering in the phase transition observed at $T_c = 210 \pm 2$ K in stage-4 $SbCl_5$-GIC by monitoring the time evolution of the CCSR linewidth around T_c. We found that below and above T_c the time broadening of the linewidth shows a scaling behavior ($\sim t^n$) which we attributed to the time growth of the average linear domain size of a weakly incommensurate $(\sqrt{39} \times \sqrt{39})R(\pm 16.1°)$ superlattice of $SbCl_3$ molecules, resulting from the intercalation process of $SbCl_5$ in graphite.[7]

For details of the handling and sample preparation, x-ray characterization, and ESR experiments of the stage-4 $SbCl_5$-GIC sample, the reader is referred to our previous work (see Ref. 8).

Figure 1 shows the thermal hysteresis of the CCSR linewidth observed in the stage-4 $SbCl_5$-GIC sample. In this figure we include part of the data shown in Fig. 1 of Ref. 8 and new data from a much slower experiment (rate of the temperature change between 0.1 and 1 K/min). The complete description of this hysteresis cycle can also be found in Ref. 8.

Figures 2 and 3 show the time dependence of the CCSR linewidth within the irreversible region ($180 < T < 245$ K) at various temperatures $T \le T_c$ and $T \ge T_c$, respectively. For these data in all cases, the time evolution of the linewidth was taken as follows: after a

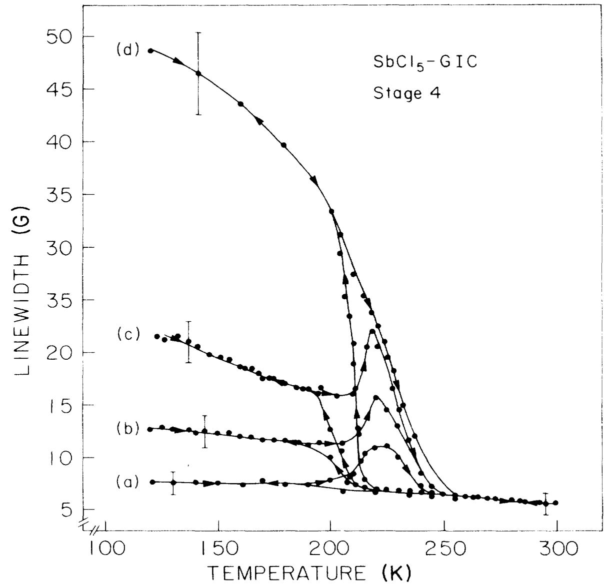

FIG. 1. Thermal hysteresis of the linewidth in the stage-4 $SbCl_5$-GIC. The rates of the temperature change in the regions *a*, *b*, *c*, and *d* were 5, 1, 0.5, and 0.03 K/min, respectively.

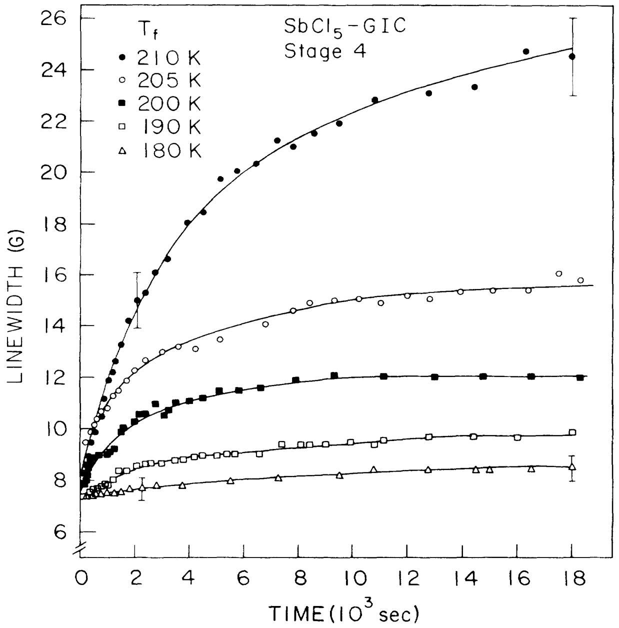

FIG. 2. Time broadening of CCSR linewidth in the stage-4 SbCl$_5$-GIC at various temperatures below the critical temperature $T_c = (210 \pm 2)$ K.

