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Neutron-diffraction study on the kinetics of the atomic order in Ni_3Mn

N. Wakabayashi
Department of Physics, Keio University, Yokohama 223, Japan
and Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

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In order to study the kinetics of the order-disorder transition in Ni_3Mn, we investigated the time dependence of the (110) superlattice peak by neutron scattering techniques. The integrated intensity and the peak width were measured for various types of temperature-change sequences. The time dependence of the intensity was found to be strongly affected by the size of the ordered region, and it is shown to be described by a phenomenological model involving a relaxational-time dependence modified by the size effect.

I. INTRODUCTION

The kinetics of first-order phase transitions is a subject of considerable interest. Phase separation, in particular, has been studied rather extensively by measuring the time dependence of the small-angle x-ray and neutron scattering patterns.[1] Such measurements have made it possible to compare theoretical predictions with experimental observations much more quantitatively than electron-microscopic studies have allowed. It seems to be well established that the transition in the unstable region is due to the spinodal decomposition and that in the metastable region the nucleation and growth mechanism is responsible for phase separations, although a sharp distinction between the two regions cannot always be observed.

The kinetics of the order-disorder transition of first order seems to have been studied less extensively. Cu_3Au and CuZn (β-brass) are the typical alloy systems with this kind of transition. The time development of the electrical resistivities on both alloys have been measured, and the relaxation times have been extracted from the results.[2,3] The superlattice peak associated with the ordered state for Cu_3Au has been investigated as a function of time by means of the x-ray diffraction technique and an interesting, dynamical scaling has been reported.[4] In the pioneering work of Marcinkowski and Brown[5] the time-dependence measurements of neutron-diffraction peaks were carried out at room temperature on a quenched Ni_3Mn sample. In the present report a neutron-diffraction study of the kinetics of the ordering in Ni_3Mn is presented. The time dependences of the (110) superlattice-peak intensity and width were measured with the sample at various temperatures and for various types of temperature-change sequences. The time dependences of intensity for some sequences were found not to be describable as simple relaxational processes. All the data are interpreted on the basis of a phenomenological model.

II. EXPERIMENT AND RESULTS

A polycrystalline sample in the form of a plate with dimensions of $20\times40\times3$ mm^3 was used. The sample was mounted on a copper block which contained a heater and a thermocouple which was used to control the temperature. An additional thermocouple was attached to the sample in order to determine the sample temperature. Since the transition temperature should be about 500 °C, the sample was heated to 590 °C for more than 20 min whenever it was necessary to bring the sample into the disordered state. Measurements were carried out on the HB-1A triple-axis neutron spectrometer installed at the High Flux Isotope Reactor of the Oak Ridge National Laboratory.

The (110) superlattice peak was measured as a function of time after the sample temperature had been changed from an initial temperature T_i to a final temperature T_f. θ-2θ scans were performed in order to maintain the symmetric reflection geometry during the measurements. Each scan typically took about 40 min to be completed. An example of the time development of the peak for $T_i = 590$ °C and $T_f = 467$ °C is shown in Fig. 1. The time denoted in the figure corresponds to the midtime of the scan. The intensity is plotted against the neutron momentum transfer Q in units of $Å^{-1}$. The width Γ_M and the

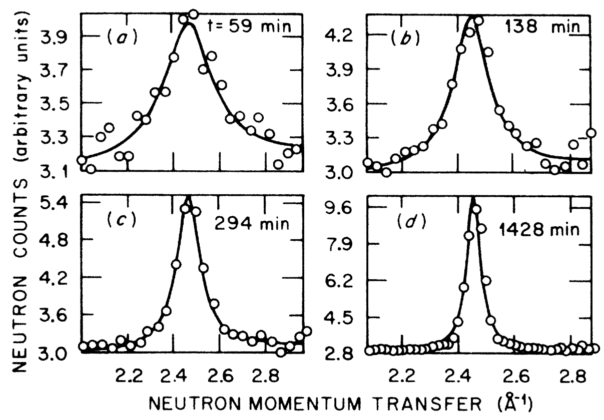

FIG. 1. (110) superlattice peaks at various times after the sample temperature was lowered from 590 to 467 °C. [The abcissa for (d) is slightly expanded in comparison to other figures.]

integrated intensity of each peak were determined by fitting the peak with a Lorentzian. The (111) fundamental peak was found to be well fitted by a Gaussian, and it was used to determine the instrumental resolution. The instrumental width for the (110) peak, Γ_R, was estimated to be 0.031 Å^{-1}. The intrinsic width Γ is assumed to be given by $\Gamma=(\Gamma_M^2-\Gamma_R^2)^{1/2}$.

