Nucleation, Growth, and Scaling in a Pressure-Induced First-Order Phase Transformation: RbI

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(Received 14 June 1984)

We have investigated the kinetics of the NaCl-to-CsCl phase transformation in RbI at room temperature ($P_c \approx 3.5$ kbar) by monitoring the time-dependent changes in neutron powder diffraction peaks. Above P_c the rate of growth of the stable phase increases with increasing pressure, but the growth curves display a universal shape, consistent with the Kolmogorov model of nucleation and growth, when plotted versus a scaled time parameter $\tau = t/\tau_0(P)$.

PACS numbers: 64.70.Kb, 61.12.Dw, 62.50.+p

In recent years there has been a renewed interest in the process of nucleation and growth at first-order phase transformations.[1] A key concept in modern understanding of these phenomena is that of scaling behavior. Computer simulations of the kinetics of order-disorder transformations[2] and spinodal decomposition[3] show a time evolution from metastable to stable equilibrium which satisfies structure-factor scaling laws. Experiments on spinodal decomposition in binary fluids and alloys also support this scaling behavior.[4]

At high pressures many alkali halides transform from the NaCl ($B1$) structure to the CsCl ($B2$) structure. Of the many studies devoted to this reconstructive first-order phase transformation, few have been concerned with the kinetics.[5-7] Daniels and Skoultchi[6] conclude that for freshly cleaved monocrystals of RbI, the transformation proceeds through nucleation at the surface. Hamaya and Akimoto[7] suggest that for polycrystalline KCl the transformation is controlled by homogeneous bulk nucleation for pressures not too close to P_c.

In this Letter we study the transformation of polycrystalline RbI, which transforms at a critical pressure $P_c \simeq 3.5$ kbar. By observing the time development of the neutron powder diffraction pattern after sudden application of hydrostatic pressure from $P < P_c$ to $P > P_c$ we directly deduce $X(t)$, the fraction of the sample converted from metastable to stable phase as a function of time. We show that over a wide range of characteristic times, $\tau(P)$, $X(t)$ obeys a simple scaling relation, $X(t,P) = X(t/\tau(P))$, and that the universal shape of the growth curve is well represented by a simple model of nucleation and growth.[8,9]

The sample was high-purity RbI purchased from Johnson Matthey Chemicals, Ltd. The largest detected metallic impurity was 40 ppm K. No analysis of anionic impurities was available. The material was used as received and had a granularity similar to common table salt. A 0.6-g sample was mounted in an aluminum alloy cell of a type previously described[10] with He gas as the pressure-transmitting medium. The pressure was measured, by use of a calibrated Manganin resistor located in the high-pressure intensifier, with a precision of ±30 bars. The accuracy of the measurement is believed to be about ±100 bars. All measurements were performed at room temperature with increasing pressure.

The neutron diffractometer at the Brookhaven high-flux beam reactor upon which the diffraction measurements were performed was equipped with a He-gas-filled multiwire area detector with a resolution of about 1 mm and located about 1 m from the sample. By means of a filtered 14-meV neutron beam it was possible to observe simultaneously Debye-Scherrer peaks from both high- and low-pressure phases with sufficient intensity with counting times of the order of 30 sec.

A typical example of the observed time development of a portion of the diffraction pattern is shown in Fig. 1. The peak corresponding to the (110) reflection of the CsCl-type ($B2$) structure gradually builds up while that of the (200) reflection of the NaCl-type ($B1$) diminishes. The resulting integrated intensities of both reflections plotted versus time for various pressures are summarized in Fig. 2. The fraction of sample transformed is given by

$$X(t) = \frac{I(t) - I(0)}{I(\infty) - I(0)} = \frac{I'(\infty) - I'(t)}{I'(\infty) - I'(0)}, \qquad (1)$$