quenching of approximately 400 K/min from room to low temperature ($T \simeq 110$ K), the temperature was quickly raised to a final temperature T_f between 180 and 245 K, where the time evolution of the resonance was monitored during approximately four hours. This procedure was repeated for various temperatures within that interval.

In order to show that for $T_f > T_c$, but still within the irreversible region, the kinetics upon cooling is much slower than during the heating of the sample, we show in Fig. 4 the time broadening of the linewidth at $T_f = 222.5$ K when this temperature is reached from the high- and low-temperature side.

Figure 5 shows that within the irreversible region but for $T_f \leq T_c$, the time broadening of the linewidth is, within the accuracy of the experiment, the same when the temperature T_f is reached from the high- and low-temperature side. Note that this is not the case for $T_f > T_c$ (see Fig. 4) and also that it is contrary to the stage-7 AlCl$_3$-GIC behavior for $T_f < T_c$.[9]

Figure 6 shows that for temperatures below and above T_c the CCSR linewidth shows a time broadening with a scaling behavior

$$[\Delta H(t) - \Delta H(0)] \sim t^n \; . \qquad (1)$$

The exponent n is obtained from the best fit of the experimental data to a plot of $\ln[\Delta H(t) - \Delta H(0)]$ versus $\ln t$ for long times, such that contributions from the initial time can be neglected. Table I gives the exponents obtained within the interval $180 < T < 235$ K except for $T \simeq T_c$. For $T \simeq T_c$ a much faster kinetics is observed (see Figs. 2, 3, and 5) which may indicate the presence of critical behavior near T_c (see below). A more sluggish kinetics is observed after an elapsed time of approximately 50 min (see Table I and Fig. 6). For temperatures $T_f < 190$ K the data (see Fig. 2) show that, although a time broadening of the linewidth is still clearly seen, the kinetics becomes initially much slower, indicating, probably, the existence of a frozen-in nonequilibrium phase at low temperature.

According to Elliot's theory[10] the main contribution to

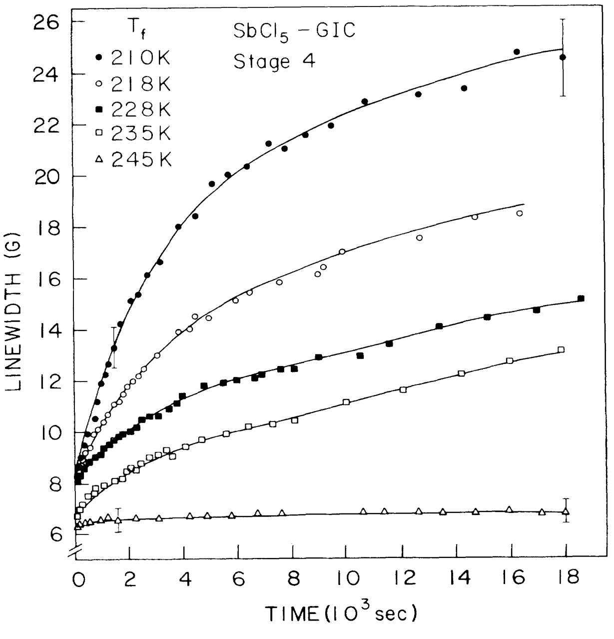

FIG. 3. Time broadening of CCSR linewidth in the stage-4 SbCl$_5$-GIC at various temperatures above the critical temperature $T_c = (210 \pm 2)$ K.

