

On the electronic and mechanical instabilities in Ni_{50.9}Ti_{49.1}

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Abstract

Both the superelastic and the shape memory properties of the cubic NiTi alloy known as Nitinol arise from two-phase transitions; from a simple cubic austenite phase to a trigonal R-phase and to a lower symmetry martensite phase. In this article, we speculate that two competing forces drive these transitions. One is “mechanical” in nature and it takes the cubic austenite structure of NiTi to a denser packing arrangement. The other one appears to be “electronic” in nature and it modifies the cubic austenite structure by correlated “Jahn–Teller” type distortions, and perhaps a fluctuation of charge density.

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1. Introduction

The phenomena of superelasticity and shape memory in Nitinol, a nearly equiatomic alloy of Ni and Ti, is thought to be driven by diffusionless phase transitions. Even after more than 30 years since its discovery, the current literature still contains many new reports on phases and phase transformations in Nitinol under application of thermal and mechanical loads. The reason for such a prolific literature is that a minor change in the alloy composition, heat treatment or the loading condition dramatically alters the nature and evolution of phases. In this study, we use ultra-high-resolution synchrotron diffractometry, in conjunction with X-ray absorption spectroscopy (a relatively new technique to the investigations of NiTi phase chemistry) to explore the relationship among the various Nitinol phases, and attempt to understand their evolution in terms of the “electronic” and “mechanical” instability of the high symmetry structure of Nitinol.

The high symmetry structure of NiTi, often called the austenite phase, is thought to be a simple cubic structure similar to the structure of CsCl (Pm-3m). On cooling or

application of mechanical stress, the symmetry of the cubic structure is lowered. If the transformation is triggered by temperature then it is the shape memory effect, whereas if it is triggered by stress then it is the superelastic effect. Many studies have suggested that the lowering of the symmetry often takes place in two stages [1]. The first breakage of symmetry transforms the material into a trigonal structure, often referred to as the “R-phase”. The presence of the R-phase has been mostly reported and characterized in studies where the transformations were driven by temperature. However, there is evidence that the transformation into R-phase will occur during mechanical loading, as seen by a change of slope or elastic modulus in the stress–strain curve of NiTi at low strains [2]. On further cooling or loading, the structural symmetry is further lowered. This lowest symmetry phase of NiTi is commonly referred to as the martensite phase. Several studies in the early 1980s identified the NiTi martensite as a monoclinic distortion of a structure arising from the shuffle of the {1 1 0} planes of b.c.c.-like austenite towards a more close-packed atomic arrangement [3].

The transition from austenite to R-phase is preceded by softening of a transverse phonon mode and the growth of incommensurate superlattice reflections that ultimately lock in at the (1/3 1/3 0) positions. Several groups, over the last 10 years, have undertaken the task of identifying the structure of the R-phase of NiTi [4–7]. Even though there is still some

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controversy regarding the precise symmetry of the R-phase, there is agreement on the fact that the R-phase structure has at least three distinct Ni and Ti atoms while the CsCl-like austenite structure of NiTi has only one unique Ni and Ti atom. Thus, the austenite to R-phase transition transforms one type of Ti and Ni ion into three distinct types. Therefore, we predict that this phase transition must be associated with an electronic (charge or valence driven) transition.

2. Experimental

Studies were performed on Ni_{50.9}Ti_{49.1} plate, annealed in vacuo for 30 min at 850 °C and furnace cooled to room temperature. Synchrotron X-ray diffraction experiments on this plate were performed at the high-resolution powder diffraction beamline at the Stanford Synchrotron Radiation Laboratory (SSRL). The plate was clamped in the copper mount bolted to the cold finger of a liquid He flow cryostat. The energy to ionize an inner shell electron critically depends on the electronic structure of the ion. Hence the position and the shape of the absorption edge of Ni and Ti in NiTi is a sensitive probe of their electronic structure. We measured the Ti and Ni X-ray absorption near-edge structure (XANES) spectra at their k-edges at different temperatures. Diffraction measurements on the same samples had been previously performed at the high-resolution X-ray spectroscopy beamline at SSRL. A liquid He flow cryostat was used to achieve the desired temperature. The measurements were performed in fluorescence, but a small amount of incident beam was allowed to miss the sample and impinge on a Ti or a Ni metal foil. The position of the Ti or Ni edge, measured in transmission on the reference foil, was used to calibrate the energy of the incident beam.

