

Structural Transitions in a TiNiFe Shape Memory Alloy

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Results for resistance versus temperature, differential scanning calorimetry (DSC), Mössbauer spectroscopy, and magnetic susceptibility measurements in a $\text{Ti}_{50}\text{Ni}_{47}\text{Fe}_3$ sample are presented. The resistance versus temperature curve shows a sharp increase at 245K and then rises slowly until a maximum is attained at $\approx 150\text{K}$. The DSC curve also exhibits a peak at the former temperature. The room temperature Mössbauer spectrum consists of a single line. As the temperature is lowered to 270K, a small asymmetric quadrupole doublet appears. The isomer shift and quadrupole splitting values of this doublet increase with decreasing temperature until almost constant values are achieved at temperatures $\approx 100\text{K}$. The magnetic susceptibility curve shows a sharp decrease that begins at 255K and then an unexpected increase at 90K. We relate these observations with a charge density wave-driven premartensitic transition in this system, and with the final martensitic phase.

INTRODUCTION

The discovery that the addition of small quantities of Fe to the TiNi alloy produces different shifts in the martensitic and pre-martensitic phase transition temperatures (T_M and T_p , respectively) [1] allowed separate study of both phases. In fact, substitution of 3% Fe for Ni depresses T_M about 100°C more than T_p . Furthermore, the substitution of nickel atoms by iron atoms in the structure allows the use of Mössbauer spectroscopy to investigate minute changes in the local surroundings at the crystal sites where the Fe atoms are [2]. As is well known, this spectroscopy is extremely sensitive to internal electric fields, and these, in turn, will vary with structural changes. On the other hand, the magnetic properties of this system are due solely to the paramagnetic character of the electrons near the Fermi surface, so that careful magnetic susceptibility

measurements will give information about the variations of the electronic density of states at that surface.

EXPERIMENT

A TiNiFe alloy was prepared by melting a 50g load (50%Ti, 47%Ni, and 3%Fe nominal composition) in an evacuated arc furnace. Homogenization was performed at 1000°C in an evacuated fused quartz capsule, followed by quenching in water at room temperature. Carefully cut slices were used, after reheating and quenching, in each of the measurements. The resistance versus temperature curve was obtained, by the usual four-point technique, in a closed-cycle helium refrigerator. The calorimetric measurements were performed with a differential scanning calorimeter. In order to obtain adequate transmission Mössbauer spectra, a thin slice

of the material was cut with a diamond cutter and then laminated and polished by hand until its width was 0.05mm. Once this slice was obtained, it was rehomogenized in the method described earlier and then placed in a closed-cycle helium refrigerator suitable for Mössbauer spectroscopy. The spectra were obtained with a constant acceleration spectrometer, with a ^{57}Co in Rh source kept at room temperature. All measurements were taken first while the temperature was lowered, and again during the heating process. Direct current magnetic susceptibility curves were obtained with a superconducting quantum interference device-based magnetometer. The procedure used was the following: In a zero magnetic field, the sample was cooled down to 4K; once the sample was in thermal equilibrium at this temperature, a magnetic field of 1000G was applied, and the measurements were taken from 4 to 330K and back to 2K to get a complete cycle. Demagnetization field corrections are almost negligible, because the shape of the sample used was a cylindrical rod with diameter d , whose length l is much larger than d , and the field H was applied parallel to the cylinder axis, so the only corrections can be due to misalignment between these two directions.

RESULTS AND DISCUSSION

In Fig. 1, a clear increase in the resistivity is observed at 245K; the resistivity changes from $8.4 \times 10^{-5} \Omega\text{-cm}$ at this temperature to a maximum value of $9.0 \times 10^{-5} \Omega\text{-cm}$ at about 150K. This represents a change of about 8%. A specific heat fluctuation is also observed at the same temperature (Fig. 2). These features have been associated with the onset of the incommensurate (I) to commensurate (C) transition, and the temperature at which the maximum resistance is attained, with the T_M temperature [3]. Also interesting in the resistivity curve are the small hysteresis observed during the I-C transition (220–240K) and in the 30–90K temperature range, where the martensitic transformation occurs [3].

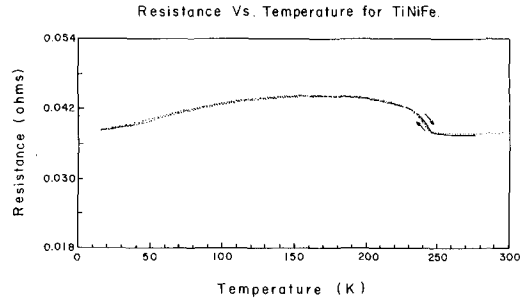


FIG. 1. Resistance versus temperature.

The transformed fraction as a function of temperature can be obtained by integration of the DSC curve [4] and, when this is done, a shift of about 2K between the peak positions is obtained during the cooling and heating processes (Fig. 3). In the same way, we computed δH values $\approx 4 \text{ J/g}$, which indicates that this anomaly corresponds to the R-phase formation.

