Scaling in the kinetics of the order-disorder transition in Ni3Mn

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The kinetics of the atomic ordering in Ni3Mn has been investigated by time-resolved neutron-diffraction techniques. The results obtained show that dynamical scaling holds in the ordering process. The characteristic length grows consistently according to a power law. In addition, the growth exponent indicates a crossover, which can be attributed to the transition from coalescence of the ordered regions to migration of the domain walls. The scaling function for the structure factor is obtained and compared with the results of theories and computer simulations.

I. INTRODUCTION

The kinetics of first-order phase transitions, that is, the development of order in a rapidly quenched system, has recently received considerable attention as a problem of far-from-equilibrium phenomena. Such studies are classified into the following two classes: transitions in which the order parameter is conserved as in phase separation, and those in which the parameter is not conserved as in order-disorder transitions. For these growth processes the idea of self-similar growth—dynamical scaling—has been explored by many works.[1] This universality is expressed as follows. The growth of the characteristic length $R(t)$ as a function of time t is characterized by a power law,

$$R(t) \propto t^a \quad (t \geq t_0), \tag{1}$$

where a is some universal exponent which depends on the growth mechanism of the process, and the quantity t_0 denotes some initial transition time. Furthermore, the nonequilibrium structure factor behaves as

$$S(q,t) = R^d(t)F(qR(t)) \quad (t \geq t_0). \tag{2}$$

Here d is the dimensionality, q is the wave vector, and F is a scaling function. For the case of a nonconserved order parameter, several computer simulation studies have succeeded in verifying this idea,[2-6] but experimental work has not been done extensively.[7-9] The scaling behavior has not been examined in detail except in a recent study of Cu3Au by Noda, Nishihara, and Yamada.[10]

In order to investigate dynamical scaling in ordering kinetics further, we chose the Ni3Mn alloy for the following reasons. Firstly, the time constant is fairly long, which is advantageous for a study of the initial stage of the ordering process. Secondly, Ni and Mn atoms have similar sizes; hence, the elastic strain involved in the transition should be small. This is good for a comparison with theories or simulations. Thirdly, the transition is of first order, but seems to be close to second order.[8,11] It is, therefore, considered that both the singularity of critical fluctuations in the second-order transition and the com-

plexity of the nucleation and growth process in the metastable state in the first-order transition are relatively small. Accordingly, when the quench is done to a temperature fairly below the transition temperature T_c, we can easily avoid the singularity and complexity near T_c mentioned above; and moreover, we can investigate continuous ordering in the unstable state below the instability temperature T_i. (See Fig. 1, which schematically shows the free energy for a first-order transition as a function of the order parameter. The instability temperature T_i is defined as a temperature where the height of the potential barrier is zero; that is, the ordered state is not metastable but unstable below that temperature.)
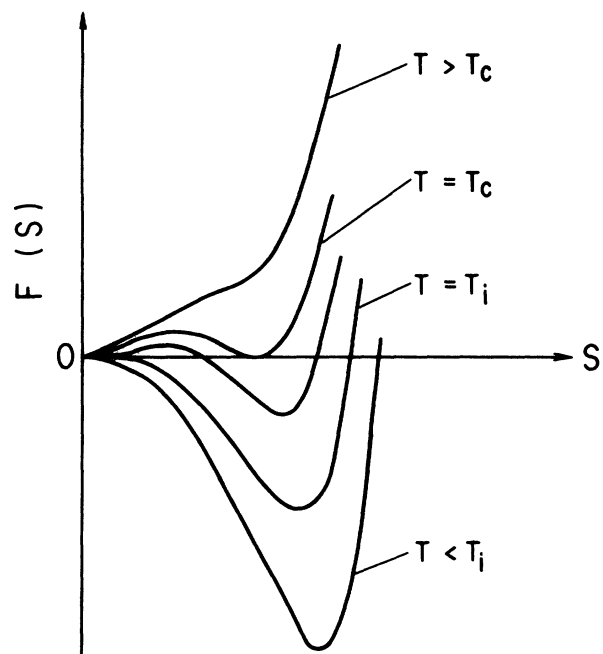

FIG. 1. Free energy vs the order parameter S at different temperatures for a first-order phase transition (schematic). The temperature T_c shows the transition temperature, and that T_i does the instability temperature.

