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Kinetics of ordering in the order-disorder phase transition of $AlCl_3$-intercalated graphite studied using ESR

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Conduction-carrier spin-resonance experiments allowed us to study with some detail the kinetics of ordering in a quasi-two-dimensional "order-disorder" phase transition observed at $T_c = 170$ K in stage-7 $AlCl_3$-intercalated graphite. After quenching from the disordered phase ($T \gg T_c$) the time broadening of the linewidth reveals a scaling behavior ($\sim t^n$), which we attribute to the time growing of the average linear domain size of a weakly incommensurate superlattice. The best fit of the experimental data gives $n = 0.42 \pm 0.06$ which corresponds to slow domain growth of highly degenerate Q-state Potts systems. Evidence for more sluggish kinetics is observed after an elapsed time of approximately 40 min, and at lower temperatures evidence of a glasslike state is also observed.

In a recent report[1] we showed that conduction-carrier spin-resonance (CCSR) experiments in the stage-7 $AlCl_3$-graphite intercalation compound ($AlCl_3$-GIC7) revealed a striking phase transition at $T_c = 170$ K. We have attributed this to a quasi-two-dimensional (2D) "order-disorder" first-order phase transition experienced by the intercalant $AlCl_3$ molecules within the graphite galleries, and speculated about the kinetics of the transformation between the high-temperature liquidlike phase ($T \gg T_c$) and the low-temperature ordered-solid-like phase ($T < T_c$). The observation of a well-defined thermal hysteresis cycle in the resonance parameters (linewidth, intensity, and diffusion time), induced us to admit the existence of an intermediate phase below the transition temperature, observable only during the heating process, and which we named the disordered-solid-like phase.

The aim of this work will be to study the kinetics of ordering in this quasi-2D order-disorder phase transformation by monitoring in detail the time evolution of the CCSR linewidth below the transition temperature. To the best of our knowledge, this is the first time that CCSR experiments regarding the kinetics of ordering in an order-disorder phase transformation in GIC's are reported.

For the details of the sample preparation, x-ray characterization, and the ESR experiments, and a description of the hysteresis cycle observed in the $AlCl_3$-GIC7 sample, the reader is referred to our previous work (see Ref. 1). For the present work, in all cases, the data were taken as follows: After a quenching of approximately 400 K/min from room to low temperature ($T \sim 100$ K), the temperature was quickly raised up to a final value T_f, between 120 and 170 K, where the time evolution of the resonance was monitored during approximately two hours. This procedure was repeated for various temperatures within that interval.

Figure 1 shows the time dependence of the CCSR linewidth for various temperatures T_f between 120 and 170 K. In order to emphasize the different kinetics observed when this temperature is reached after cooling or heating the sample,[1] we show in Fig. 2 the time broadening of the linewidth at $T_f = 160$ K when the temperature T_f is approached from the high-temperature side and from the low-temperature side of the transition. From these results it is evident that the system is "memorizing" its previous

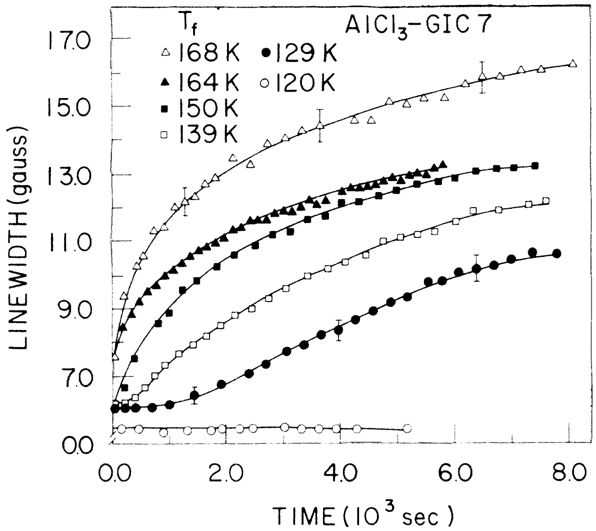

FIG. 1. Time dependence of the CCSR linewidth in the stage-7 $AlCl_3$-GIC at various temperatures below the critical temperature $T_c = 170$ K.