3. Results and discussion

3.1. Austenite to R-phase transition

The austenite to R-phase transition is a first order transformation followed by continued distortion. The final strains associated with the transformation can exceed 0.5%. Fig. 1 shows the XANES spectra for the two elements. The XANES spectrum for the Ti edge shows small but significant changes as the material transforms from the austenite to the R-phase. The Ni spectrum for the two phases also shows changes, but these are smaller. Therefore, we conclude that there must be a change in the electronic structure of NiTi accompanying the structural phase transition from austenite to the R-phase. This valence transition, perhaps a charge disproportionation of Ti (and Ni), leads to a charge density wave and it is the origin of three distinct Ti and Ni atoms in the R-phase structure. It is known from the R-phase structure proposed by Schryvers and Potapov [4] that the average Ti–Ni bonds for the three distinct ions differ by 0.05–0.10 Å.

In addition, strong Jahn–Teller type displacements distort the co-ordination sphere of both Ni and Ti sites. Fig. 2 shows the volume (per formula unit) of NiTi as a function of temperature. A small and anomalous increase in the unit cell volume at the onset of the transition to the R-phase was observed. The volume expansion is small, but we believe, it was detected in this study because of the high precision offered by the synchrotron instrumentation used. Kulkov and Mironov [5] see a similar volume expansion on a different (the austenite to R-phase transition in their study is more than 50 K higher) NiTi alloy. Ling and Kaplow [2] also investigated the temperature dependence of the austenite to R-phase transition. However, the resolution of their sealed tube diffractometer was significantly lower (one order of magnitude less) than that of the high-resolution synchrotron based instrument employed in this study and in the study of Kulkov and Mironov. Consequently, they could have not detected the volume change, as the precision with which they were able to determine the unit cell volume is lower than the magnitude of the observed anomaly. In most materials, volume and entropy are positively correlated, and hence the volume contracts on cooling. The anomalous volume expansion of the R-phase would indicate that the common positive correlation between entropy and volume is broken at the transition by creation of a more ordered state. For example, a charge disproportionation (or ordering) phenomenon that transforms a system into multivalency, could result in larger average interatomic bond distances but still result in a lower energetic ground state. A multivalency transition or perhaps a Jahn–Teller transition will result in a discontinuous volume expansion at the onset as the correlation between volume and entropy is broken, but then will be followed by a gradual volume contraction as a new volume–entropy correlation is established in the transformed material. The austenite to R-phase appears to be such a transition.

3.2. R-phase to martensite transition

Extra peaks appear in the R-phase diffraction pattern at 200 K; their intensities increase with decreasing temperature, but by about 150 K they reach stable and maximum values. The diffraction pattern is essentially unchanged to the lowest probed temperature (~30 K).

Fig. 3 shows the experimental X-ray diffraction pattern (+ points) from the fully annealed Ni_{50.9}Ti_{49.1} plate at 55 K and the simulated diffraction pattern (dash curve) for the monoclinic (P2₁/m) NiTi martensite phase. However, the agreement between the simulation and the experimentally observed diffraction pattern is very poor ($\chi^2 = 79.51$, $R_{wp} = 54.88\%$).

It is evident from the comparison between the experimental diffraction pattern and the fit that the P2₁/m structure is not adequate to model the low temperature structure of Ni_{50.9}Ti_{49.1} in this case.

It is evident from the misfit between the experimental pattern and the P2₁/m structure that either the structure of

