Neutron-Scattering Study of Premartensitic Behavior in Ni-Al Alloys

S. M. Shapiro and J. Z. Larese

Brookhaven National Laboratory, Upton, New York 11973

Y. Noda

Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

S. C. Moss

Physics Department, University of Houston, Houston, Texas 77004

and

L. E. Tanner

Chemistry and Materials Science Department, Lawrence Livermore National Laboratory, Livermore, California 94550

Phonon dispersion curves for the [110] $\langle \bar{1}10 \rangle$ TA_2 branch in Ni_xAl_{100-x} ($50 < x < 65$) reveal a pronounced minimum whose position in q space is composition dependent but whose frequency does not change appreciably with temperature. In the same q range, substantial elastic scattering also appears which is associated with localized embryos of a low-temperature phase. The diffuse scattering from the elastic displacement field about these embryos is highly anisotropic, giving rise to the striated strain contrast (tweed) in the electron microscope image. A common electronic origin of these effects is proposed.

First-order structural phase transformations in metallic alloys have been extensively studied[1,2] and invariably display both measurable volume changes accompanying an abrupt change of symmetry, and extensive hysteresis. Much effort has been devoted to understanding the variety of precursor or premonitory effects that occur prior to the actual transformations.[3,4] Prominent among these effects are tweedlike striations[5] in transmission electron microscope (TEM) images formed from electron-diffraction (ED) patterns of alloys above their structural transformation temperature. This tweed pattern, shown in Fig. 1(a) for a Ni-Al alloy, develops well above the actual transformation and becomes increasingly more pronounced as the transformation is approached.[6-8]

The ED pattern in Fig. 1(b) is characterized by rather narrow [110] ridges of pronounced diffuse scattering which, when double-diffraction conditions are minimized, have been shown to arise from transverse atomic displacements along [$\bar{1}$10], which is transverse to the [110] direction.[7] This direction and polarization correspond to the ($q = 0$) elastic constant $c' = \frac{1}{2}(c_{11} - c_{12})$ for a cubic system. Related to the development of the tweed pattern is also a slight decrease in c' with decreasing temperature, well above any transformation, which has been identified with pretransitional behavior.[5] A good deal of effort has also been expended over the years to develop a microscopic, or lattice-dynamical, basis for these transformations which would explain the premonitory behavior.[3,4,9,10] The present Letter addresses these issues in Ni-Al alloys.

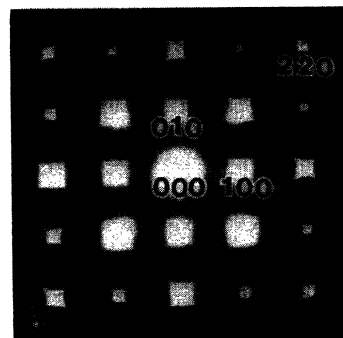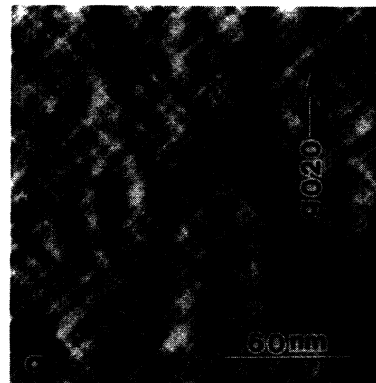The metallic alloys Ni_xAl_{100-x} ($50 < x < 65$) which

FIG. 1. (a) TEM of $Ni_{63}Al_{37}$. Bright-field (001) orientation; strong two-beam conditions for (0,2,0). Tweed strain-contrast striations lying parallel to {110} planes. (b) ED pattern with [001] perpendicular to the plane.

display a prominent tweed pattern have been extensively studied by electron[6] and x-ray diffraction,[11] ultrasonic absorption,[12] and calorimetric measurements.[13] In a series of excellent papers, Robertson and Wayman (RW)[6] indicated that the diffuse streaking [Fig. 1(b)], which leads to the tweed structure in the image, arises from static displacements induced by localized tetragonal perturbations of the lattice. The period in the tweed structure depends quite critically on the exact orientation of the beam and crystal foil, much as with the fringe contrast associated with a stacking fault.[14] It should therefore be viewed more as an artifact than as indicative of a fundamental structure. The origin of the proposed tetragonal perturbation was not isolated by RW, but it is clear from their detailed analysis that the diffuse scattering which is being "imaged" must be considerably more ridgelike along $\langle \bar{1}10 \rangle$ than pure thermal diffuse scattering, and hence must be static in origin.