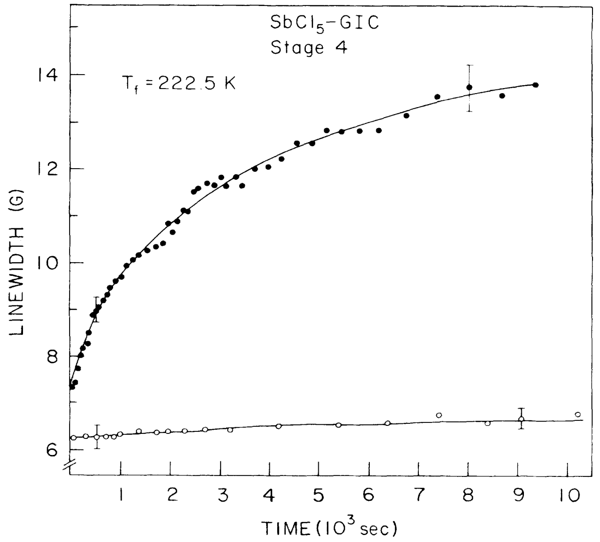

FIG. 4. Time broadening of CCSR linewidth in the stage-4 SbCl$_5$-GIC at $T = (222.5 \pm 2)$ K. Open circles correspond to data taken when the temperature T_f was approached from the high-temperature side, and solid circles correspond to data taken when the temperature T_f is approached from the low-temperature side.

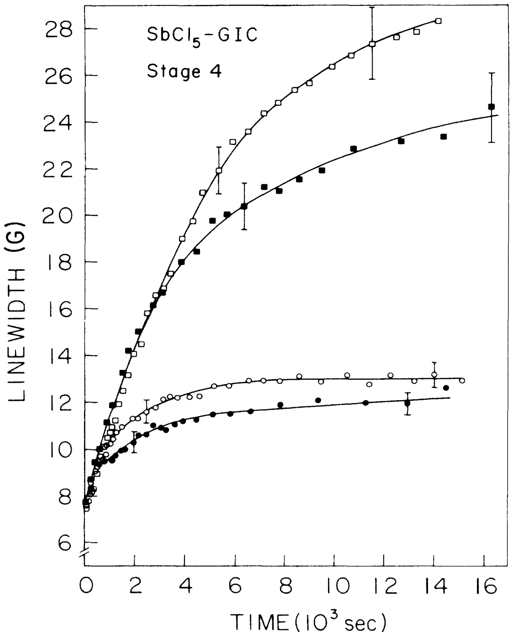

FIG. 5. Time broadening of the CCSR linewidth in the stage-4 SbCl$_5$-GIC at $T_f=(200\pm2)$ K, open circles, and $T_f=(210\pm2)$ K, open squares, when the temperature T_f is approached from the high-temperature side and at $T_f=(200\pm2)$ K closed circles, and $T_f=(210\pm2)$ K, solid squares, when the temperature T_f is approached from the low-temperature side.

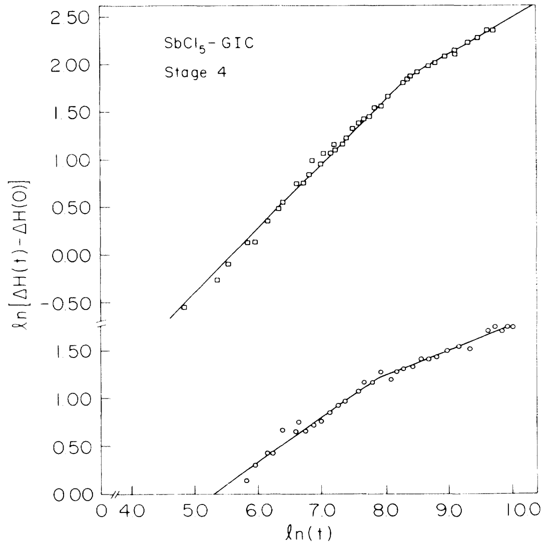

FIG. 6. Time evolution of CCSR linewidth in the stage-4 SbCl$_5$-GIC at $T_f=(218\pm2)$ K, open squares, and $T_f=(200\pm2)$ K, open circles. The solid lines are fits to scaling behavior [Eq. (1)].

