## Neutron Scattering Study of the Martensitic Transformation in a Ni-Al $\beta$ -Phase Alloy

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A high-resolution neutron scattering study of Ni<sub>62.5</sub>Al<sub>37.5</sub> shows that the martensitic transformation is associated with a homogeneous distortion and a nearly sevenfold modulation of the cubic lattice which is predicted by an observed phonon anomaly above  $T_M$ . In the low-temperature 7R phase a nonuniform spacing of superlattice reflections and unusual line shapes are observed which are believed to arise from stacking faults.

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Martensitic transformations (MT) in metallic alloys have been extensively studied for nearly a century because of the important metallurgical properties of the martensitic phase.<sup>1</sup> Much of the interest in recent years has been on the precursor, or premonitory effects where anomalies in the elastic constants, phonon dispersion curves, and/or diffuse scattering in diffraction experiments give an indication of the eventual low-temperature structures. Since MT are by definition first-order phase transitions, the precursor effects do not diverge at the temperature  $T_M$  (or  $M_s$ ) and there is a range of temperatures where the high-temperature, or parent, phase coexists with the low-temperature, or product, phase. Because of this coexistence the actual structure of the product phase is not always well known. Also, most of the diffraction studies have used electron or x-ray diffraction techniques which require very thin samples and are very surface sensitive. Neutron-diffraction techniques have the advantage that the entire bulk sample, complete with the inherent defects, is probed.

The Ni<sub>x</sub>Al<sub>1-x</sub> alloy is a prototypical material exhibiting a MT for 60 < x < 64 at.%.<sup>2</sup> For  $T > T_M$  the structure is called the  $\beta_2$  phase which is a simple ordered B2 or CsCl-type structure, where the excess nickel is randomly distributed over the Al sites.<sup>3</sup> Precursor effects (e.g., Huang diffuse streaking) have been observed in the electron diffraction patterns and the corresponding image shows a typical tweed strain contrast pattern characteristic of martensitically transforming alloys.<sup>4</sup> Recently the phonon dispersion curve of the [ $\zeta\zeta 0$ ] transverseacoustic mode (displacements along [ $\overline{110}$ ]) measured in the Ni<sub>x</sub>Al<sub>1-x</sub> alloy was shown to have an anomaly at wave vector  $\zeta$  which is x dependent.<sup>5</sup>

We report in the following the temperature dependence of the phonon dispersion curve for x = 62.5 at.% and show that a marked, but incomplete, softening occurs at wave vector  $\zeta \approx \frac{1}{6}$ . At the same time an elastic central peak develops whose intensity increases at  $T \rightarrow T_M$ .<sup>6,7</sup> Below  $T_M$  a large distortion of the cubic structure occurs accompanied by the appearance of superlattice reflections along the [*HKO*] direction of the low-temperature phase whose nonuniform spacing is nearly, but not exactly, equal to  $\frac{1}{7}$ .

The single crystal of Ni<sub>62.5</sub>Al<sub>37.5</sub> was grown at United Technologies Research Center and was carefully heat treated in order to reduce compositional inhomogeneities. The sample was cubic in shape  $(5 \times 5 \times 5 \text{ mm}^3)$  with each face parallel to a (1,0,0) plane. The crystal was of exceptionally good quality (< 6 min mosaic) and had a room-temperature lattice parameter of  $a_0 = 2.858$  Å. It was wrapped in Al foil and glued to an Al rod. The sample was placed in a sealed Al can filled with He gas, then mounted onto the cold finger of a Displex refrigerator. The sample was oriented with a [100] direction vertical. The neutron-diffraction experiments were performed on the H7 triple-axis instrument at the Brookhaven National Laboratory's High Flux Beam Reactor. Different incident energies and collimations were used for the elastic and inelastic scans.