Thus the results can be compared with those of recent theories and/or numerical simulations which usually dealt with this kind of continuous ordering. Finally, the neutron cross sections are favorable for these measurements because of the negative scattering length of Mn which enhances the intensity of the superlattice reflections.

In Ni_3Mn, Mn atoms can occupy any of four equivalent sites of the fcc lattice; therefore, the degeneracy of the order parameter is 4. Thus the ordered state consists of domains of those four kinds, as shown by electron microscopy.[12] Many recent works have shown that those domains coarsen by the motion of their interfaces, and the characteristic length $R(t)$ has a $t^{1/2}$ time dependence.

Previously, neutron diffraction studies on this alloy have been done by Collins and Teh,[8] and by Wakabayashi.[9] However, since they used a conventional furnace and diffractometer, it took more than 30 min to complete a stepwise temperature change and to obtain the first diffraction pattern. Therefore, their studies were restricted to the late stage of the ordering process. In the present work, we used a special furnace which can change the temperature very rapidly,[13] and a new kind of diffractometer, the wide-angle neutron diffractometer (WAND), installed at the High Flux Isotope Reactor at the Oak Ridge National Laboratory.[14] Since this diffractometer consists of a curved one-dimensional position-sensitive detector covering a 130° angle, we are able to do time-resolved neutron-diffraction experiments. As a result, we could investigate the whole process of the kinetics from the very initial to the final stage.

II. EXPERIMENTAL DETAILS

The polycrystalline Ni_3Mn alloy was prepared by melting 99.99%-pure Ni and Mn in an argon-arc furnace. To homogenize the ingot it was melted several times. Since the loss of weight was small, the nominal concentration (25.1 at. % Mn) was adopted. The sample which had a cylindrical form with dimensions of 6 mm diameter and 40 mm length was placed in the furnace. The sample was heated to 600 °C and kept at this temperature for 30 min to achieve the disordered state, and then the temperature was abruptly changed to 470 °C across the transition temperature T_c around 510 °C. By the quench, the temperature of the sample could reach the final temperature in about 15 s over that temperature difference. The transition temperature was estimated by measurements of the integrated intensity of the superlattice reflections in the equilibrium state. The value we determined is consistent with those reported in the literature.[15]

The following are reasons why the annealing temperature of 470 °C was selected. Experiments on the relaxation process show that the relaxation time is relatively fast around this temperature;[8,11] that is, the effect of the critical phenomena near T_c is not significant. Moreover, since the temperature 470 °C is fairly below T_c, that temperature is expected to be lower than the instability temperature T_i. This assumption is reasonable in consideration of the nature of the transition of this alloy, i.e., weak first-order character.

The growth of the superlattice reflections which appear below the transition temperature was investigated by the WAND. To observe the initial stage of the ordering kinetics up to 30 min, time-resolved measurements with 1 min increments were performed. In order to attain sufficient counting statistics, the identical measurements were repeated 30 times and each data set was accumulated in the memory of the data-acquisition system. For the later stage, time-resolved measurements for 6 min increments were repeated five times.