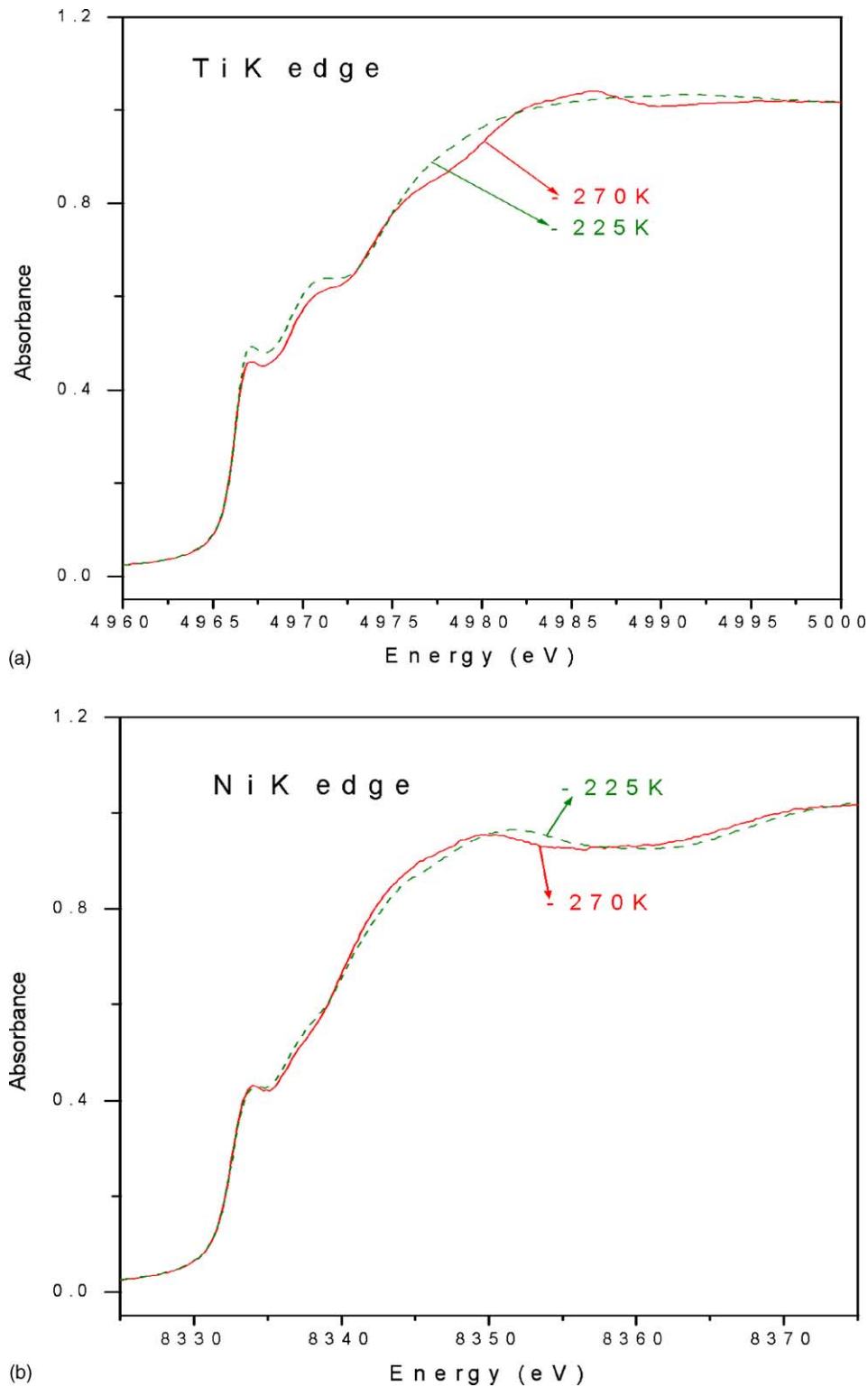


Fig. 1. Measured Ti (a) and Ni (b) X-ray absorption near-edge structure spectra at their k-edges.

low temperature phase of $\text{Ni}_{50.9}\text{Ti}_{49.1}$ has a symmetry lower than the well-known monoclinic martensite (we will call this **Hypothesis 1**), or that the curvature of the phase boundaries (see schematic in Fig. 6) is such that this composition of NiTi (with the reported annealing conditions) cannot fully

transform to the monoclinic martensite (we will call this **Hypothesis 2**).