Figure 1(a) shows the phonon dispersion curve of the  $[\zeta\zeta 0]$ -TA branch (displacements along [110]) measured different temperatures above  $T_M \sim 80$  K about the (1,1,0) Bragg peak. (The actual transition temperature depends upon the rate of cooling and any external stresses.) It is seen that the phonon energy develops a minimum around  $\zeta \approx \frac{1}{6}$  as  $T \rightarrow T_M$ . Figure 1(b) shows the elastic scattering measured along the same [ $\zeta\zeta 0$ ] direction. An elastic central peak develops at the same wave vector as the phonon softening. Figure 2(a) shows an elastic scan starting from the ( $\bar{2}$ ,2,0) Bragg peak toward the ( $\bar{1}$ ,3,0) Bragg peak. Two broad satellite peaks (FWHM=0.17 Å<sup>-1</sup>) are seen at a distance  $\zeta$ =0.162



FIG. 1. (a) The temperature dependence of the  $[\zeta\zeta 0]$ -TA phonon branch for Ni<sub>62.5</sub>Al<sub>37.5</sub>. (b) The temperature dependence of the elastic scattering associated with the photon branch measure in q.

± 0.004 from the nearest Bragg peaks, a result which is similar to that shown in Fig. 1(b). A similar observation was made by electron diffraction.<sup>7</sup> As  $T \rightarrow T_M$ , the satellite intensity, as well as the underlying Huang diffuse scattering, increases along with the tweed amplitude observed in the TEM images. High-resolution imaging (phase contrast) at room temperature reveals that the atomic configurations underlying the tweed are in the form of distorted domains of approximate size 40-60 Å. The local atomic displacements within each domain are of the {100}  $\langle 1\bar{1}0 \rangle$  type and superimposed is a diffuse



FIG. 2. (a) The elastic scattering measured along the  $[\zeta\zeta 0]$  direction from the  $(\bar{2},2,0)$  to the  $(\bar{1},3,0)$  Bragg peak for Ni<sub>62.5</sub>Al<sub>37.5</sub> for  $T > T_M$ . (b) The same scan as in (a) only for  $T < T_M$ .

banded modulation parallel to {110} traces of ~13-Å spacing.<sup>7</sup> This value corresponds to the inverse of the q value of the satellite peaks shown in Figs. 1(b) and 2(a).

Below  $T_M \sim 80$  K the  $\beta_2$  lattice transforms and the symmetry is reduced. The position of the (0,1,0) cubic Bragg peak remains nearly unchanged, but the (1,0,0) Bragg peak splits into two peaks: one above and one below the scattering plane with a shorter and longer reciprocal-lattice vector, respectively. The relationship between the cubic reciprocal-lattice vector and that of the new pseudo-orthorhombic low-temperature structure is shown in Table I. The new  $A^*$ ,  $C^*$  axes correspond to  $a^* + \delta$  and the change  $\delta$  corresponds to a 5% distortion. The volume of the unit cell is, therefore, nearly the same as in the cubic phase. In addition to the change in lattice parameters, there is a slight change in the angle between  $A^*$  and  $B^*$  which becomes 89.56° instead of 90° in the cubic phase.

In addition to the homogeneous strain, a long-period modulation is observed in the martensite as shown in Fig.

| TABLE I     | Ι. | Relationship | between | cubic | cell | and | 7R | cell | of |
|-------------|----|--------------|---------|-------|------|-----|----|------|----|
| martensitic | ph | ase.         |         |       |      |     |    |      |    |

| Cubic                        | Pseudo orthorhombic   | 7R (monoclinic)                                 |
|------------------------------|---|---|
| $a^* = 2.199 \text{ Å}^{-1}$ | $(\overline{A}^*, 0, 0) = 2.079 \text{ Å}^{-1}$<br>$(0, B^*, 0) = 2.208 \text{ Å}^{-1}$<br>$(0, 0, C^*) = 2.319 \text{ Å}^{-1}$ | $(1,0,3)_m$<br>$(1,0,\bar{4})_m$<br>$(0,1,0)_m$ |
| $\gamma^* = 90^{\circ}$      | $\gamma^* = 89.56$  | $(1,0,3)_m \wedge (1,0,\bar{4})_m$              |

