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Thermodynamic character of the order-disorder transition in nickel-manganese alloys[*]

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X-ray investigation of a nickel-manganese alloy (26.8-at.% Mn) shows the existence of an extensive two-phase field between the disordered and ordered forms. Recent observations of "critical slowing down" in this system must therefore be interpreted with caution.

It has recently been reported by Collins and Teh[1] that the rate of disordering of a nickel-manganese alloy showed "critical slowing down," as if the transition were of higher order than first. Since a number of crystallographically identical transformations have been shown[2] to be of first order, as required by Landau's rules,[3] it seemed to us that characterization by more direct means was desirable.

A latent heat of transformation is associated with the coexistence of two phases of different densities and, in binary systems, generally of different compositions. Only at an extremum (with respect to composition) of the transition temperature do the phases have the same composition, and alloys like Ni$_3$Mn usually show a maximum at the A_3B composition. Our purpose being to demonstrate by x-ray diffraction the presence (or absence, within limits) of a region of heterogeneity, we chose an alloy richer in manganese than the ideal composition. The effects on density of ordering and composition difference would then be of the same sign, if, as usual, the ordered phase had the higher density. The specimen, containing 26.8-at.% Mn, was a grain 4×4 mm in size at the edge of a disk 1 cm diam and 1 mm thick. This grain was found to have [110] 12° from the normal to its surface. The disk was mounted in a suitable holder enclosed by a furnace supported on a goniometer[4] in high vacuum. Openings in the furnace and surrounding radiation shields permitted observations of the (110) and (220) Bragg reflections of Cr$K\alpha$ x-rays, selected by diffraction from a bent pyrolytic-graphite crystal. The sample temperature was read by a Pt-Pt-10%-Rh thermocouple clamped to the holder. Because sample and thermocouple temperatures differ by an unknown amount, no significance should be attributed to the absolute values given in what follows. However, none of our conclusions is dependent on a knowledge of more than relative temperatures, which should be fairly reliable. Further, since the side of the sample facing the x-ray beam was opposite to that on which the thermocouple junction was located, and received thermal radiation from the hotter half of the furnace, all temperatures given are probably *lower* limits to the true sample temperature.

The intensity of the (110) reflection is proportional to the square of the long-range-order parameter and, in a two-phase field, to the volume fraction of the ordered phase.[5] The observed temperature dependence is shown in Fig. 1, where the open circles are peak intensities measured in a series of experiments extending over a period of four days. On the fifth day it was found that the reflection had narrowed appreciably because of antiphase-domain growth, so the series was terminated. The solid circles are data taken with improved angular collimation and pulse-height discrimination, and using a balanced vanadium-titanium filter. These changes were needed to eliminate the contribution from the (220) half-wavelength reflection, which was increasingly troublesome as the superlattice reflection weakened. A factor has been applied to these points to join them smoothly to the first series in the range 510–520 °C. The

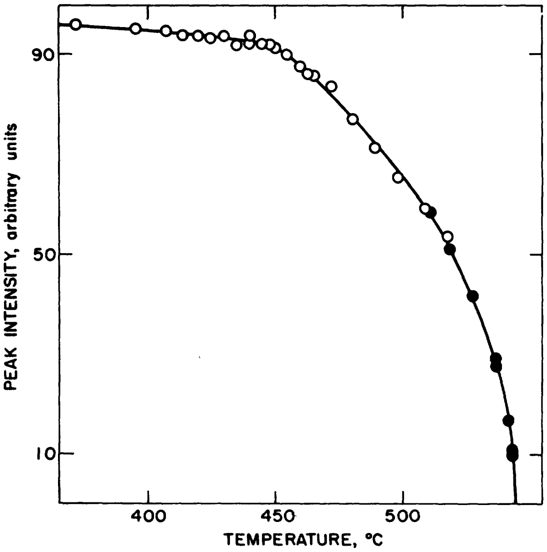

FIG. 1. Peak intensity of (110) superlattice reflection vs temperature. For clarity, many points appearing in Fig. 2 have been omitted or averaged.

