Time-Resolved X-Ray Diffraction Study of One-Dimensional Nucleation and Growth in the First-Order Transition

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The kinetics of nucleation and growth in the first-order transition belonging to the one-dimensional nonconserved-order-parameter system has been studied by time-resolved synchrotron x-ray diffraction measurements of the stacking transition in stage-1 rubidium-graphite intercalation compounds. The volume of the growing phase can be scaled by the theoretical function of Avrami. The line shape is scaled by a squared Lorentzian which is consistent with a recent theory. The nuclear size has a nearly logarithmic time dependence which is in contrast to the linear time dependence in the usual theories.

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The nonequilibrium kinetics of the first-order phase transition has been studied extensively by theories, computer simulations, and experiments.[1] The results suggest the existence of a scaling law even for the kinetic properties of a nonequilibrium process. The scaling function depends on the universality class, which is categorized by the dimensionality of a system, the conservability of the order parameter, and the degeneracy p of the ground state.

The development of the stable phase in the first-order transition consists of two successive growing processes, namely, the nucleation and growth (NG) and the domain growth (DG) processes. In the nucleation process, nuclei of the stable phase larger than a critical size come out in the metastable-phase matrix, while in nuclear growth they grow in size at the expense of the metastable phase: A growing nucleus consists of one of p-degenerate domains. The NG process continues until domains of the stable phase contact each other, and eventually these domains merge into larger ones, which is the DG process. Kinetic studies in nonconserved-order-parameter (NCOP) systems have been made so far for DG in 1D,[2] 2D,[3] and 3D[4] systems while NG processes have been studied only in 3D[5] systems.

We have studied the nonequilibrium process of the stacking transition in stage-1 rubidium-graphite intercalation compounds (C_8Rb), and report in this Letter the first observation of the scaling in the 1D NCOP system for volume fraction and structure factor in the NG process. Furthermore, we show that the mean nuclear size R in NG has a slow time dependence, $R(t) \sim \ln(t)$, which is in contrast to phenomenological theories.

C_8Rb has two solid phases, with four-layer stacking ($\alpha\beta\gamma\delta$) and two-layer stacking ($\alpha\beta$). Both solids have the in-plane (2×2) triangular lattice commensurate with graphite. The four sublattices α, β, γ, and δ differ from each other by an in-plane displacement of the graphite unit vector. The ground-state $\alpha\beta\gamma\delta$ solid is stable in a low-temperature (T) and a high-pressure (P) region due to repulsive interaction between Rb atoms, while the $\alpha\beta$ solid becomes stable in a high-T and low-P region because of its excess entropy.[6] The stacking sequence $\alpha\beta\alpha\beta\cdots$ can be obtained from the $\alpha\beta\gamma\delta$ phase by a simple lateral displacement $\frac{1}{2}(\mathbf{a}_1+\mathbf{a}_2)$ of the two-layer package $\gamma\delta$ to the $\alpha\beta$ position, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the in-plane unit vectors of this compound. Namely, the stacking sequences $\alpha\beta\alpha\beta$ and $\alpha\beta\gamma\delta$ are equivalent to ferromagnetic and antiferromagnetic states, respectively, when we regard the two-layer package $\alpha\beta$ as spin-up and $\gamma\delta$ as spin-down states. Thus the stacking configuration of Rb layers corresponds to the 1D Ising system, so that the transition belongs to the 1D NCOP system and the degeneracy $p=2$ (Ref. 7). The observed in-plane coherence length (typically 1000 Å) does not change throughout the transition while the stacking coherence length increases, so that we conclude that our system can be regarded as a good one-dimensional system.[8] This stacking transition has been confirmed to be first-order by Metoki and Svematsu[9] from the observation of a discontinuous change of the Bragg intensity and the thermal hysteresis at the transition point.