III. RESULTS AND DISCUSSION

A. Growth law

The time evolution of the (211) superlattice diffraction pattern is shown in Fig. 2, where the intensity is plotted against the wave vector. This superlattice line could be observed most accurately on our experimental condition. Since this pattern is symmetric, only half of it is shown. The data of this figure were obtained by smoothing the raw data using a least-squares fit to a third-order polynomial. The background level was also estimated by that fit as the level where the profile converges to a horizontal
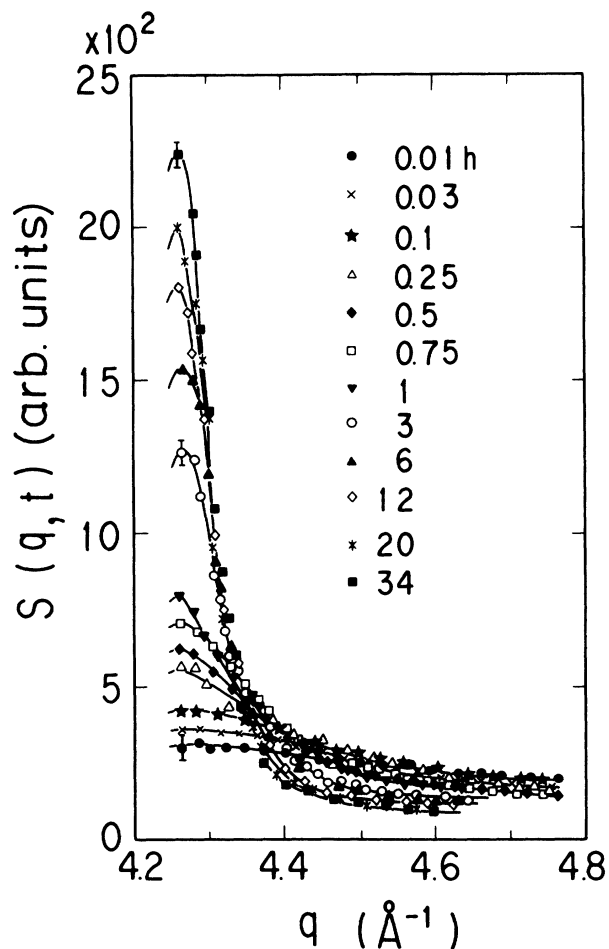
FIG. 2. Time evolution of the (211) superlattice diffraction pattern of Ni_3Mn (arbitrary units) after the temperature was abruptly changed from 600 °C to 470 °C.

line. As will be discussed later, since a simple analytical form of the profile which superimposes on the background is not clear at present, that procedure is the only way to estimate the background. (While we tried to fit the experimental result to simple Gaussian and Lorentzian curves, small but systematic deviations from these curves were obtained in the fit.)

As seen in the figure, a peak over a wide wave-vector range is observed already at the very initial stage after the quench. With time, the width of the peak becomes narrow [i.e., the size of the ordered region $R(t)$ grows], and the background level decreases. The integrated intensity of the measured profiles minus the background is shown in Fig. 3 as a function of time. This figure indicates that the intensity is nonzero at the initial stage, then it rapidly increases and approaches a constant value. The broad peak and the large integrated intensity which are observed instantaneously after the quench indicate that a large number of small ordered regions of four kinds are formed at this stage; however, the high background level at the same stage shows that the other portions are still disordered. Since it is considered that the state at 470 °C is in the unstable state as mentioned before, an analogy with spinodal decomposition in phase separation may be permitted. That is, small ordering fluctuations are formed spontaneously, and those diffuse regions of increasing order become sharp. The initial increase of the intensity probably corresponds with the rapid growth of ordering fluctuations. The disordered regions suggested by the high background level may be related with those fluctuations and may also involve the portions near the surfaces of the ordering regions. With time, these ordering regions with the fluctuations soon become well ordered and grow into domains. Such domains coarsen by the motion of their walls, and finally the ordering becomes complete.