The single crystal of nominal composition $Ni_{63}Al_{37}$ used in the present experiment is from the same boule used in the electron diffraction studies of RW.[6] The sample for the neutron studies was approximately cylindrical (6 mm diameter×5 mm height), showed a macroscopic cellular growth pattern, and had a mosaic spread of $\sim 1°$. This alloy has the β-phase CsCl structure at room temperature with the lattice parameter $a = 2.866$ Å. Inelastic-scattering measurements were also performed on two other compositions of Ni_xAl_{100-x} with $x = 58$ and 50.

The neutron-scattering experiments were performed at the high-flux beam reactor at Brookhaven National Laboratory with use of a triple-axis spectrometer. A fixed final energy of $E_f = 14.7$ meV was employed with 20' collimation in the instrument except for 40' in front of the detector. The energy resolution was 0.5 meV full width at half maximum (FWHM). The sample was mounted in a Displex refrigerator with [001] perpendicular to the scattering plane.

The TEM and ED were carried out at room temperature on a JEOL 200CX instrument at Lawrence Livermore National Laboratory. The diffuse striated strain contrast (tweed pattern) in Fig. 1(a) lies along traces of {110} planes and shows a minimum spacing of about 20 Å for these imaging conditions and resolution. In the symmetrical (001) zone-axis ED pattern of Fig. 1(b), the streaks at the origin and those parallel to $\langle 110 \rangle$ at {hh0} Bragg peaks are due to multiple scattering.[8] Densitometer traces along $\langle \zeta\zeta 0 \rangle$ show that the streak intensity falls off with q and reveal a weak broad satellite at $\zeta \sim 0.13$. In Fig. 2(a) we show the elastic neutron scattering measured on the $x = 63$ sample about the (2,0,0) Bragg peak along the $[\zeta\zeta 0]$ direction. On either side of the intense Bragg peak are similar broad satellite peaks near $\zeta \approx 0.13$ that are localized along narrow $[\bar{1}10]$ ridges. On cooling, these peaks sharpen, shift and become more intense. Figure 2(b) shows the intensity at
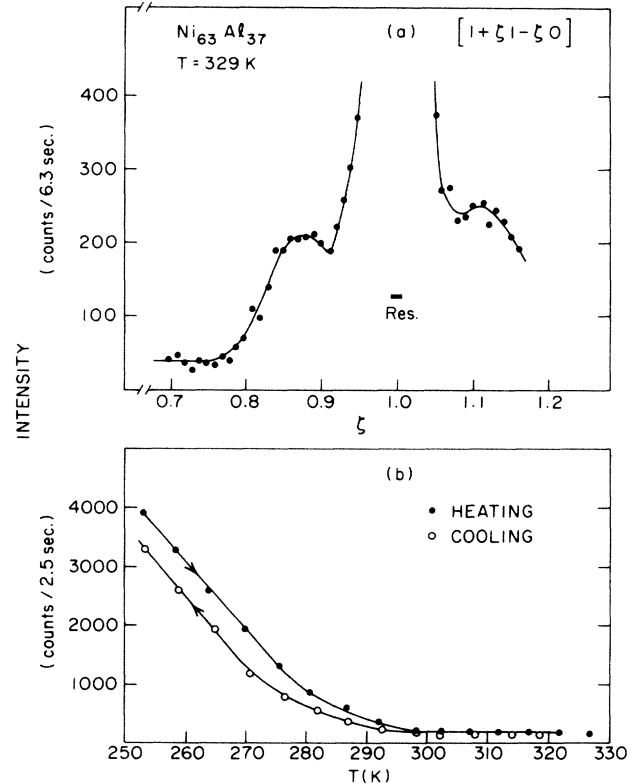

FIG. 2. (a) Elastic neutron-scattering spectra along $[\zeta\zeta 0]$ direction about the (2,0,0) Bragg peak. (b) Temperature dependence of the intensity measured at $Q = (2.11, -0.11)$ measured on heating and cooling.