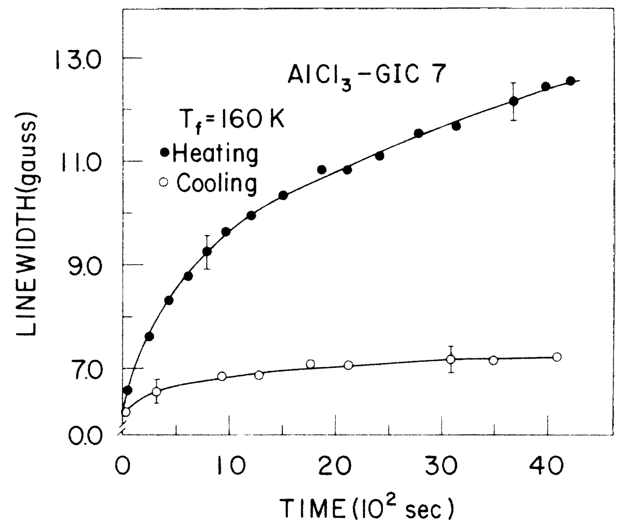

FIG. 2. Time dependence of the CCSR linewidth in the stage-7 AlCl$_3$-GIC at $T_f = 160$ K. Open circles correspond to data taken when the temperature T_f was obtained by quenching from room temperature, and closed circles correspond to data taken when the temperature T_f was obtained by heating from a low temperature $T \sim 100$ K, which was previously obtained by quenching from room temperature.

thermal history, suggesting a first-order character for this order-disorder phase transformation.

Figure 3 shows that for temperatures just below T_c the time broadening of the linewidth shows a scaling behavior

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

The best fit of the experimental data at 164 and 168 K gives $n = 0.42 \pm 0.06$. More sluggish kinetics can be observed after an elapsed time of approximately 40 min (see Fig. 3). For temperatures $T_f < 164$ K the data indicate that, although a time broadening of the linewidth can be clearly observed, the kinetics become slower toward low temperatures. In this work we shall be mainly concerned with the kinetics observed in a temperature region lying just below T_c, where the thermal broadening of the linewidth shows a scaling behavior.

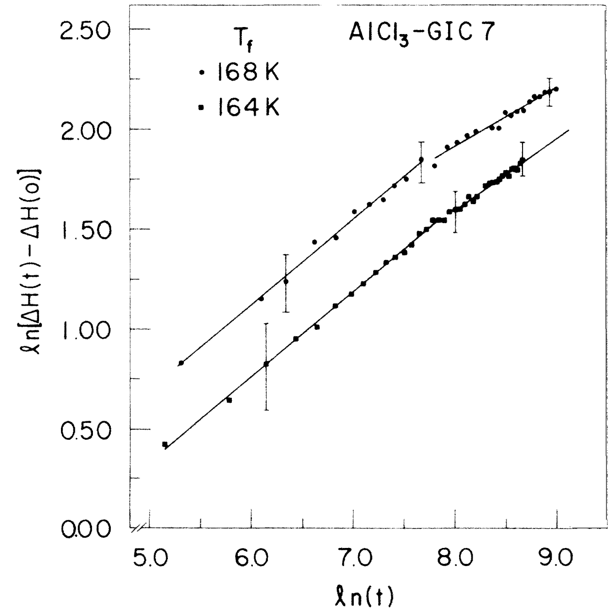

FIG. 3. Time evolution of the CCSR linewidth in the stage-7 AlCl$_3$-GIC at 164 K (squares) and 168 K (circles). The solid lines are fits to scaling behavior (see text).

According to Elliot's theory[2] 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 ($\Delta H \sim \lambda^{-1}$). In our previous work[1,3] we attributed the observed hysteresis cycle in the CCSR linewidth to an order-disorder first-order phase transition, experienced by the AlCl$_3$ molecules in the intercalant layers, which in turn may affect the in-plane conduction-carrier mobility.