Three different types of measurements were performed depending on T_i and T_f: type I, $T_i>T_c>T_f$; type II, $T_c>T_i>T_f$; and type III, $T_c>T_f>T_i$, where T_c is the transition temperature. Figure 2(a) and 2(b) represent the integrated intensity and the width Γ_M, respectively, as functions of the time elapsed after the sample temperature was decreased from $T_i=590\,°\text{C}$ to T_f indicated in the figures (type I). Since it took about 15 min for the sample temperature to reach T_f, there is an uncertainty in the position of the time origin, i.e., $t=0$, but it is believed to be of the order of 15 min. The saturation intensity is higher for lower T_f but it takes a longer time to reach saturation, as can be seen clearly from the data for $T_f=430\,°\text{C}$. The widths also change more slowly at lower T_f's. Figure 3 shows two examples of measurements carried out in the type-II temperature sequence after the sample had remained at T_i for 20–30 h. This heat treatment produced rather small widths already at $t=0$ in this type of measurement [see Fig. 2(b)]. The subsequent change in Γ at T_f is correspondingly small, although the widths are significantly larger than that due to the instrumental resolution. There are two distinct time developments in the type-III sequence as shown in Figs. 4 (III*A*) and 5 (III*B*). In the type-III*B* measurements, the sample temperature was lowered to T_i from 590 °C and was held at the temperature for about 30 h before it was raised to T_f. This procedure corresponds to initiating the measurements at the end of the type-I measurements for $T_f=430$ and 440 °C (Fig. 2). Before starting the type-III*A* measurements, the sample was kept at 480 °C for about 40 h until the widths became very narrow, and the temperature was subsequently lowered to T_i. After the intensity corresponding to the equilibrium intensity for T_i was attained, the measurement was started by raising the temperature to T_f. The intensities shown in Fig. 5 do not exhibit simple relaxational time dependences, in contrast to those of Fig. 4. It should be noted that the widths shown in Fig. 5 are larger and change significantly during the time of obser-

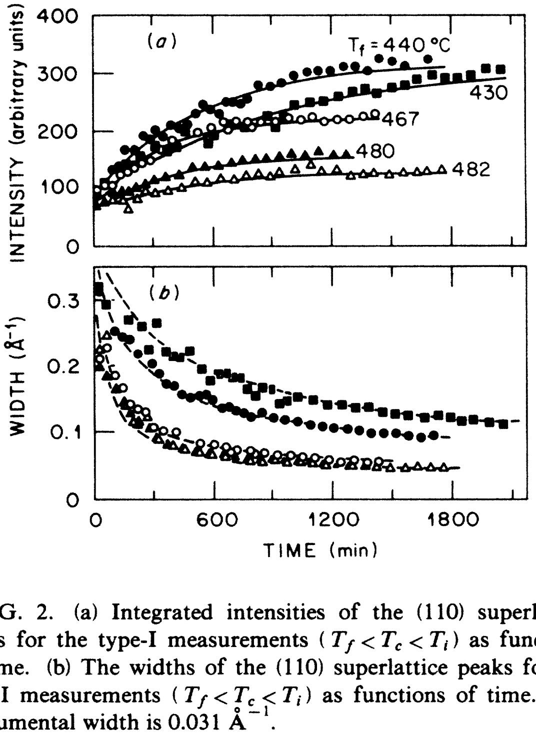

FIG. 2. (a) Integrated intensities of the (110) superlattice peaks for the type-I measurements ($T_f<T_c<T_i$) as functions of time. (b) The widths of the (110) superlattice peaks for the type-I measurements ($T_f<T_c<T_i$) as functions of time. The instrumental width is 0.031 Å^{-1}.