The stacking structure of the Rb layer was studied by x-ray diffraction along the $\mathbf{c}^*$ axis around the (103) and (104) superlattice reflections, which arise from the $\alpha\beta\gamma\delta$ and $\alpha\beta$ solids, respectively. The index is referred to the reciprocal lattice of the $\alpha\beta\gamma\delta$ phase. The linewidth of these high-l diffraction peaks is less affected by the mosaic spread of the sample. Time-resolved measurements were carried out by using synchrotron radiation x rays monochromatized by an Si(111) double monochromator at the Photon Factory (beam line 7C), KEK, Tsukuba. A single-crystal sample was synthesized in a horizontal two-zone furnace mounted on a two-axis goniometer. The furnace enabled us to control independently the sample temperature T_G and Rb vapor pressure P_{Rb}. The response time was about 1 min. The intercalation reaction was controlled very carefully to maintain a small mosaic spread of the sample ($=1.5°$) which practically determined the experimental resolution, typically about 0.01 Å^{-1}. The dimension of stage-1 crystallites was about 1000 Å along the c axis. Starting with a single-phase state in equilibrium (which was confirmed by observing no trace of the counter phase), P_{Rb} (corresponding to chemical potential μ) was changed quickly at $t=0$ with T_G held constant. After that, the time dependence of the diffraction spectrum was measured for some values of ΔP_{Rb}, the excess pressure above (+) or below (−) the critical pressure. The measuring time for a spectrum was typically 1 min.

Figure 1 shows the time dependence of the $(10l)$ x-ray diffraction spectrum for $\Delta P_{\text{Rb}} = -1.6$ Pa in the transition from the $\alpha\beta\gamma\delta$ to the $\alpha\beta$ phase. The (104) peak intensity of the $\alpha\beta$ solid, stable at $t>0$, increases with time while the (103) peak of the metastable $\alpha\beta\gamma\delta$ solid decreases. The (104) reflection shows a sharp Bragg peak from the beginning of the transition although its linewidth decreases steeply as the transition proceeds. These facts indicate that at the beginning of the transition, nuclei of the $\alpha\beta$ phase stabilized in the matrix of the metastable $\alpha\beta\gamma\delta$ phase have a grain size large enough to give the Bragg reflections. During the transition neither peak is accompanied by diffuse scattering, which indicates that there is no fluctuation at the transition and the stable and metastable phases are separated by a sharp phase boundary without a disordered state. Therefore, we conclude that the growing process in this period is the NG process. After the complete replacement of the $\alpha\beta$ phase, we observed no appreciable narrowing of linewidth, which means no appreciable DG process occurs.

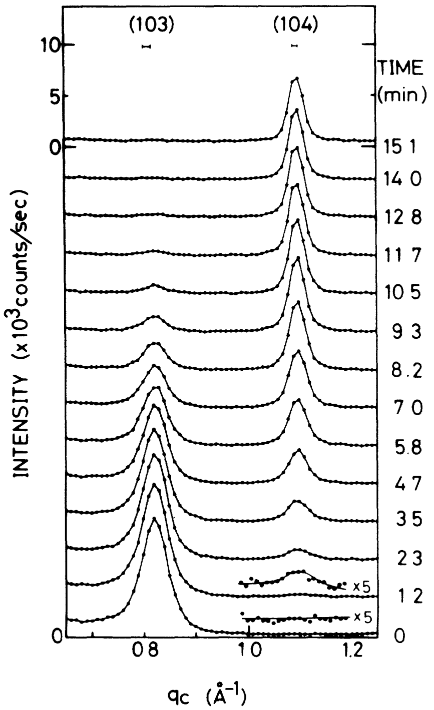

FIG. 1. The time dependence of the $(10l)$ x-ray diffraction spectra for $\Delta P_{\text{Rb}} = -1.6$ Pa at $T_G = 378.0\,°\text{C}$. Horizontal bars indicate the resolutions.