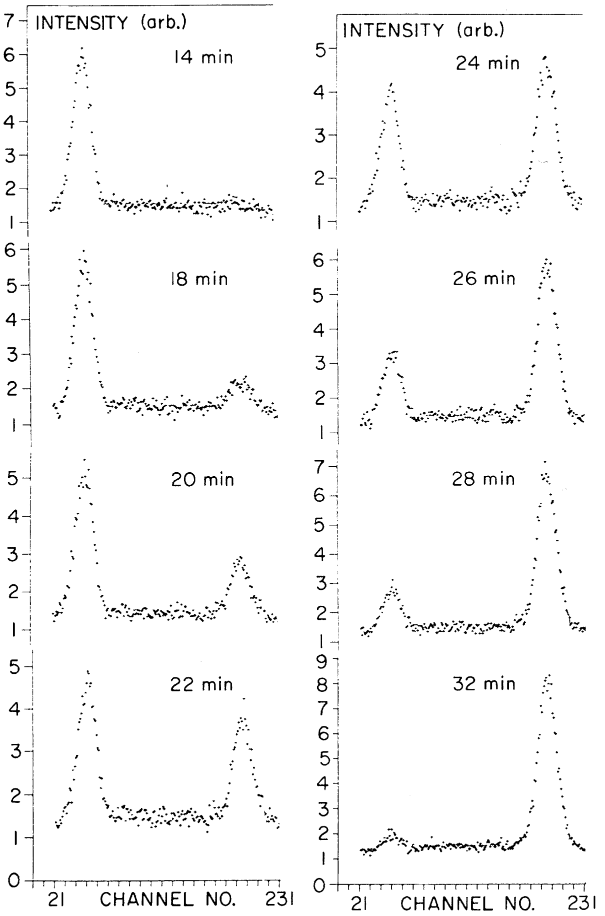

FIG. 1. A typical example of time sequence of the diffraction pattern obtained by integrating the output of the position sensitive detector along a line tangent to the Debye-Scherrer cone. The horizontal axis is the channel number of the detector. Note the change of scale of the vertical axis.

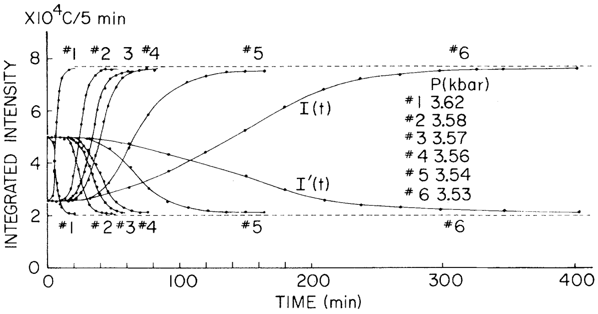

FIG. 2. Time dependence of $I(t,P)$ [integrated intensity of $(110)_{\mathrm{CsCl}}$] and $I'(t,P)$ [integrated intensity of $(200)_{\mathrm{NaCl}}$]. The dashed lines indicate the saturated values.

where $I(t)$ $[I'(t)]$ are the integrated intensities of the high- (low-) pressure phase. Values of $X(t)$ derived independently from $I(t)$ and $I'(t)$ agree to within $\sim 3\%$, which can be taken as a limit on the absolute (random plus systematic) error of the measurements.

At each pressure we define a characteristic scaling time $\tau_{1/2}$ for the transformation through the relation $X(\tau_{1/2}) = \frac{1}{2}$. Note from Fig. 2 that $\tau_{1/2}(P)$ diverges as P approaches $P_c \approx 3.5$ kbar. Figure 3 demonstrates that over a wide range of pressures $X(P,t)$ displays a universal shape when plotted versus a scaled time parameter, $\tau'(P) = t/\tau_{1/2}(P)$. We shall now discuss the possible implications of this scaling behavior, as shown through this universal growth curve, on the mechanism of the transformation. We will then return to a brief discussion of the scaling violation which occurs at $P = 3.53$ kbar, closest to P_c.

Perhaps the simplest picture of nucleation and growth which satisfies the required scaling is the following. When the pressure is instantaneously raised above P_c, infinitesimal grains of stable phase are produced randomly within the sample at a constant rate, Γ, per unit volume. Although $\Gamma(P)$ is time independent the nucleation rate decreases with time proportionally to the fraction of metastable phase remaining, $1 - X(t)$. Once formed, a grain grows isotropically with constant domain-wall velocity, $v(P)$, until it is impeded by impinging on neighboring domains. The required scaling follows directly from dimensional analysis. Since the model is completely characterized by two parameters Γ (with dimension $T^{-1}L^{-d}$ in a d-dimensional space) and v (dimension LT^{-1}), it follows that there exists a single characteristic time scale and length