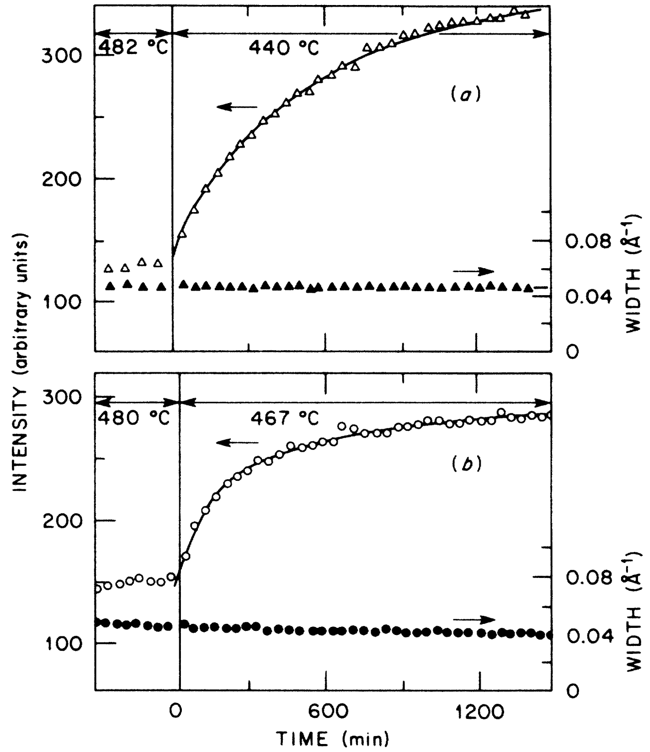

FIG. 3. Widths (solid symbols) and the integrated intensities (open symbols) of the (110) superlattice peaks for the type-II measurements ($T_f<T_i<T_c$).

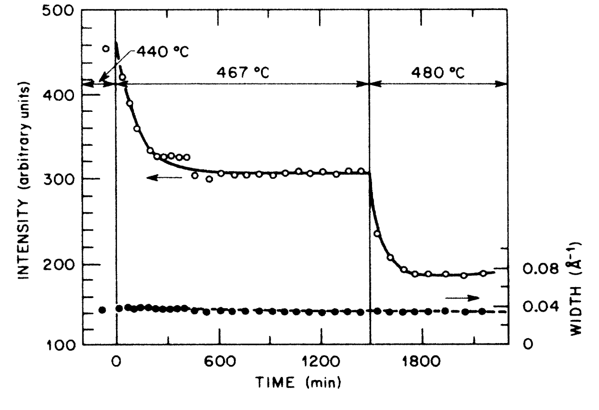

FIG. 4. Widths (solid circles) and the integrated intensities (open circles) of the (110) superlattice peaks for the type-III*A* measurements ($T_i<T_f<T_c$).

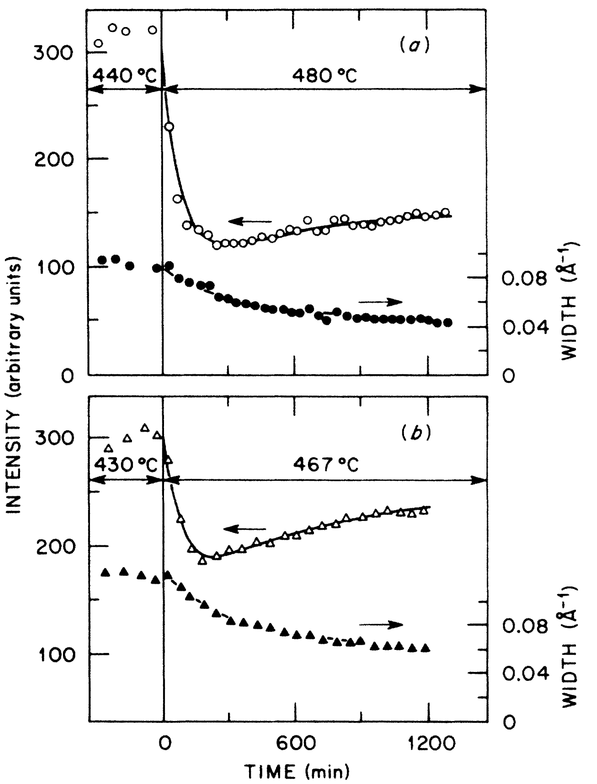

FIG. 5. Widths (solid symbols) and the integrated intensities (open symbols) of the (110) superlattice peaks for the type-IIIB measurements ($T_i < T_f < T_c$).

vation, whereas those of Fig. 4 are essentially resolution limited. It seems, therefore, that the unusual time dependence of intensity is associated with the large width of the peak.