The volume fraction of the growing phase, $X(t)$, which was determined from the integrated intensity, is a function dependent on ΔP_{Rb}. However, as shown in Fig. 2, it can be scaled by a unified function when t is normalized by $\tau = t/t_{1/2}$, where $t_{1/2}$ is the time that $X(t)$ grows to a half the intensity at the completion of the transition. This fact indicates that a scaling law is realized for the t dependence of the volume fraction in the NG process of the 1D NCOP system. In Fig. 2 we also show the results of the phenomenological theory of Avrami[10] for NG in a d-dimensional system,

$$X(\tau) \propto 1 - \exp(-\tau^{d+1}) . \tag{1}$$

The calculated function for $d=1$ is in quite good agreement with the experimental results except for small ΔP_{Rb}.

At small ΔP_{Pb} (<0.5 Pa) the experimental result shows much slower kinetics than Eq. (1), and $X(t)$ asymptotically approaches an exponential relaxation, $1-\exp(-\tau)$. Avrami's theory is based on the assumptions of (a) a constant rate of nucleation and (b) a constant growing speed of the nuclear size. If we assume the cell model[11] instead of (a), the power of $d+1$ in Eq. (1) is replaced by d and the present slow kinetics can be understood: In the cell model the number of nuclei is given only at $t=0$ and nucleation at $t>0$ is not allowed.

The characteristic relaxation time $t_{1/2}$ shows two steep functions of ΔP_{Rb} which appear to diverge at $\Delta P_{\text{Rb}}=0$ (Fig. 3). The data points for $\Delta P_{\text{Rb}}<0$ (>0) are obtained for the transition from a starting P_{Rb} which is a little higher (lower) than the critical pressure P_{Rb}^c (15.0

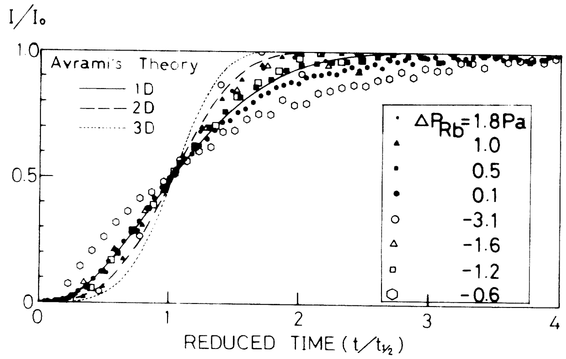

FIG. 2. The time dependence and the scaling function of the volume fraction of the growing phase. The results of Avrami's theory are shown for 1D (solid line), 2D (dashed line), and 3D (dotted line).

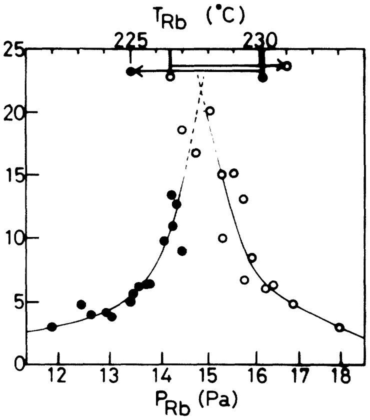

FIG. 3. The ΔP_{Rb} dependence of relaxation time $t_{1/2}$.

Pa) to the final P_{Rb} indicated in Fig. 3. The relaxation shows a remarkable slowing-down phenomenon.

The nuclear size $R_{\alpha\beta}$ of the growing $\alpha\beta$ solid is determined from the inverse of the linewidth corrected by the experimental resolution. $R_{\alpha\beta}(t)$ shows a remarkable t dependence from a critical size (~60 Å) to the final size (~300 Å). However, the observed t dependence is far from a linear function. In Fig. 4 a logarithmic plot is used as a trial function; the fit is good over a limit t range. The slope of $R_{\alpha\beta}(t)$ in the logarithmic plot decreases with decreasing ΔP_{Rb}. The observed logarithmic t dependence of the nuclear size is inconsistent with Avrami's assumption (b), although the volume fraction $X(t)$ is consistent with his prediction for the NG process. Assumption (b) is a reasonable consequence of the fact that the free-energy gain does not depend on t in the NG process, and it is also the basis of recent microscopic theories. The very slow t dependence of NG observed here is quite unique.