In order to compare the results with the power law— Eq. (1)—the second moment $q_2(t)$ which corresponds to the mean square of the peak width [thus it is inversely proportional to the square of $R(t)$] was calculated. The moment q_2 is given as
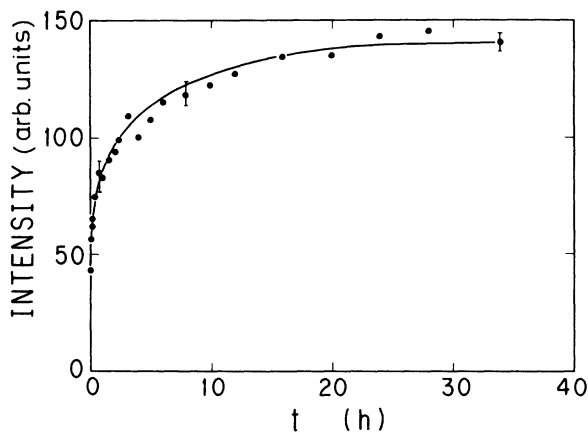
$$q_2(t) = \sum_q q^2 S(q,t) \Big/ \sum_q S(q,t) .$$ (3)

This procedure was taken because a simple analytical function which represents the profile is not clear at present; therefore, we cannot estimate the width of the profile by a conventional manner such as fitting to Gaussian or Lorentzian line shapes. Before the calculation, the background level estimated as mentioned before was subtracted. Furthermore, for the structure factor $S(q,t)$ we used the pure profile which was obtained by the deconvolution of the experimental profile using the (220) fundamental reflection as a measure of the instrumental resolution. Here an iterative method of successive folding was employed for the deconvolution.[16] The result is shown in Fig. 4 on a double logarithmic scale. On the calculations of q_2, the following point is made. The value of the moment is sensitive to the choice of the background level. In particular, when there are fluctuations in the intensity at large q, the background has to be chosen carefully. We, however, believe that reasonable values were obtained as the background levels by the procedure mentioned before. Those levels were changed within a reasonable range as a parameter, and errors of the value of the moment were estimated. Those errors are shown in the figure by error bars. As is clearly seen in this figure, the square root of the second moment $q_2^{1/2}$ decreases gradually but its entire time evolution cannot be expressed by a single power law. The result indicates that the growth of the ordered regions is slow at the initial state, then becomes faster and comes to an end. The final state is a mixture of four kinds of ordered domains. Our experiment indicates that the size of these domains at this stage is of the order of a few hundred Å.

As mentioned above, the data in Fig. 4 cannot be expressed by a power law with a single exponent. However, by choosing appropriate data points at the later stage, those data can be fitted by a straight line. The slope shown in the figure is $-\frac{1}{2}$. The fitted slope in this time range is -0.46 ± 0.03. This result is consistent with the prediction of Allen and Cahn for the growth process which involves the migration of domain walls driven by their curvature.[17] This exponent has been verified by many computer simulations and experiments. Accordingly, this growth mechanism is now generally accepted.
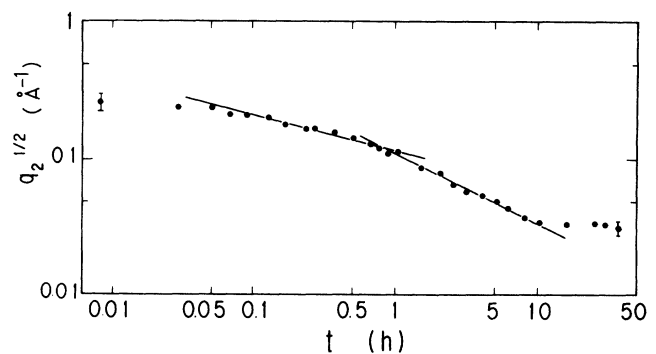

FIG. 3. Time dependence of the integrated intensity.

FIG. 4. Time dependence of the square root of the second moment $q_2^{1/2}(t)$. The solid lines show the exponent of the power law $a = \frac{1}{4}$ at the early stage and $\frac{1}{2}$ at the late one. The fitted slopes in the respective time region are -0.24 ± 0.02 and -0.46 ± 0.03.