Recent in-plane diffuse x-ray scattering experiments in SbCl$_5$-GIC's by Homma and Clarke[4] revealed that one of the coexisting intercalated molecular species of SbCl$_3$ experiences an order-disorder phase transition at $T_c = 230$ K. They identified the low-temperature solidlike phase as an almost commensurate (2% off) $(\sqrt{39} \times \sqrt{39})R(\pm 16.1)$ superlattice. Ultrasonic experiments[5] and ac calorimetry[6] in SbCl$_5$-GIC's, have also attributed the observed transition at ~ 230 K to a disordered-liquid to incommensurate-solid phase experienced by the intercalant molecular species SbCl$_3$.

Following these ideas we suggest that in our stage-7 AlCl$_3$-GIC, upon cooling through the first-order phase transition at $T_c = 170$ K, the supercooled-liquid–like phase may freeze in many small domains or islands of a weakly incommensurate structure of AlCl$_3$ molecules. If the linear sizes of these domains are much smaller than $(l+\Delta l)(l+\Delta l)/\Delta l \simeq l^2/\Delta l$,[5,7] which corresponds to a characteristic domain with the molecules occupying all the positions between the bottom and the top of the graphite potential, most of the intercalant molecules will be registered near the bottom 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 T_c but before 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 molecules will be shifted from the bottom of the graphite potential wells. This will probably modify 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. Therefore we claim that the time broadening of the linewidth directly measures the time growing of the average linear domain size (L),

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

This is supported by the observed power-law evolution of the experimental time broadening of the linewidth, as shown in Fig. 3.

Monte Carlo simulations, performed by Sahni *et al.*,[8] of the kinetics of domain growth in 2D systems quenched from high temperature ($T >> T_c$) to low temperature

$(0.5T_c < T < T_c)$, 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 value of $\frac{1}{2}$ $(Q=2$, Ising limit) predicted by Lifshitz[9] and Allen and Cahn[10] 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 T_c 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 T_c, however, our results show that the kinetics becomes slower, and at even lower temperatures $(T \leqslant 140$ K) the domain configuration seems to be initially frozen (see Fig. 1). Although Monte Carlo simulations[8] for square or honeycomb lattices show strong pinning effects at low temperatures, and although Lifshitz[9] and Safran[11] have already discussed the difficulty in equilibrating systems with high degeneracy, we cannot associate one of these structures with our low-temperature phase. First, as we said before, there are no Monte Carlo simulations of the kinetics of domain growth for weakly incommensurate phases, and second, the structure for $T < T_c$ is not known experimentally for $AlCl_3$-GIC's. Therefore we suggest that the time evolution of the CCSR linewidth observed near T_c can be attributed to the time growing of the average linear domain size of an unknown, yet weakly incommensurate superlattice (likely a triangular one) with high Q degenerancy, $Q > 10$.[8] At lower temperatures $(T \leqslant 140$ K) the observation of a slower ordering kinetics could be due either to a configuration of frozen-in microdomains forming a quasi-2D glasslike state, similar to those reported in electron microscopy and x-ray diffuse scattering experiments in $SbCl_5$-GIC's,[12,13] or (unlikely) to pinning effects due to square or honeycomb superlattices.

The sluggish kinetics observed after an elapsed time of 40 min near the transition temperature, $n \simeq 0.32 \pm 0.06$ (see Fig. 3), can be attributed, following Homma and Clarke's ideas,[14] to a pinning of the domain boundaries on defects introduced into the graphite by intercalation when the average domain size becomes comparable with the average defect separation. Our data do not reveal any effect of critical fluctuations near the transition temperature.[15]

In summary, we believe that the observed time broadening of the CCSR linewidth can be explained in terms of time growing of the average domain size of a weakly incommensurate superlattice, which we called the intermediate disordered-solid–like phase.[1] Obviously, in-plane diffuse x-ray scattering experiments are necessary in order to characterize more precisely the nature of this low temperature phase in $AlCl_3$-GIC7. In any case we showed that CCSR experiment can be a very helpful technique for studying the kinetics of quasi-2D domain ordering in GIC's.

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