III. DISCUSSION

In each measurement of type I, the smallest value of t for which an intensity measurement could be made was about 0.3 h, and therefore it was impossible to follow the time dependence during the initial period. As indicated by the results in Fig. 2(a), the integrated intensity increases very rapidly within the initial period, and thereafter a more gradual intensity change occurs. Thus there is a natural division of the observed time development into two periods. Since the initial period is very short, no meaningful time-dependence measurements could be performed, and the present data can give information only about the later period. The ordering kinetics are considered to have two extreme stages. The initial stage develops extremely rapidly and should be describable by a linear theory analogous to that of the spinodal decomposition.[6] This stage may correspond to the initial periods of type-I measurements. The other extreme is the final stage, and it is characterized by the existence of sharp antiphase boundaries and the dynamics of these boundaries should be described on the basis of a model such as the drumhead model.[7] The diffraction peak intensity in this stage is not expected to be time dependent and the peak width may be too small (or the size of the ordered region is too large) so that its time dependence may be impossible to detect with a standard diffractometer. Since we always observed a time variation of the intensity, it may be concluded that the present measurements correspond to the intermediate stage between the two extreme cases.

The peak width is determined by the average size L of the ordered region. Consequently, for our purposes L can be estimated from $2\pi/\Gamma$, where Γ is given in Å^{-1}. The size of the ordered region L as a function of time has been discussed on the basis of various models for the kinetics.[8] The theory of Kawasaki and Ohta based on the drumhead model predicts the relationship[9]

$$L^2 - L_0^2 = 2kt \ , \tag{1}$$

where L_0 is the size at $t=0$. However, this type of time dependence seems to be valid even at the stages prior to the one that is describable by the drumhead model.[10] In the present analysis Eq. (1) is assumed to give the time dependence of the size throughout the period corresponding to each sequence of observation. By properly choosing the values for k and L_0 in Eq. (1), the time dependence of the measured width could be reproduced reasonably well as shown by dashed lines in Figs. 2(b) and 3—5.

The time dependence of the integrated intensity observed in the type-I measurements can be expressed as $I = I_0(1-e^{-t/\tau})$, if the initial part of the intensity change is subtracted as a constant. (In the following analysis of the type-I data, this subtraction is always performed.) However, the values of the relaxation time τ which reproduced the intensity data were found to be larger by a factor of 2—7 than those estimated from the results of the neutron-diffraction study of Collins and Teh.[11] On the other hand, the data of type IIIA and those of the type II for $T_f = 440°$ C [Fig. 3(a)] could be reproduced by

$$I = I_0(1-e^{-t/\tau}) + I_1 \ , \tag{2}$$

with $\tau = 50$, 100, and 460 min for $T_f = 480$, 467, and 440 °C, respectively. These values are in much better agreement (within 30%) with those of Ref. 11. It is evident that the data of type IIIB cannot be described by Eq. (2). The essential difference between the data of type IIIA and IIIB is that the widths of the type-IIIB measurements are very large (i.e., the ordered regions have small sizes), while those of the type IIIA measurements are nearly equal to that due to the instrumental resolution. Therefore, the values of τ reported in Refs. 3 and 11 seem to correspond to those of a system in which the ordered region is essentially macroscopic in size. It may be assumed that, even in earlier stages of ordering kinetics, these values of τ determined above characterize the time dependence of the ordering within an ordered region of microscopic size. However, a portion near the surface of the region is expected to be significantly disordered and does not fully contribute to the intensity, and a factor representing the size dependence of the intensity should be taken into consideration. The fraction of this type of disordered volume is proportional to surface/volume $\propto 1/L$. Thus one can write