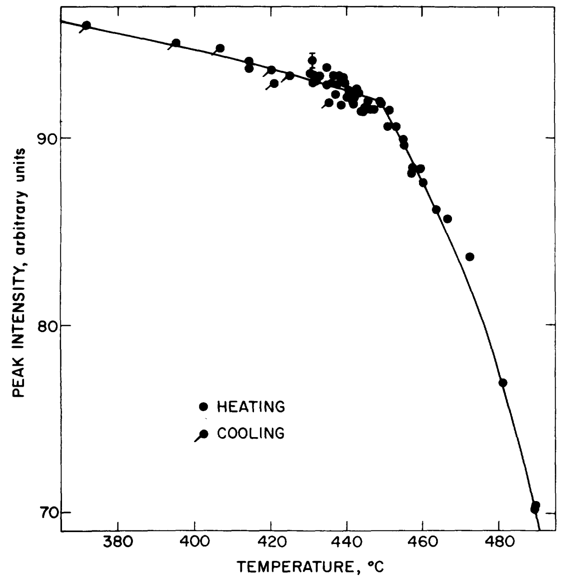

FIG. 2. Peak intensity of (110) reflection, vertical scale expanded to show behavior near 450 °C better. Error bar shows statistical uncertainty for majority of points; some points are averages with smaller errors.

intensities from 528 °C up vary approximately as $(T_0 - T)^{1/2}$, with $T_0 = 544.5$ °C.

In Fig. 2, the data near 450 °C are shown on a greatly expanded scale. It seems inescapable that there is a cusp at about 448 °C marking the lower end of a two-phase field which terminates at 544.5 °C for this composition.

In the two-phase region, we observed broadening of the superimposed (220) reflections of the ordered and disordered phases (the orientation of the original crystal apparently was retained throughout a number of disordering and reordering sequences). At room temperature, with additional collimation in the incident beam, the $K\alpha_1$ and $K\alpha_2$ components of (220) were well separated, and the full width at half-maximum of the former was 0.105° at a Bragg angle of about 64°. The breadth increased to a maximum of 0.154° at 500 °C, and fell again to 0.12° at 578 °C. After reordering for three days at 477 °C, the width was again only 0.112°. The maximum broadening observed is that which would be produced by superposition of the reflections from equal amounts of two phases differing by 0.05% in lattice parameter.

The lattice parameter calculated from the mean Bragg angle of the (220) reflection is an average of that of the phases present, weighted roughly as their volume fractions. From Fig. 3 it can be seen that the average lattice parameter increases from room temperature to 300 °C at a normal rate, but that the apparent expansion coefficient rises to a maximum around 500 °C, and falls again to nearly a normal value above 580 °C. If the transition were of higher order, the maximum (probably infinite) would have occurred at the temperature of disappearance of the long-range order (544.5 °C). The maximum that seemingly occurs midway in the transition range coincides with the maximum in rate of conversion of the ordered phase into the disordered, rather than with any anomaly in the expansion coefficient of the separate phases.[6]

It seems clear, on the basis of measurements of three independent properties of this sample, that the transition is first order. Nevertheless, a characterization as such would be incomplete and misleading. First, if the ordered phase retained a typically high degree of order right up to the phase boundary, the (110) intensity would vary linearly with temperature in the limit $T \rightarrow T_0$. The observed vertical slope must be due to a rapid drop of the long-range order itself as $T \rightarrow T_0$ and at the (unknown) composition of the ordered phase in equilibrium with the disordered phase at our composition. Marcinkowski and Brown[7] also show the superlattice reflection intensity vanishing with vertical slope for their sample (22-at.% Mn) at 520 °C. This temperature and our value (545 °C) are both *higher* than that given by Collins and Teh at an intermediate composition[8] (25.8-at.% Mn). If all