2(b). The pseudo-orthorhombic  $[\bar{2}20]$  Bragg peak has practically disappeared and six intense superlattice peaks appear between the  $(\overline{2},2,0)$  and  $(\overline{1},3,0)$  Bragg peaks. The spacing of these peaks is nonuniform and *almost*, but not exactly, equal to  $\frac{1}{7} = 0.143$ . The peak closest to  $(\bar{2},2,0)$  is at  $\zeta = 0.153 \neq \frac{1}{7}$  and the second peak is at a period of twice the first, but the third is not at the thirdharmonic position. In addition, the peak nearest the  $(\bar{1},3,0)$  is at a different spacing ( $\zeta = 0.144$ ) than the peak near  $(\overline{2},2,0)$ . Another feature is the large asymmetry in the line shapes and linewidths of the peaks. Figure 3 shows a summary of the relative intensities of the observed superlattice peaks superimposed on the pseudoorthorhombic reciprocal (0,0,1) plane. Only the peaks for  $|H| + K \ge 3$  are shown because only for these scattering vectors is it possible to separate the monoclinic twins corresponding to  $\gamma^*$  less than or greater than 90°. The thin lines correspond to the reciprocal lattice of the 7R structure determined from the averaged peak positions of the observed reflections produced in  $\beta_2$  Ni-Al under tension. The relationship between the pseudoorthorhombic  $(A^*, B^*, C^*)$  cell and the 7R monoclinic cell is given in Table I and shown in Fig. 3. From this, the reciprocal lattice of the monoclinic structure is  $a_m^* = 1.512 \text{ Å}^{-1}$ ,  $b_m^* = 2.319 \text{ Å}^{-1}$ , and  $c_m^* = 0.4353 \text{ Å}^{-1}$ , with  $\beta_m^* = 85.18^\circ$ . Converting to real-space coordinates, we obtain lattice vectors in excellent agreement with those obtained by Martynov et al.<sup>8</sup> for Ni-Al.

The incomplete softening of the [110]-TA<sub>2</sub> mode is typical of most  $\beta$ -phase alloys where the degree of softening varies from system to system.<sup>9</sup> In all the  $\beta$ phase materials, there is a weak restoring force for the long-wavelength displacements associated with this mode. This leads to an ease of shearing of the {110} planes stacked along the  $\langle \overline{1}10 \rangle$  direction and the various stacking sequences of the {110} planes results in different martensitic structures.<sup>10</sup> Depending upon the stacking sequence it is possible to generate an fcc, hcp, or nR(n=3, 7, 9, 12, or 18) structure. In Ni-Al under tension Martynov et al.<sup>8</sup> showed that the product 7R structure with a  $(5,\bar{2})$  stacking<sup>11</sup> was most consistent with the measured x-ray intensities. Our observed intensities are consistent with this stacking but the nonuniform spacing and varying linewidths cannot be explained by a simple stacking model. Conventional and high-resolution TEM confirm the sequence of the  $(5,\overline{2})$  stacking but also see

![](_page_2_Figure_7.jpeg)

FIG. 3. Scattering plane show the relationship between the pseudo-orthorhombic  $(A^*, B^*)$  notation and the monoclinic  $(a_m^*, c_m^*)$  notation. The solid circles are indicative of relative strength of the superlattice peaks. S denotes strong, M denotes medium, and W denotes weak.

evidence for other sequences.<sup>7</sup>

These latter features are the most novel and significant results of our experiment. The presence of stacking faults is known to play a key role in martensitic transformations in  $\beta$ -phase alloys<sup>12</sup> and the associated shape memory effects.<sup>13</sup> In the present case, the stacking fault consists of a distribution of various stackings such as (6,1), (4,3), (4, $\overline{1}$ ,1, $\overline{1}$ ), etc., which coexist with the (5, $\overline{2}$ ), all of which give a periodicity of 7. The admixture of these stacking sequences leads to the well-known Hendricks-Teller (HT) type of line shape<sup>14</sup> observed in intercalated graphite<sup>15</sup> and quasicrystals.<sup>16</sup> The characteristics of the HT line shapes are a series of lines of different widths and spacings arising from a random mixture of phase differences; features very similar to Fig. 2(b).

In conclusion, we show that the martensitic transformation in Ni-Al  $\beta_2$  phase is associated with a homogeneous strain accompanied by a modulation of the lattice whose wavelength is predicted by an observed phonon anomaly above  $T_M$ . This is precisely what recent theories require to describe martensitic transformations.<sup>17</sup> In addition, peculiar line shapes are present in the modulated phase which are most likely due to stacking faults. Our diffraction pattern will serve as a rigorous test of any model describing this type of martensitic transformations and structure.

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