Hypothesis 1. It has to be noted that the peaks in the observed diffraction pattern are significantly broadened by the

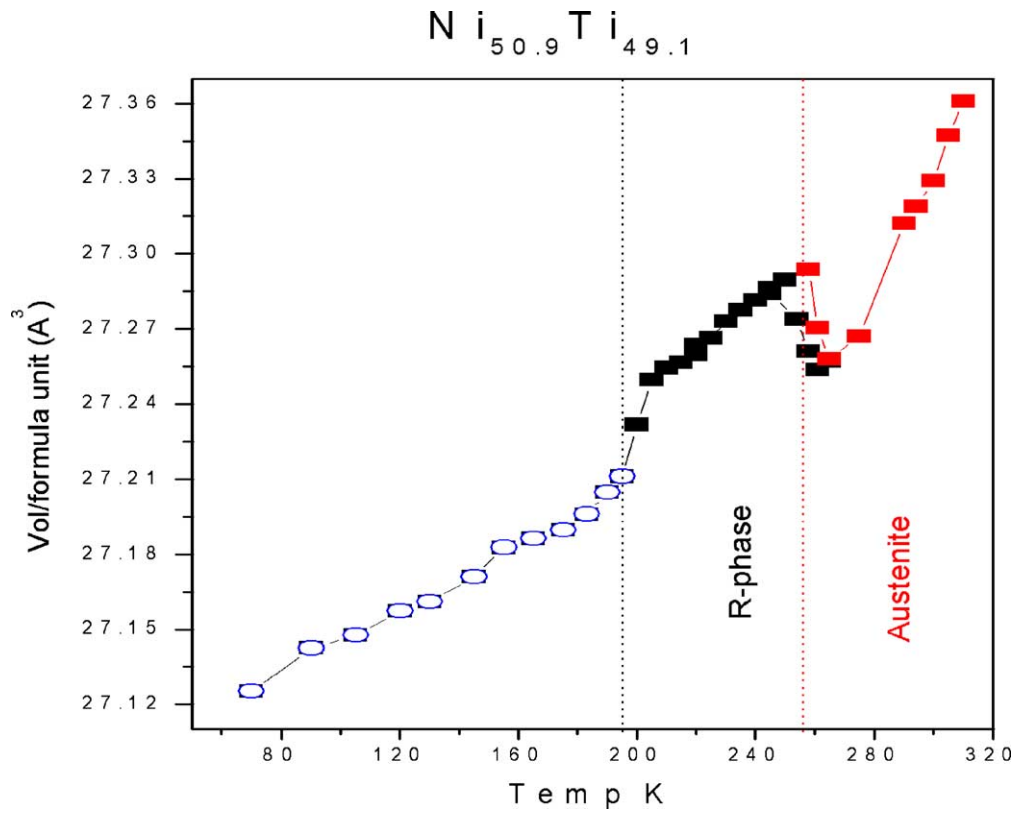


Fig. 2. Unit cell volume as a function of temperature.