$\zeta \cong 0.11$ as a function of temperature measured on heating and cooling. A hysteresis is present and the heating and cooling curves merge near 295 K, which is close to the martensitic phase transition reported for this composition (i.e., $x = 63$).[13] Extending the measurements to lower temperatures produced an unusual nonmonotonic behavior in the intensity about various reciprocal lattice points, which is a consequence of the variation in composition throughout our sample. However, TEM and electrical-resistivity measurements[15] show consistently that the martensitic transformation (T_M) is near 200 K, suggesting that the bulk of the coarse cellular segregation structure of this crystal is at a slightly lower composition, viz. $\sim 62.5\%$. Because of this difficulty, the remainder of this Letter deals essentially with our interpretation of the premonitory effects well above any transformation temperature.

Figure 3(a) shows the phonon dispersion curve for the $[110]$-TA_2 branch, for three compositions of Ni_xAl_{100-x}, $x = 63$, 58, and 50 at.%. This is the same branch that characterizes the diffuse ridges observed in Figs. 1(b) and 2(a). For $x = 63$, the slope for the small-ζ region agrees well with the velocity of sound[12] but near $\zeta \sim 0.05$ the phonon energy deviates from a linear behavior with ζ. The deviation is strongest for $0.05 < \zeta < 0.25$. In or-
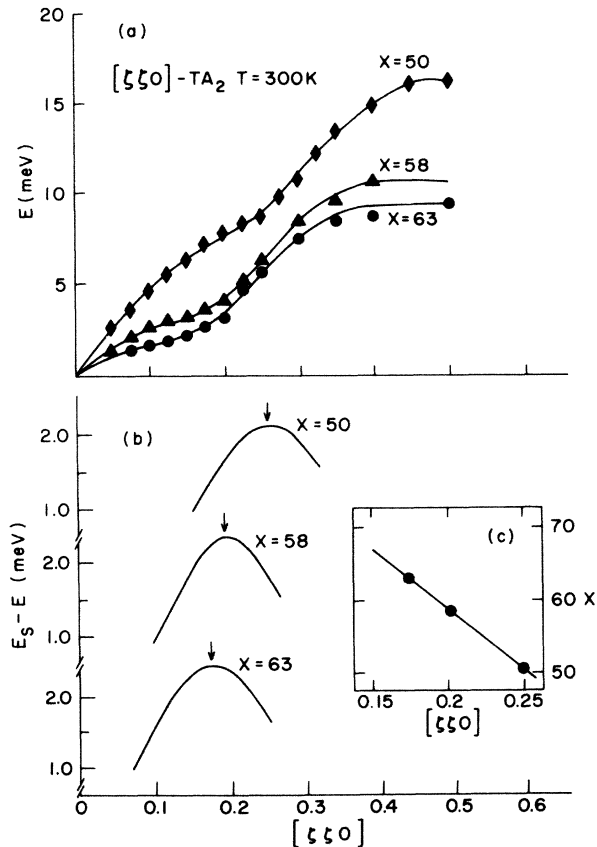
FIG. 3. (a) Dispersion curves of [110]-TA₂ (displacements along [110]) branch of Ni_xAl_{100-x} for $x = 63,58,50$. (b) Deviation of the measured phonon frequency E from that determined by assuming a sine wave dispersion, E_s. (c) Variation of the maxima of $E - E_s$ with concentration, x.

der to examine the concentration dependence of the ζ value in the anomalous region, we calculated the deviation of the measured phonon energy, E, from that determined by our assuming $E_s \propto v_s \sin\pi\zeta$ where v_s is the velocity of sound.[16] In Fig. 3(b) we plot $E_s - E$ vs x. The maxima correspond to the largest deviation, which shifts linearly with x as shown in Fig. 3(c), but is similar in magnitude at all three values.