the CCSR linewidth is given by the spin-lattice relaxation through a phonon scattering via conduction-carrier spin-orbit coupling. Elliot's calculation leads to a linewidth which is proportional to the spin-orbit coupling parameter and to the inverse of the conduction carrier's mean free path. As in our previous work[8] here we attribute the observed hysteresis cycle in the CCSR linewidth to an "order-disorder" first-order phase transition experienced by the SbCl$_3$ molecules within the graphite galleries, which via spin-orbit coupling affect the conduction-carrier spin-flip scattering.

Recent in-plane diffuse x-ray scattering experiments in SbCl$_5$-GIC's by Homma and Clarke[7] revealed that the SbCl$_3$ molecules, one of the coexisting intercalated molecular species, experience an order-disorder phase transition at $T=230$ K. They identified the low-temperature "solid-like" phase as an almost commensurate (2% off) $(\sqrt{39}\times\sqrt{39})R\,(\pm16.1°)$ superlattice. Ultrasonic experiments[3] and ac calorimetry[6] in SbCl$_5$-GIC's, also attribute the observed transition at $T_c=230$ K to a "disordered-liquid" to "incommensurate-solid" phase transformation experienced by the intercalant molecular species SbCl$_3$.

Following these ideas we suggest that, in our stage-4 SbCl$_5$-GIC, upon cooling through the first-order phase transition at $T_c=(210\pm2)$ K the "supercooled-liquid"-like phase may freeze in many small domains or islands of a weakly incommensurate $(\sqrt{39}\times\sqrt{39})$ structure of SbCl$_3$ molecules. If the size of these domains is much smaller than a domain with a characteristic size of $l^2/\Delta l$,[8] which corresponds to a domain with its molecules occupying all the positions between the bottom and top of the graphite potential, most of the intercalant molecules will be located near the bottom of the graphite potential wells, yielding probably to an almost unperturbed potential on the graphite layers and consequently to an almost unchanged CCSR linewidth at the transition. Now, when the temperature is raised we claim that around T_c, 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 $l^2/\Delta l$ most of the SbCl$_3$ molecules within these domains will be shifted from the bottom of the graphite potential wells, and a large charge density may be induced on the graphite layers, with different periodicity than that corresponding to the carbon atoms, which in turn could shorten the conduction-carrier mean free path. On the other hand, as a consequence of the observed disproportionation in SbCl$_5$-GIC's (Ref. 7) and the domain growth, there might be regions, within the Daumas-Herold domains, of high Sb concentration relative to C concentration which, via spin-orbit coupling may cause an increase in the

TABLE I. Quasi-2D domain growth power-law exponents.

T (K) (±2 K)	n (±0.05) $t\lesssim50$ min	$t\gtrsim50$ min
180	0.49	0.20
190	0.51	0.23
200	0.47	0.27
200[a]	0.50	0.17
205	0.49	0.26
218	0.67	0.39
222.5	0.54	0.34
228	0.59	0.46
235	0.54	0.57

[a] Corresponds to the open circles in Fig. 5.

conduction-carrier spin-flip scattering. Both mechanisms could be in principle responsible for the observed time broadening of the linewidth. In consequence we claim that the time broadening of the CCSR linewidth measures directly by the time growth of the average linear domain size (L),

$$[\Delta H(t)-\Delta H(0)]\sim\lambda^{-1}\sim L\ . \tag{2}$$

This is supported by the observed power-law evolution of the experimental time broadening of the linewidth shown in Fig. 6.