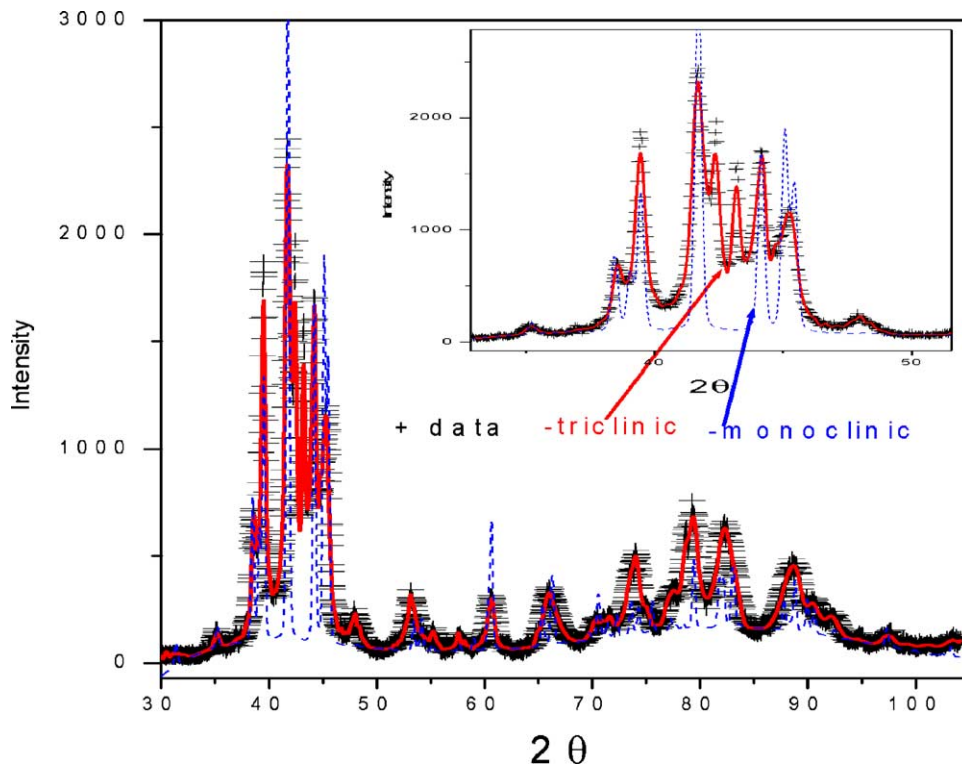


Fig. 3. XRD experimental pattern (black crosses) and triclinic (continuous line) and the monoclinic (dotted line) martensite structural simulated fits to the 55 K phase of NiTi.

small particle size of the martensite “needles” ($\leq 1 \mu\text{m}$), and by the associated transformation strain. (The instrumental resolution of the high-resolution powder diffraction beamline is an order of magnitude higher than the observed peak widths.) Due to this “microstructural” broadening of the peaks, even the lower angle peaks in the observed diffraction pattern of the martensite phase are composed of several overlapping peaks. This makes unique identification of the structural symmetry ambiguous. However, we can speculate that the austenite to R-phase transformation is driven by an “*electronic*” instability, whereas the austenite to monoclinic

martensite transformation is driven by a “*mechanical*” instability that makes the structure denser. We thus speculate that the low temperature structure observed is obtained by applying a mechanical shuffle to the R-phase distortion. Hence, the triclinic distortion can be viewed as a distortion of the austenite symmetry, arising from the “*electronic*” instability, followed by the distortion arising from “*mechanical*” instability. The application of the “close packing” mechanical shuffle to the R-phase structure enlarges the unit cell, as shown in Fig. 4, and lowers the symmetry to triclinic. The solid curve in Fig. 3 shows a LeBail fit to the experimental