A similar logarithmic t dependence has been observed in the 1D antiferromagnet $Rb_2Co_{0.7}Mg_{0.3}F_4$ by a neutron diffraction study.[2] However, it is observed in the DG process after having ordered in antiferromagnetic domains, but not in the NG process, unlike the present case. This logarithmic t dependence in the 1D DG process has been explained by Kawasaki and Nagai[12] in a theory taking account of the interaction between 1D kink-type domain boundaries. In the 2D and 3D NCOP systems, a $t^{1/2}$ dependence is deduced from experiments[3,4] and theories,[13] which originates from the surface-tension effect due to finite curvature in these dimensions.

Although the linewidth of the (104) Bragg peak depends on t, the structure factor $S(q)$ can be scaled by a unified function, as shown in Fig. 5, when q is reduced by $\eta=(q-q_0)/\Delta_q$, Δ_q being the full width at half maximum of a peak. The experimental function $S(\eta)$ shows a significant difference from Gaussian or Lorentzian, but seems to be fitted by the squared Lorentzian (SQL), as indicated by the solid line. This scaling law in $S(q)$ is consistent with the recent theoretical result of Axe and Yamada[14] for Avrami's NG system. They proposed a correlation function which is quite similar to the Fourier transform of SQL in the 1D case.[15]

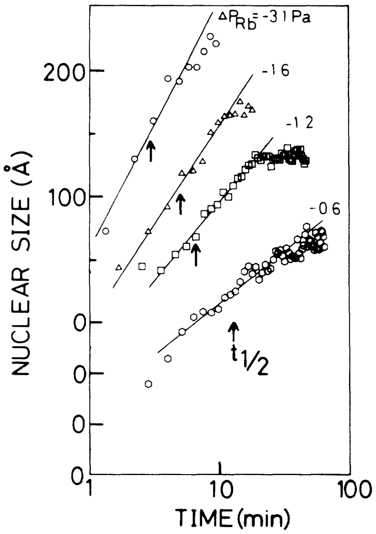

FIG. 4. The time dependence of nuclear size $R_{\alpha\beta}$. Note that the origin is vertically shifted for each ΔP_{Rb} for clarification.

For the DG process in the 1D NCOP system, Kawasaki and Nagai[16] proposed that $S(q)$ is approximated by SQL (the purely 1D case in their paper). It is very interesting that the NG process in the present 1D system has the same kinetics in $R(t)$ and $S(q)$ as those proposed for the DG process though they are quite different mechanisms.

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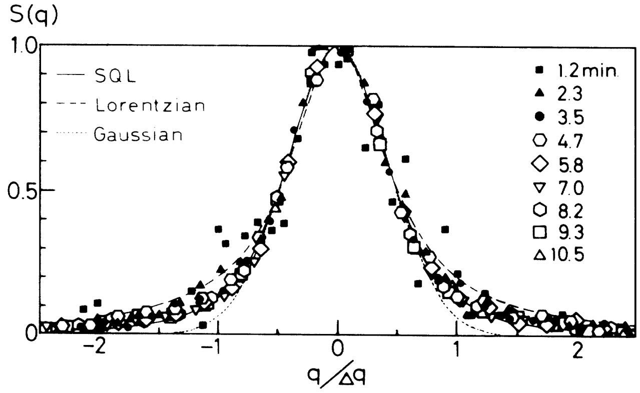

FIG. 5. The scaling function of the structure factor $S(q)$. All the (104) spectra in Fig. 1 are superposed; the intensity and width are normalized by the peak intensity and FWHM, respectively. Data points for $t=1.2$ min (solid squares) scatter from the others because of the weak intensity of the peak.

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