$$I=[1-\alpha/L(t)][I_0(1-e^{-t/\tau})+I_1]\ , \qquad (3)$$

where α is a parameter which depends on T_f. τ in Eq. (3) is assumed to be equal to the values given above as determined from the data for which the region size L is so large that the size effect α/L is negligible. The type-I and type-IIIB data, as well as those shown in Fig. 3(b), were then fitted by Eq. (3) for various values of α. Table I contains the values of α which best describe the data. The sum $I_s=I_0+I_1$ is the intensity at $t=\infty$ and should correspond to the intensity of the system in equilibrium. This quantity seems to be uniquely determined for each T_f, except for that obtained from the data of Fig. 3(b). This fit also has an unusually large value of α, and more reasonable values of α and I_s could be found if the quality of the fit is slightly sacrificed. From the plot of I_s versus T_f, the transition temperature was estimated to be 500±10 °C. The solid lines in Figs. 2(a) and 3–5 are those corresponding to the values of the parameters given in Table I. It should be noted that the model can describe the "undershoot" of the data in Fig. 5. Owing to the small size of the ordered region at $t=0$, the size factor $1-\alpha/L$ is quite small for small values of t. Since τ is rather small at these T_f's, the intensity decreases rapidly toward a small value $(1-\alpha/L)I_s$. It eventually increases as the region size becomes larger, thus producing a minimum in the intensity at an intermediate time. It may be concluded that, aside from the behavior observed at the initial stage of the type-I measurements all of the observed time development can be characterized by a relaxation time appropriate to T_f if the effect due to the finite size of the ordered region is taken into consideration. The initial stage for the type-I measurements may be described by the linear theory which predicts that the growth is described by an exponential function with a positive exponent.[6]

Collins and Teh[10] did not give information about peak widths, but they reported that a simple time dependence given by Eq. (2) could not be observed if the initial state was not already in equilibrium, which indicates the importance of the size effect. A similar experiment on Cu_3Au by the x-ray diffraction method was carried out by Nishihara *et al.*[4] Their measurements correspond to the type-I sequence and $\Delta T=T_f-T_i$ was between 4 and 11 K. The results of their intensity measurements were reported to be represented by Eq. (2) except for T very close to T_c. They also found a scaling of the intensity-time curve in terms of the incubation time τ_t. In the present measurements the definition of τ_t was not clear and no attempt has been made to test the validity of the scaling law for Ni_3Mn.

IV. CONCLUSION

The time development of the (110) superlattice peak intensity of Ni_3Mn is described by an expression which involves the relaxation time and the size effect. A more microscopic justification of the expression of Eq. (3) is obviously needed. However, there is, at present, no microscopic theory which deals with the intermediate stage of ordering, and measurements similar to the type-IIIB measurements in this paper should be useful in developing such theories. The very initial stage of ordering was not resolved in the present experiment. A furnace which is capable of more rapid changes in the sample temperature is essential in such a measurement. Also, a position-sensitive detector which collects intensity data simultaneously for a wide angular range is needed. In these respects, the x-ray diffraction method may be more suitable in some alloys, although the method is unsuitable to measurements on Ni-Mn alloys. However, the very fact that Ni and Mn are difficult to distinguish in the x-ray diffraction method offers a possibility for detecting, unambiguously, the diffuse scattering due to lattice distortions which may accompany the order-disorder transition. A similar possibility exists in the Cu-Au system for the

TABLE I. Values of the model parameters.

Type	T_i (°C)	T_f (°C)	τ (min)	α (Å)	I_0+I_1	L_0 (Å)	k ($\text{Å}^2\,\text{min}^{-1}$)
I	590	482	46[a]	57.8	138	33[b]	9.0
I	590	480	46[a]	39.8	178	33[b]	9.0
I	590	474	60[a]	72.5	231	30[b]	7.6
I	590	467	100[a]	29.8	259	35	6.0
I	590	455	180[a]	29.1	354	20[b]	3.3
I	590	440	460[a]	10.6	355	13	1.5
I	590	430	690[a]	11.5	356	9[a]	0.71
II	480	467	100[a]	100.5	518	186	6.0
II	482	440	460	0	341	188	1.5
IIIA	440	467	100	0	305	268	6.0
IIIA	467	480	46	0	187	329	9.0
IIIB	440	480	46[a]	39.4	189	81	9.0
IIIB	430	467	100[a]	32.2	319	54	6.0

[a] Fixed in fitting the data.

[b] α/L_0 is very large, so that the calculated intensity near $t=0$ may not be meaningful.

neutron-diffraction method since the neutron scattering length of Cu is almost identical to that of Au. Such experiments will be carried out in the near future.

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