For the earlier stage we can fit the data to a straight line with the slope of $-\frac{1}{4}$. The fitted slope in this range is -0.24 ± 0.02. Thus the exponent indicates a crossover, which was observed also in the studies of phase separation of Fe-Cr and Al-Zn alloys.[18,19] Therefore, it is thought that this kind of crossover is universal in the growth process. Theoretically, Furukawa predicted universal exponents for a system with the nonconserved order parameter.[20,21] In his theory, the exponent of the coalescence process by thermal energy k_BT is $\frac{1}{3}$ for bulk diffusion and $\frac{1}{4}$ for surface diffusion. Since our result indicates $\frac{1}{4}$, it is suggestive that coalescence dominated by surface diffusion takes place during this stage. It should be noted here that the growth mechanism by coalescence in the early stage has been suggested for a long time, and it was pointed out again recently.[22] Moreover, quite recently Furukawa observed a similar crossover of the exponent in the computer simulations for the two-dimensional ordering kinetics.[23]

At the initial stage earlier than about 3 min, the time dependence of q_2 is very weak. In this time range it is considered that the ordered regions are being formed; that is, the ordering fluctuations are growing in amplitude without changing their sizes and soon the boundaries of these regions are becoming sharp similar to the process in spinodal decomposition.

Thus the present result indicates that the ordering process changes from the first stage of the formation of ordered regions to the stage of the growth by the coalescence of these regions (the exponent $\frac{1}{4}$) and then to that by the migration of domain walls (the exponent $\frac{1}{2}$). Finally, the growth of those domains may terminate on grain boundaries, dislocations, and so on: The system comes to an equilibrium state.

The present result is very similar to that of Hashimoto et al. for the Cu_3Au alloy; that is, the initial stage in their result also shows slow growth. Although they interpreted their result by assuming the formation of small ordered regions (about 25 Å) at the moment of the transition (i.e., $t=0$), our detailed experiment indicates that fairly small ordered regions (about 10 Å) at the initial stage actually grow with time according to a power law. The results of Noda et al. for Cu_3Au are, however, considerably different from these. They observed a very fast growth in the early stage. While the reason for such a difference is not clear at present, it should be noted that Noda et al. performed extensive diffraction experiments especially near the transition temperature, and they interpreted their results by the nucleation-growth mechanism.

B. Scaling function

To extend the comparison with the scaling theory, we have calculated the normalized scaling function $\bar{F}$, according to Eq. (2). Since the square root of the second moment $q_2(t)$ is inversely proportional to $R(t)$, the normalized scaling function is calculated as follows:

$$\bar{F}(q/q_2^{1/2}(t))=(q_2^{3/2}(t))\bar{S}(q,t) ,$$ (4)

where the normalized structure factor $\bar{S}(q,t)$ is defined as

$$\bar{S}(q,t)=S(q,t)\Big/\sum_q q^2 S(q,t)\delta q .$$ (5)

Here δq is the wave-vector increment in the calculation of the sum, and again the structure factor $S(q,t)$ is the deconvoluted profile with background subtracted. The normalization is necessary to compare the result with the scaling theory, because the background level of the profile was subtracted from the measured intensity whereas the theory does not involve the scattered intensity from the disordered part. The plots of $\bar{F}(x)$, where $x=q/q_2^{1/2}$, for different times are shown in Fig. 5. It is found that the scaling is well satisfied after the initial transient time; after about 10 min when the exponent $\frac{1}{4}$ is followed well. Moreover, the result indicates that the scaling function becomes a little sharper at the late stage, roughly corresponding to the crossover of q_2. However, the change is not drastic, as seen in Fig. 5, compared to the result observed in phase separation of an Fe-Cr alloy.[18] This suggests that the factors such as cluster shapes or correlations between clusters in the present case are not changed drastically over the whole process.