Monte Carlo simulations, by Sahni *et al.*[11] of the kinetics of domain growth in 2D systems quenched from high temperature ($T \gg T_c$) to low temperatures ($0.5T_c < T < T_c$), for both small and large Q degeneracies, show a universal or lattice-independent power-law behavior for all values of Q but with exponents falling gradually from the classical values of $\frac{1}{2}$ ($Q=2$, Ising limit) to a constant value of 0.41 for large Q ($Q>30$). In terms of scaling and since no simulation for incommensurate structures has been done yet, our time broadening of the linewidth around T_c agrees only qualitatively with Monte Carlo simulations for either triangular, square, or even honeycomb lattices. At temperatures below T_c, however, our results show that the kinetics becomes slower, and at even lower temperatures ($T_f < 190$ K) the domain configuration seems to be initially frozen (see Fig. 2). Although Monte Carlo simulations[11] for square or honeycomb lattices show strong pinning effects at low temperatures we can not associate either of these structures with our low-temperature phase because: firstly these are no Monte Carlo simulations of the kinetics of domain growth for weakly incommensurate phases, and secondly, the phase structure for the $SbCl_3$ molecules at $T<T_c$ is known experimentally to be hexagonal.[4,7] Therefore we suggest that the time evolution of the CCSR linewidth observed below and above T_c could be attributed to the time growth of the average linear domain size of a weakly incommensurate $(\sqrt{39}\times\sqrt{39})R\,(\pm 16.1^\circ)$ superlattice.

The slow kinetics of ordering observed at low temperatures ($T_f<180$ K) could be an indication of the existence of a configuration of frozen-in microdomains which may be forming a quasi-2D metastable state.

The sluggish kinetics observed after an elapsed time of approximately 50 min (see Fig. 6 and Table I) may be attributed to a pinning of the domain boundaries on the Daumas-Herold domain walls. It is also observed that this pinning effect tends to be more effective for $T<T_c$ than for $T>T_c$ (see Figs. 2, 3, and Table I for $t>50$ min).

For $T\simeq T_c$ Figs. 2, 3, and 5 show that the time broadening of the linewidth increases abnormally fast. The data can only be fitted to Eq. (1) for exponents which are much larger than those given in Table I. It is possible that for $T\simeq T_c$ a critical behavior could be responsible for this fast time broadening of the linewidth, but we think that careful experiments, with a more accurate temperature control than ours ($\Delta T=\pm 2$ K), should be done in order to decide if around T_c the domain growth shows critical behavior.

It is interesting to comment that although $AlCl_3$ and $SbCl_3$ molecules are similar species they show different order-disorder transition temperatures, 168 and 210 K for stage-7 $AlCl_3$-GIC's and stage-4 $SbCl_5$-GIC's, respectively. We attribute this difference to the fact that in the case of $SbCl_5$-GIC's the $SbCl_3$ molecules should move within the graphite galleries in the presence of an ordered $(\sqrt{7}\times\sqrt{7})R\,(\pm 19.11^\circ)$ superlattice of $SbCl_6$ molecules.[7] The presence of the $SbCl_6$ molecules (or even other species) may also be the reason for the different time broadening of the linewidth observed around T_c for these two systems. Stage-4 $SbCl_5$-GIC shows approximately the same time broadening of the linewidth for $T_f \le T_c$, when T_f is reached from both sides (see Fig. 5), and also a time broadening of the linewidth for $T_f > T_c$ (see Fig. 3), in both cases contrary to the observed behavior in stage-7 $AlCl_3$-GIC. It is possible that the presence of various molecular species within the graphite galleries makes the order-disorder transformation much smoother in $SbCl_5$-GIC's than in $AlCl_3$-GIC's.[9]

In conclusion we believe that for $SbCl_5$-GIC's the time broadening of the CCSR linewidth, the time dependence of the x-ray intensity,[4] and the time dependence of the c-axis shear elastic constant,[3] all have the same origin, i.e., the time growth of the average linear domain size of weakly incommensurate superlattices of antimony chlorine molecules. For temperatures well below T_c the weakly incommensurate microdomains may form a quasi-2D metastable state, and the fast kinetics observed at $T\simeq T_c$ may suggest a critical behavior for the domain growth.

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