For $x = 63$, the [110]-TA₂ phonon branch exhibited only a slight decrease with temperature, and never approached zero, even though a phase transition eventually occurs as evidenced by the elastic intensity shown in Fig. 2(b). This behavior is similar to that observed in several metallic alloys that undergo martensitic phase transformations,[9,10] none of which should, *inter alia*, be called "soft-mode" transitions.

From these preliminary neutron-scattering measurements we infer that the strain centers responsible for the elastic scattering in Fig. 2(a) and thus the tweed contrast are related to the phonon anomalies in Fig. 3. Similar anomalies, though often much less pronounced, occur in many metallic systems as a result of electron-

phonon coupling.[17-19] In the Kohn[17] case, the q values are directly connected to the Fermi wave vectors, $2k_F$, which span large nesting sections of the Fermi surface, whereas in the alternative Varma and Weber[18] picture the anomalies may arise in the q dependence of the electron-ion form factor for scattering close to the Fermi surface.[20]

In the present alloy the broad frequency dip in the region $\zeta \sim 0.1$-0.2 that shifts with the Al content is presumably of electronic origin. The associated elastic scattering is then proposed to arise from the local accommodation of the structure to singular terms in the electron energy in the vicinity of $2k_F$. Because the range of ζ where the phonon energy is low ($\zeta = 0.14$) includes a seven-plane [110] stacking sequence of the NiAl $B2$ parent phase, which transforms to a $7R$ martensite upon cooling,[21] we envision the room-temperature equilibrium state of our alloy as heterogeneous, consisting of uniformly distributed localized regions of these near-tetragonal ($7R$) embryos or domains, coherent with the cubic matrix and straining it to produce the streaking in Fig. 1(b).

Such a heterogeneous equilibrium state has been suggested by Krivoglaz[22] to be the nonuniform response of a metallic alloy, above a first-order phase transition, to singular terms in the electronic energy at $2k_F$. The signatures of these terms according to Krivoglaz[22] are both the phonon anomaly and the elastic scattering associated with the embryos. If we take the size of a localized tetragonal fluctuation or embryo to be given roughly by the FWHM in Fig. 2(a) of the satellite at $\zeta \simeq 0.13$, this size is about 40 Å at 329 K. A similar heterogeneous state has recently also been proposed by Yamada[23] for the pretransitional structure in a NiTi crystal. *Within* the tweed structure, under appropriate lattice imaging conditions, one should therefore be able to discern a more or less uniform distribution of localized regions with a structure resembling $7R$ (with an internal periodicity of ~ 14 Å). This indeed appears to be the case, especially as the temperature is lowered.[15] Raising the temperature dissolves the premartensitic structure and removes the attendant strain-contrast tweed[15] though the phonon spectrum is not drastically changed. However, as the Al concentration increases, the anomaly shifts to larger ζ and the contrast at room temperature is weaker since the transformation becomes more remote, i.e., T_M shifts to a lower temperature.

Although we suggest that a common origin of the phonon anomalies, elastic scattering, and associated tweed contrast is connected with the electronic structure of the alloy, it need not be unique. For metals, however, it seems quite plausible and we therefore suspect that it is rather common as indicated earlier by Mori, Yamada, and Shirane[9] and Nakanishi, Hayashi, and Murakami[24] for β-phase alloys.[25]

We wish to thank G. Barsch, J. A. Krumhansl, G. Ol-

[1]W. Warlimont and L. Delaey, *Martensitic Transformations in Copper-, Silver- and Gold-Based Alloys* (Pergamon, New York, 1975).

[2]See papers in "Pretransformation Behavior Related to Displacive Transformation in Alloys," American Society of Metals–Materials Science Division Symposium, New Orleans, March 1986, Met. Trans. A (to be published).

[3]S. C. Moss, J. Phys. (Paris), Colloq. **38**, C7-440 (1977).

[4]Y. Morii and M. Iizumi, J. Phys. Soc. Jpn. **54**, 2948 (1985).

[5]L. E. Tanner, A. R. Pelton, and R. Gronsky, J. Phys. (Paris), Colloq. **43**, C4-169 (1982), and to be published.

