BNL-25917

CONF-790341--6

A NEUTRON SCATTERING STUDY OF PREMARTENSITIC PHASES OF TiNi(Fe)

M. B. Salamon, M. Meichle, C. M. Wayman, C. M. Hwang
University of Illinois, Urbana, IL 61801

S. M. Shapiro
Brookhaven National Lab, Upton, NY 11973

Contributed paper for the International Conference

on Modulated Structures, Kona, Hawaii

March 22-25, 1979

MASTER

(to be published by the AIP)

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64.60.-i

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ABSTRACT

The premartensitic phases of TiNi(Fe) have been studied by means of neutron diffraction, specific heat, and electron microscopy. Evidence for an incommensurate charge density wave has been found, with a wavevector near, but not at, (h/3, k/3, 0) positions. A lock-in transition occurs at lower temperatures, accompanied by the formation of needle-shaped domains oriented along [110] directions.

TEXT

The intermetallic compound TiNi has long been known to undergo a martensitic transformation near M_s = 300 K. This transition, however, exhibits atypical resistivity and structural anomalies above the M_s temperature—the so-called premartensitic transition.[1] Recently Matsumoto and Honma[2] noted that substitution of up to 3% Fe for Ni depresses the M_s temperature more strongly than the premartensitic temperature T_o, revealing a distinct premartensitic phase.

We report here the results of neutron diffraction, specific heat, electron diffraction, and electron microscopy studies on nominal $Ti_{50}Ni_{47}Fe_3$ in the premartensitic phase. We find evidence for the formation of an incommensurate superlattice at T_o with a lock-in at lower temperatures, very similar to incommensurate charge density waves (CDW) in layered compounds.

Neutron diffraction studies were performed on a single crystal obtained from Raychem Corporation, the composition of which was determined to be $Ti_{50.1}Ni_{46.7}Fe_{3.2}$ by microprobe analysis. Resistivity indicates that M_s is below 80 K, well separated from T_o, which is near 230 K. The high temperature phase was confirmed to be an ordered CsCl structure with a lattice constant of 3.015 Å.

Both electron and neutron diffraction show the appearance of distinct superlattice peaks at temperatures below 231 K, slightly shifted from (h/3, k/3, 0). Neutron diffraction peaks with $h \neq k$ are much stronger than for $h = k$, indicating that the distortion giving rise to the superlattice is phonon-like, and transverse to the [110] direction in reciprocal space. The intensity of the peak nominally at (2/3, 1/3, 0) is shown in Fig. 1. The considerable tailing of the intensity makes it difficult to locate the transition temperature, but an extrapolation of the linear portion of the curve gives T_o = 228 K. The data of Fig. 1 were taken on cooling. There is some hysteresis in the intensity with cycling, especially in the vicinity of 220 K, where there seems to be some structure in the

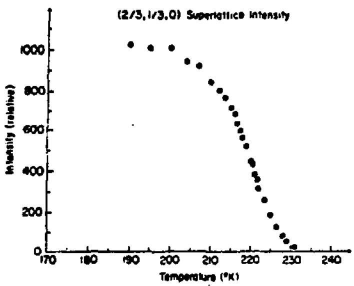

Fig. 1. Superlattice peak intensities.

intensity curves. Associated with T_o is an apparent rhombohedral distortion, evidenced by splitting of (110) and (111) peaks, but no splitting of (100) peaks. The (100) positions rotate, however, without a change in lattice constant.

The actual position of the superlattice peak of Fig. 1 is at ((2+δ/3), (1-δ)/3, 0). We have plotted the deviation δ in Fig. 2. The shift is small, having its maximal deviation from the one-third position at T_o, and then decreasing. The δ shown does not take into account the slight rotation of the (100) positions due to the rhombohedral distortion. When this is considered, the deviation approaches zero near 215 K and remains "locked-in" below. There is some evidence, therefore, for the existence of a lock-in transition between 215 K and 220 K.