For a system with the nonconserved order parameter, the scaling function $F(x)$ was calculated by Ohta, Jasnow, and Kawasaki[24] on the basis of the motion of domain walls by the mechanism of Allen and Cahn. On the other hand, experimentally, Noda et al.[10] proposed the squared Lorentzian curve for the fit to their experimental results for the Cu_3Au alloy. Both of these curves have a $1-x^2$ dependence at small x and a x^{-4} dependence at large x. Our result also shows that these x dependences in each x range; that is, the asymptotic behavior of the experimental results agree with those two
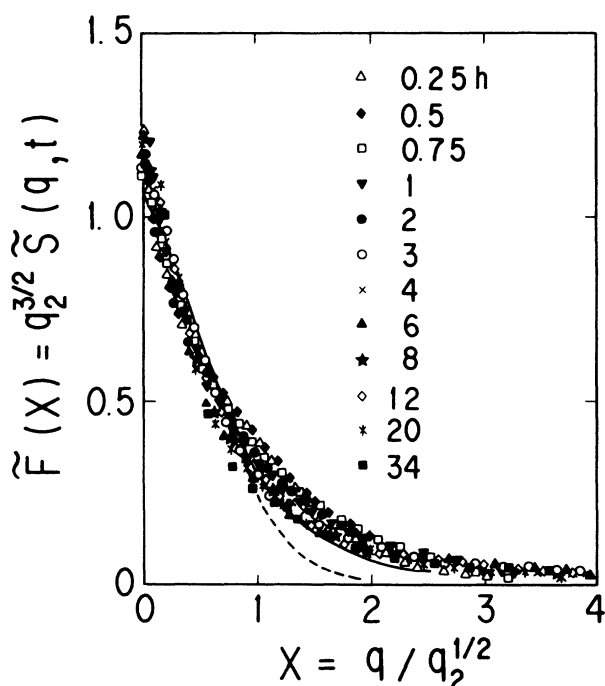

FIG. 5. The scaling function of the normalized structure factor. The dashed curve represents the result of the theory by Ohta et al., and the solid one is the squared Lorentzian.

curves. However, for a more precise comparison there is an ambiguity in the scales of the vertical and horizontal axis. We have introduced adjustable parameters for these scales. In Fig. 5 the dotted curve is the result of Ohta *et al.*, and the solid one is the squared Lorentzian. Note that for each curve $F(0)$ is put equal and $F(x) \simeq 1 - x^2/c + O(x^4)$ at small x, where c is a constant. The experimental result seems to indicate a small deviation from the theory of Ohta *et al.*; rather, the squared Lorentzian represents the result well.

A similar situation is observed also in the comparison between those two curves and the results of computer simulations or a renormalization theory in the two-dimensional system; that is, the squared Lorentzian rather than the result of Ohta *et al.* shows a very similar feature to the dynamical scaling function obtained in those studies.[5,25,21] While we did not directly compare the present scaling function with the results of computer simulations or of the renormalization theory because of the difference in the dimensionality, the results mentioned above suggest that the squared Lorentzian can explain the scaling function observed in this experiment as well as that deduced in the simulations or the renormalization theory. However, the squared Lorentzian was firstly proposed for small-angle scattering by an inhomogeneous material.[26] Thus it is not clear whether or not the assumption in that theory (randomly distributed clusters in the material) is applicable to the case of ordered domains. A more detailed theory is required.

IV. CONCLUSION

The whole process of the ordering kinetics in Ni_3Mn was investigated from the very initial to the final stage by time-resolved neutron diffraction. The experimental results can be interpreted as the continuous ordering in the unstable state. The subsequent growth of order is explained by recent theories on the basis of scaling concepts: the self-similar growth. The growth is characterized by a power law. Moreover, a crossover in the growth mechanism is found. Since a similar crossover was also observed in the kinetics of phase separation, it is considered that this kind of crossover appears universally in the growth of order. The experimental form of the scaling function can be expressed by the squared Lorentzian. However, more extensive theoretical work on the form of the scaling function may be necessary.

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