[6]I. M. Robertson and C. M. Wayman, Philos. Mag. A **48**, 421, 443, 629 (1983).

[7]L. E. Tanner, Philos. Mag. **14**, 111 (1966).

[8]T. Kainuma and R. Watanabe, J. Jpn. Inst. Met. **35**, 1126 (1971).

[9]M. Mori, Y. Yamada, and G. Shirane, Solid State Commun. **17**, 127 (1975).

[10]G. Guénin, D. Rios Jara, M. Morin, L. Delaey, R. Pynn, and P. F. Gokin, J. Phys. (Paris), Colloq. **43**, C4-597 (1982).

[11]P. Georgopolus and J. B. Cohen, Acta Metall. **29**, 1535 (1981).

[12]K. Enami, J. Hasunuma, A. Nagasawa, and S. Nenno, Scripta Metall. **10**, 879 (1946); N. Rusovic and H. Warlimont, Phys. Status Solidi **44**, 609 (1977).

[13]J. L. Smialek and R. F. Hehemann, Metall. Trans. **4**, 1571 (1973).

[14]P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley, and M. J. Whelan, *Electron Microscopy of Thin Crystals* (Krieger, Melbourne, FL, 1977).

[15]L. E. Tanner, R. Gronsky, A. R. Pelton, and G. Van Tendeloo, to be published.

[16]M. Iizumi, J. Phys. Soc. Jpn. **52**, 549 (1983).

[17]W. Kohn, Phys. Rev. Lett. **2**, 393 (1959).

[18]C. M. Varma and W. Weber, Phys. Rev. Lett. **17**, 1094 (1977).

[19]A. W. Overhauser, Phys. Rev. Lett. **4**, 415 (1960).

[20]See, for example, D. E. Moncton, F. di Salvo, and J. D. Axe, Phys. Rev. B **16**, 801 (1977).

[21]K. Enami, A. Nagasawa, and S. Nenno, Scripta Metall. **12**, 223 (1978).

[22]M. A. Krivoglaz, Zh. Eksp. Teor. Fiz. **84**, 355 (1983) [Sov. Phys. JETP **57**, 205 (1983)].

[23]Y. Yamada, in Ref. 2.

[24]N. Nakanishi, M. Hayashi, and Y. Murakami, Trans. Jpn. Inst. Met. **48**, 1288 (1980).

[25]Other sources of localized shear strain in combination with sufficiently *anisotropic* shear softness would also provide possible origins for tweed contrast and these will certainly be more appropriate explanations of the pretransitional effects in insulators as discussed, for example, by M. Mori, Y. Noda, and Y. Yamada, J. Phys. Soc. Jpn. **48**, 1288 (1980), and by J. A. Krumhansl, private communication.
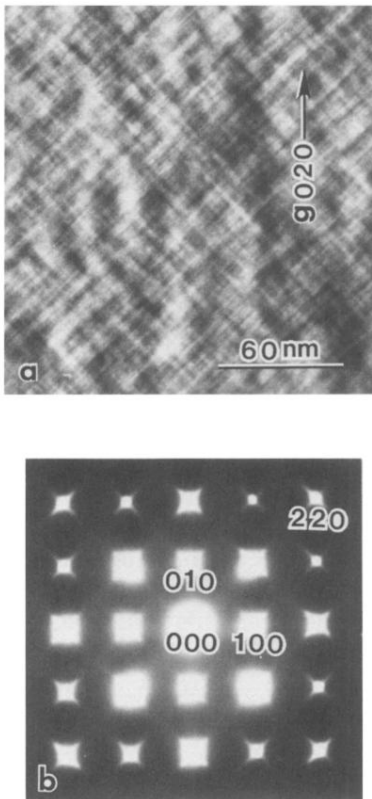
FIG. 1. (a) TEM of Ni$_{63}$Al$_{37}$. Bright-field (001) orientation; strong two-beam conditions for (0,2,0). Tweed strain-contrast striations lying parallel to {110} planes. (b) ED pattern with [001] perpendicular to the plane.