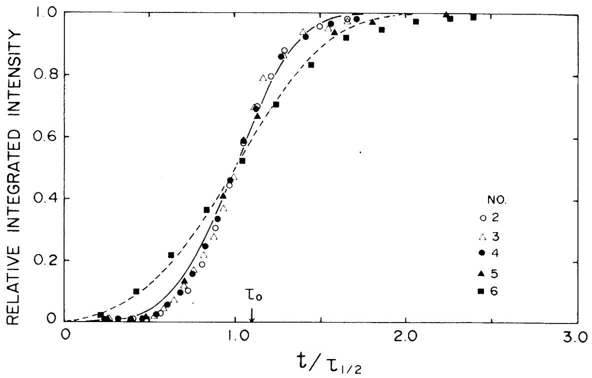

FIG. 3. The scaled curves of $I(t,P)/I_\infty(P)$ plotted in terms of $t/\tau_{1/2}$. They fall into a single universal curve except for the case of $P_f = 3.53$ kbar. The solid line is the curve $X(\tau)$ calculated by Eq. (5). The dashed line is the calculation when $\tau_c = 0.3$ (see text).

scale given by

$$\tau_0 = (\Gamma v^d)^{-1/(d+1)}, \tag{2a}$$

$$\xi_0 = (v/\Gamma)^{1/(d+1)}, \tag{2b}$$

respectively. The time development of any quantity is universal when expressed in terms of the scaled time $\tau = t/\tau_0$. Similarly any quantity associated with spatial development (e.g., domain size distribution function) is universal when expressed in a scaled length, $\xi = l/\xi_0$.

An explicit expression for $X(t)$ for this model was first given by Kolmogorov[8,11]:

$$X(t) = 1 - \exp[-\Gamma \int_0^t V(t')\,dt'], \tag{3}$$

where $V(t')$, the volume occupied by a hypothetical "free" grain (one that does not impinge on a neighboring grain) a time t' after nucleation, is

$$V(t') = D[vt']^d, \tag{4a}$$

$$D = 2, \pi, 4\pi/3 \quad \text{for } d = 1, 2, 3. \tag{4b}$$

On substitution we find the following universal shape for this model:

$$X(\tau) = 1 - \exp[-\tfrac{1}{3}\pi\tau^4], \tag{5}$$

with $\tau = t/\tau_0$ and $\tau_0 = (\Gamma v^3)^{-1/4}$ in accordance with Eq. (2) for $d = 3$. This scaled theoretical curve, Eq. (5), is compared with the experimental data in Fig. 3 and is seen to be in good agreement. The value of $\tau_0 \cong 1.11\tau_{1/2}$ can therefore be interpreted as a measure of Γv^3 for the transformation process.

It is clear from Fig. 3 that at the lowest pressure (closest to P_c), $\tau_{1/2}$ ($\simeq 145$ min) becomes very long and deviations from universal scaling appear. Among the various possibilities for this behavior we consider specifically the effect of a finite critical droplet size, r_c. Nuclei redissolve or grow according to whether their radius is less than or greater than r_c. We have thus far assumed $r_c \rightarrow 0$. The modification of Eq. (5) to include a finite r_c has been discussed by Ishibashi and Takagi,[12] who find

$$X(\tau) = 1 - \exp[-\tfrac{1}{3}\pi\{(\tau + \tau_c)^4 - \tau_c^4\}], \tag{6}$$

with $\tau_c = r_c/v\tau_0$. Since the formulation now includes two characteristic times, τ_0 and r_c/v, $X(\tau)$ is no longer universal. The dashed curve in Fig. 3 is obtained by the choice $\tau_c = 0.3$. If this interpretation is correct the observed value of τ_c indicates that the critical droplet size is already comparable to the average domain size at, say, $t = t_{1/2}$ for P close to P_c.

We are aware of the modest nature of the model assumptions which apparently represent our measurements, and we cannot justify them in detail. For example, it is well known that the rate of growth of grain boundaries depends, in general, on the local curvature of the grain interface.[13] (However, Coleman[14] has shown in the case of nucleation by quantum fluctuations that the critical domain size is large, at least compared to the thickness of the domain wall.) The shortcoming (as well as the principal appeal) of the model is its phenomenological character. If additional measurements testing the length-scaling hypothesis could be made, the characteristic size, ξ_0, so determined could be used in conjunction with τ_0 in Eqs. (2) to determine the basic model parameters $\Gamma(P)$ and $v(P)$. These quantities, particularly if measured versus temperature, would be useful in discussing the validity of more detailed microscopic models of the transformation. In the hope of testing the *length*-scaling hypothesis by diffraction measurements, we have initiated theoretical and computer simulations of the scattering function $S_q(t)$ for this model. Simultaneously we are planning to improve the experimental resolution in the hope of observing the effects of $S_q(t)$ through small-particle broadening of the powder pattern or more directly by small-angle scattering experiments.

This research was supported in part by the Division of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016, and carried out as part of the Japan–U. S. Cooperative Neutron Scattering Program (No. 8413).

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