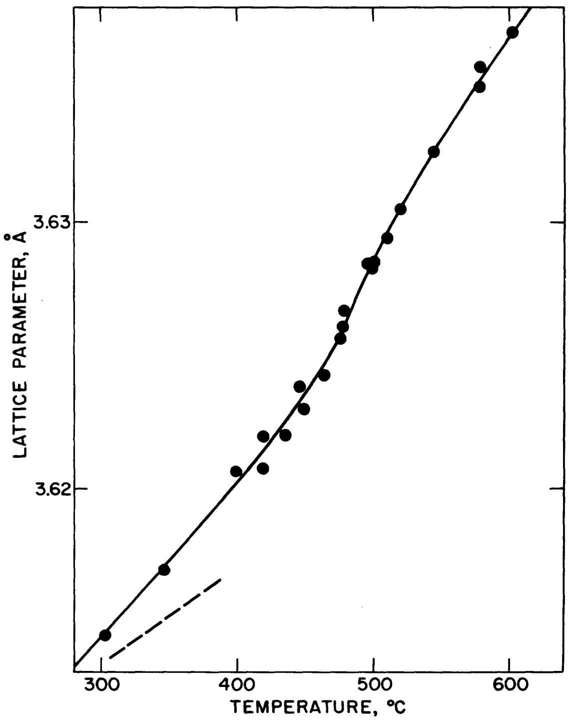

FIG. 3. Mean lattice parameter vs temperature. The dashed line indicates the average slope between room temperature and 300 °C.

these numbers are taken at face value, the equilibrium diagram must be quite different from the normal form, which would show the long-range order going to zero at a *maximum* temperature for a composition near 25-at. % Mn.[9] A thorough study of the diagram is needed.

Second, the effects of temperature and composition change along the phase boundaries must combine to produce anomalously large expansion coefficients of the separate phases. The values outside the two-phase region, though very rough, would suggest at least a 0.1% difference in lattice parameter for these phases at the same temperature, but the maximum broadening is only half this amount.

Finally, we have qualitatively confirmed the observation by Collins and Teh[1] that the rate of disordering decreases dramatically as the long-range order falls to zero. At most temperatures the rate was too large to be measured accurately in our system. However, at 543.5 °C (1 °C below T_0), during an initial period of about 1 h, the intensity fell exponentially with a characteristic time of ~45 min; the disordering was followed for some 8 h more, during which the characteristic time was about 220 min. Collins and Teh would have observed this time at about 2.5 °C below their apparent critical temperature. One would conjecture that a system having a first-order transition would show critical slowing-down, if at all, at a virtual trnasition temperature where the long-range order fell to zero in the metastable ordered phase. Apparently this virtual temperature is only a little higher than the actual limit of stability of the ordered state relative to the disordered state (i.e., the phase boundary), both at our composition and at that of Ref. 1. This observation poses a difficult conceptual problem, to us more intriguing than any likely to arise had the transition turned out to be simply one of critical type.

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[1] M. F. Collins and H. C. Teh, Phys. Rev. Lett. 30, 781 (1973).

[2] For references see: L. Guttman, Solid State Phys. 3, 146 (1956); *Critical Phenomena in Alloys, Magnets and Superconductors*, edited by R. E. Mills, E. Ascher, and R. I. Jaffee (McGraw-Hill, New York, 1971), p. 243.

[3] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958), Chap. XIV; E. M. Lifshitz, J. Phys. USSR 6, 252 (1942).

[4] The apparatus was slightly modified from that described earlier: L. Guttman, H. C. Schnyders, and G. Arai, Phys. Rev. Lett. 22, 517 (1969).

[5] Because the superlattice reflection amplitude is proportional to the *difference* between the atomic scattering factors of nickel and manganese, it is extremely weak. Even when the sample is perfectly ordered, the parameter $Q/(\mu\eta)$ is at most 10^{-3}, whereas secondary extinction begins to become significant for our geometry when this parameter is of the order of unity. We were therefore quite safe in neglecting extinction under all conditions. [See G. E. Bacon and R. D. Lowde, Acta Cryst. 1, 303 (1948).]

[6] The data shown in Fig. 3 were acquired in two series, one covering the interval from 420 to 580 °C, followed by cooling to 300 °C and reheating to 600 °C. The reproducibility of the data gives us confidence that the effects shown are not due to accidental shifts of the sample position (which are relatively unimportant anyway at this large Bragg angle), and that if there is any anomalous expansion near 545 °C, it must be small compared to the normal value.

[7] M. J. Marcinkowski and N. Brown, J. Appl. Phys. 32, 375 (1961).

[8] We are indebted to Professor Collins for informing us of the composition of his sample.

[9] However, all the results cited are in disagreement with the suggestion by Litvin *et al.* (Ref. 10) that Ni_3Mn is metastable above 400 °C relative to ordered NiMn and the disordered phase.

[10] D. F. Litvin, V. A. Udovenko, and E. Z. Vintaikin, Dokl. Akad. Nauk SSSR 198, 1316 (1971) [Sov. Phys.—Dokl. 16, 486 (1971)].