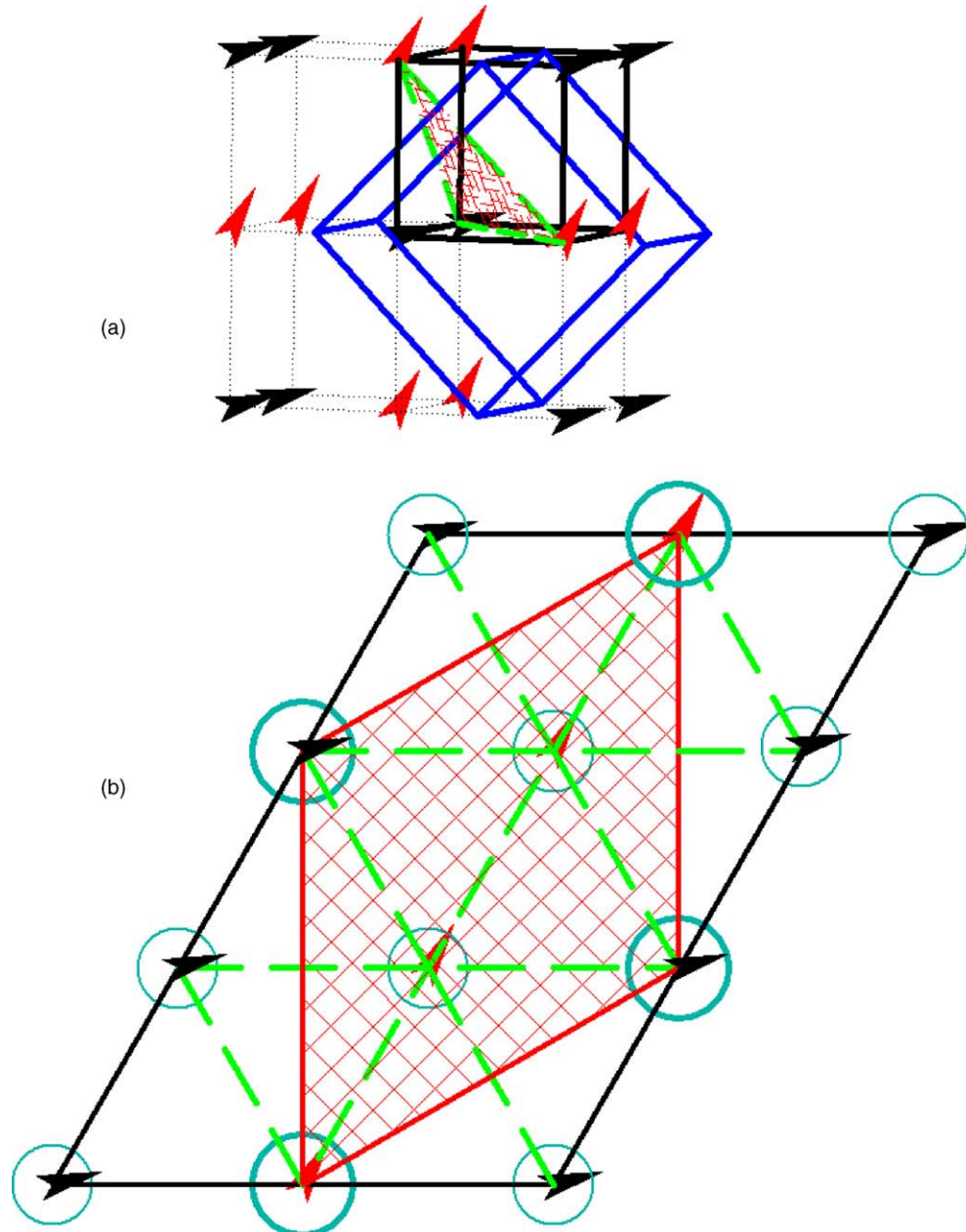


Fig. 4. In (a), the black cube represents the austenite unit cell, the light gray triangle represents the units that make the basal planes of the R-phase (see (b)), the black parallelepiped represents the monoclinic structure of the martensite phase. The gray and the black arrowheads are related by two-fold screws. In (b), the rhombus represents the basal plane of the R-phase, the black parallelogram represents the basal plane of the triclinic structure of the martensite, and the gray and black arrowheads represent sites related by a pseudo-two-fold screw.

diffraction pattern ($\chi^2 = 1.54$, $R_{wp} = 7.63\%$), from which we obtained the unit cell parameters of the suggested triclinic structure of the martensite phase of NiTi as 8.53(1) Å, 13.06(2) Å, 5.18(1) Å, 92.21(1)°, 93.66(1)°, 119.68(1)°.

In a recent study of the R-phase stabilized (Ni_{0.47}Fe_{0.03}Ti_{0.5}) shape memory alloy, Voronin et al. [8] also suggested that the structure of the martensite (at 4 K) is not monoclinic P2₁/m, but a triclinic structure similar to the one we proposed. Their structure can be obtained by transforming the cubic austenite into the trigonal R-phase via an intermediate rhombohedral structure along the cubic {111} direction ($a = 5.2$ Å, $\alpha = 73^\circ$); however, this trigonal distortion of the cubic lattice (as a result of the electronic transition) leads to a triclinic structure. A further mechanical {110} shuffle, as a result of the “mechanical” instability, would double one of the axis and crystallize the low temperature martensite. The LeBail fit to the structure ($\chi^2 = 2.26$, $R_{wp} = 9.24\%$) experimentally observed by Voronin et al. is better than that for the P2₁/m structure but inferior to the triclinic structure we propose. (The refined lattice parameters in this setting are: $\sim 5.65(1)$ Å, $12.82(1)$ Å, $5.18(1)$ Å, $73.82(1)^\circ$, $73.77(1)^\circ$, $73.78(1)^\circ$.) To fully represent the trigonal distortion of the R-phase in the orientation proposed by Voronin et al., a triclinic lattice is required. Therefore, we believe, that triclinic lattice (R-phase) proposed by Voronin et al. is incapable of fully representing the additional mechanical shuffle required to obtain the martensite phase, which is reflected in inferior LeBail fit to the experimental data. However, to uniquely characterize the martensite phase of Nitinol, the knowledge of the precise positions of the atoms in the phase is necessary.