Ac specific heat measurements have been performed on thin slices of material adjacent to the crystal used in the neutron study. The results are shown in Fig. 3. The specific heat increases sharply as the temperature is lowered below 230 K, reaching a maximum near 221 K. This rise does not appear to be a power-law increase, but rather a broadened Landau step, such as observed in TTF-TCNQ and other CDW transitions.[3] Assuming this to be the case, we fit the curve in Fig. 3 to a Landau specific heat, as shown, with T_o = 228 ± 1 K, in agreement with our estimate from Fig. 1. Superimposed on the larger specific heat maximum is a sharp peak at approximately $T_L \gtrsim$ 219 K. This feature shows considerable hysteresis, as seen in Fig. 3, and is further evidence for the existence of a lock-in transition in this temperature range.

Electron diffraction studies on similar samples show complementary results. The transition temperatures are strong functions of Fe content and stoichiometry. In electron microscopy, small irregular domains accompany the onset of the incommensurate phase, which are similar in appearance to antiphase domains in alloys. At lower temperatures, sharp, needle-shaped regions appear which are aligned with [110] axes as shown in Fig. 4. The electron diffraction spots, both Bragg spots and superlattice peaks, split when the domains appear.

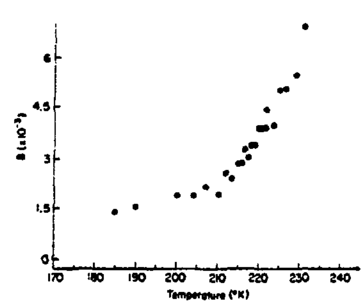

Fig. 2. Deviation of the superlattice peak of Fig. 1 from (2.3, 1/3, 0). Positions are relative to the high temperature cubic lattice.

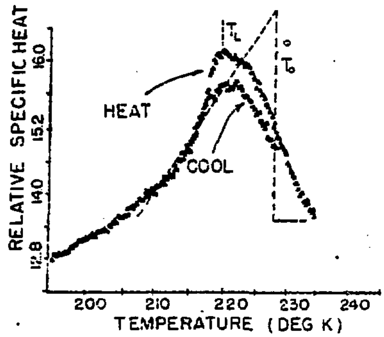

Fig. 3. Specific heat of $Ti_{50.1}Ni_{46.7}Fe_{3.2}$. X, cooling data, Δ, heating.

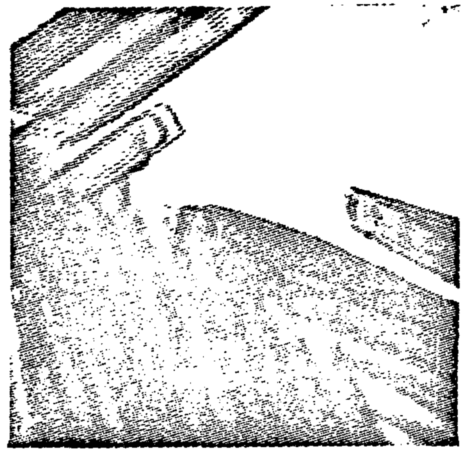

Fig. 4. Needle-shaped domains which appear below the lock-in. Orientation is along [110] (x 28k).

Dark-field images show that one of the split peaks is associated with the needles, and the other with the surrounding matrix. The domains appear to be associated with the lock-in transition, but may not be themselves the locked-in regions.

The premartensitic transition in TiNi(Fe) gives every indication of being a CDW transition, with a lock-in occuring approximately 10 K below T_0. A rhombohedral distortion accompanies the CDW transition, but the splitting and intensities of the (110) and (111) peaks are not exactly as expected for a purely rhombohedral distortion. Some of the discrepancy is due to domain effects, but we cannot yet exclude a more complicated distortion. Dynamical neutron scattering studies and elastic constant measurements are now underway in order to clarify these remaining questions.

ACKNOWLEDGEMENTS

The support of the National Science Foundation through Grant No. DMR-77-23999 (Materials Research Laboratory) and of the DOE under Contract No. EY-76-C-02-0016 is gratefully acknowledged.

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