Any alteration of the electronic structure of NiTi, by doping, with other transition metals such as Fe and Cu, or by heat treatment that results in “self-doping” via antisite defects, for example, will have a significant effect on the stability of the R-phase and consequently on the trigonal distortion of the lattice. As the proposed triclinic structure of the martensite phase of NiTi is a mechanical distortion of the trigonal R-phase, if the R-phase is suppressed, for instance by doping or by specific mechanical loading conditions [9], then the triclinic structure reverts back to the well-known single site (P2₁/m) monoclinic structure.

Hypothesis 2. The 55 K diffraction pattern can also be fitted by a two-phase mixture of the trigonal R-phase and the monoclinic martensite, as shown in Fig. 5. Note that the fit ($\chi^2 = 4.45$, $R_{wp} = 12.96\%$) is inferior to the fit to the triclinic structural model. However, it is possible that some of the misfit could arise from the very different morphology of the R-phase and the martensite; in addition, further misfit occurs if the two phases are heavily textured.

What is remarkable about this hypothesis is that, to be consistent with the observations, the phase boundaries of the R-phase and the martensite must be nearly parallel to the temperature axis below 150 K. To better illustrate this hypothesis, based on the present set of measurements, we present, in Fig. 6 a constant pressure/applied stress cut of a schematic phase diagram for NiTi.

We believe that the “electronic” and the “mechanical” instabilities are independent and orthogonal pathways for NiTi to achieve a lower ground state. The “electronic” instability appears to arise predominantly from the d-shell electronic

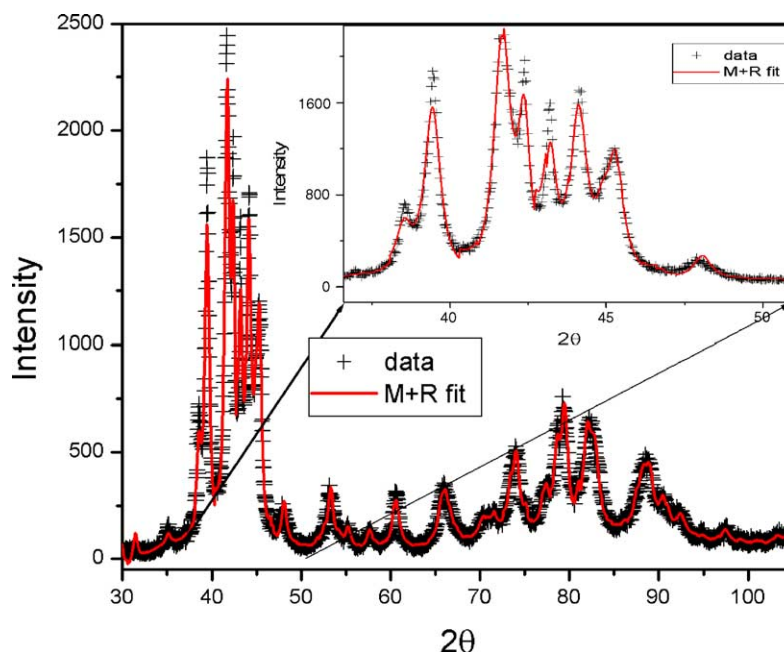


Fig. 5. XRD experimental pattern (black crosses) and two-phase (monoclinic martensite + R-phase) structural fit to the 55 K phase of NiTi.

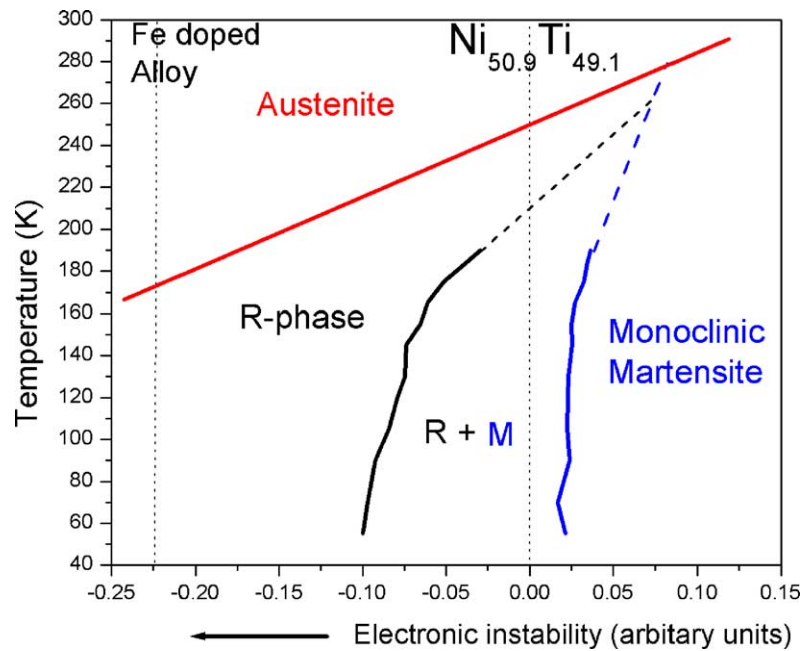


Fig. 6. Schematic diagram based on the experimental results representing the “electronic” instability, showing an isobar (or constant applied stress) cut of the phase diagram based on the two-phase model (see text for details). The “mechanical” instability axis is perpendicular to the plane of the paper.

structure of the Ti ion. The degree of the instability, and hence the stability of the R-phase, can thus be altered by changing the electronic structure of Ti site. The electronic structure of the Ti site can be altered by incorporating other transition metals, such as Fe and Cu, V, Cr or Ni. Isovalent transition metals, such as Zr and Hf for Ti, or Pd for Ni, will alter the electronic structure of NiTi only marginally, and will not, therefore, have such a significant effect on the “electronic” instability. However, substitution on Ti or the Ni site also has the effect of altering the average ionic size of the Ti site and thus can significantly alter the “mechanical” instability of the alloy as well (see below). For example, isovalent substitutions like Hf for Ti, would have little effect on the “electronic” instability, but because of the larger ionic size of Hf, they can alter the “mechanical” instability of the alloy significantly.

Unless the body-centered ion is significantly smaller in size than the corner ions in a CsCl-type structure, the CsCl-type structure is not close-packed and can be transformed to a denser structure on application of pressure. The tendency of the CsCl-type structure to transform to a denser structure would then depend on the ionic sizes of the two types of ions, and the magnitude and the direction of the applied stress. (Only the component of the stress that facilitates the $\{110\}$ type mechanical shuffle is relevant to the “mechanical” transition.)

We therefore believe that the austenite/R-phase boundary in Fig. 6 is determined by the degree of the “electronic” instability and therefore by the electronic composition of the Ti site. The size of the monoclinic martensite field in the phase diagram is dependent on the size difference between the ions on the Ti and the ions on the Ni sites, and thus, the

precise composition and the heat treatment of the alloy. But the martensite stability region is also very strongly dependent on the shear component of the applied pressure/load parallel to the $\{110\}$ cubic planes. The shear component can be combined with the ionic size difference to generate a measure of the mechanical instability. Because the “mechanical” instability is orthogonal to the “electronic” instability, the axis representing the mechanical instability comes out of the plane of Fig. 6.

4. Concluding remarks

Based on this study, it is concluded that the austenitic phase in Nitinol undergoes an “electronic” instability that results in the R-phase structure, and a “mechanical” instability that leads to a denser atomic packing arrangement, the martensitic phase. The “electronic” and the “mechanical” instabilities lead to two independent modes of distortion of the CsCl-type structure of NiTi. The transition due to “mechanical” instability leads to a denser packing, whereas the transition due to the “electronic” instability leads to a more open structure. The “electronic” instability leading to the R-phase is very sensitive to doping on the Ti site of the alloy with other transition metal ions. The “mechanical” instability is very sensitive to the sizes of the ions on the two types of sites and the shear component of the applied load parallel to the $\{110\}$ planes of the austenite. For a given degree of “electronic” instability, which is defined by the alloy composition, the “mechanical” instability can be made sufficiently large, by applying the appropriate loading conditions, so that the

R-phase region could be suppressed. Therefore, the transition of austenite NiTi into various phases is not only strongly dependent on the “*electronic*” and the “*mechanical*” instabilities but also on the competition between the two.

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