The Mössbauer spectra obtained at different temperatures are shown in Fig. 4; no magnetic splitting is observed at any temperature, so the spectral characteristics are due only to electrostatic interactions between the electric charge distribution around the Mössbauer nucleus and the nuclear charge. This interaction can be divided into two terms [5]:

(a) The isomer shift (IS), always present, is associated with the monopole interaction of the nuclear charge with the electronic charge density at the nucleus (s and $p_{1/2}$ electrons); it produces a shift of the nuclear levels of the bare nucleus and is sensitive,

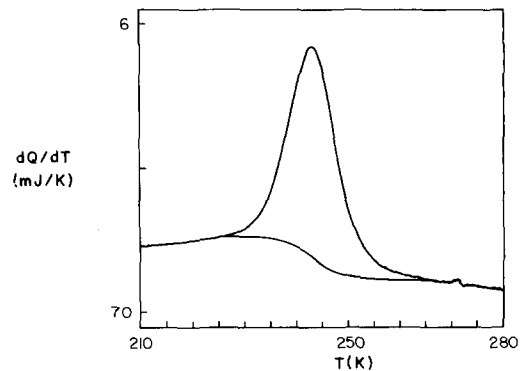


FIG. 2. Differential scanning calorimetry curve.

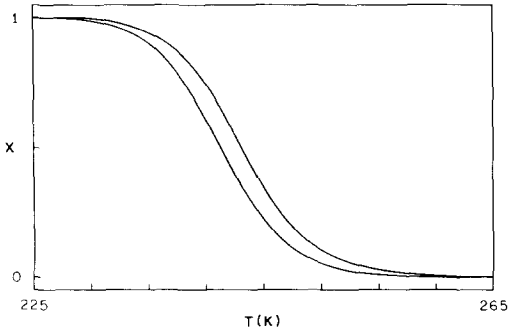


FIG. 3. Transformed fraction versus temperature.

via electronic screening of the valence electrons, to the ionic state of the Mössbauer atom.

(b) The quadrupole splitting is due to the interaction between a permanent quadrupole moment of a nucleus and the next higher multipole term associated with the charge distribution around it. This interaction is different from zero only if there is a nonspherical electric field gradient associated with the charge distribution. In the case of a cubic crystal structure, the three components of the electric field gradient are

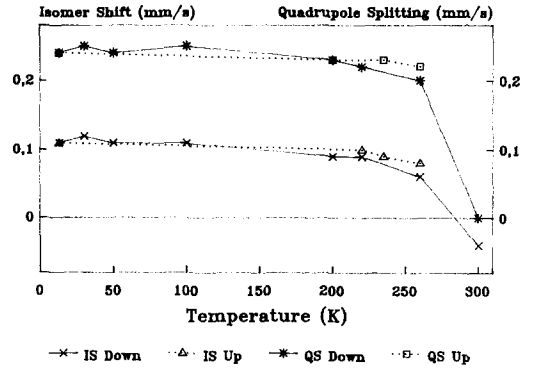


FIG. 5. Mössbauer parameters as a function of temperature.

equal, and this interaction is zero. If this is not the case, the interaction manifests itself as two lines in the Mössbauer spectra.

The solid line in Fig. 4 is the result of a fitting process that uses a constrained least-squares program and keeps the line widths fixed. At room temperature, the spectrum consists of a single line ($\Gamma = 0.26\text{mm/s}$), in accordance with the expected substitution of the iron atoms in the Ni sites of the ClCs (B2) cubic parent structure. The measured isomer shift ($IS \approx -0.3\text{mm/s}$) indicates an Fe(II) state, which is in agreement with the valence states of Ti and Ni in this alloy. When the temperature is lowered to 270K, a small quadrupole doublet ($\delta Q \approx 0.3\text{mm/s}$) appears and reveals a change in the local symmetry of the iron atoms. This temperature is slightly higher than the one at which the premartensitic transition starts, as judged from the resistance versus temperature and DSC curves, which indicates that this transition has already started in accordance with previously reported results [6].

Figure 5 shows the temperature behavior of the IS and δQ values. As the temperature is lowered, the IS value of the doublet increases until an almost constant value is attained at about 90K; however, a somewhat smaller value is obtained at 13K. One possible reason for the increasing IS values is a diminishing effect of the screening of the valence electrons (mainly *d* electrons) due to a change in the electronic background where the metallic ions are immersed, produced by the change in the density of states near the Fermi surface. During the heating

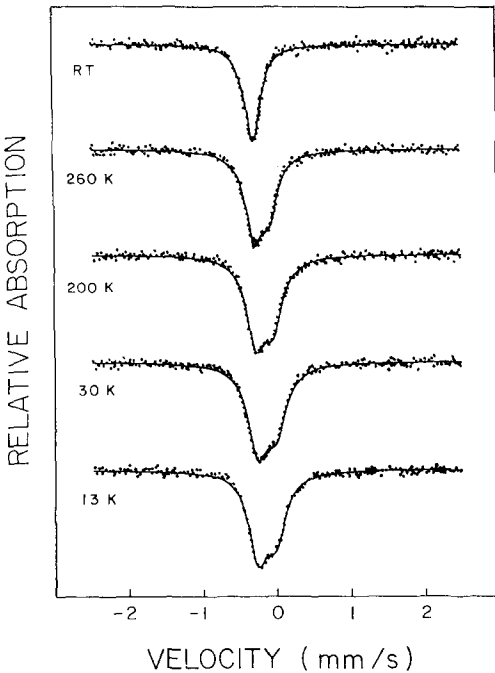


FIG. 4. Mössbauer spectra at different temperatures.

process, the IS shift decreases with increasing temperature, but in a nonreversible way; actually, there is a small "hysteresis" of about 10K at least in the 200–250K temperature range. This behavior is associated with the premartensitic phase of the system.

On the other hand, the quadrupole splitting is directly related with the crystal symmetry, so the observed increase in δQ implies an increase in the magnitude of the electric field gradient, which, in turn, is associated with a lowering of the crystal symmetry. That is to say, local rhombohedral distortions begin much before the temperature at which this distortion is "locked in" [7]. The low temperature (13–100K) value of δQ fluctuates around 0.245mm/s and does not reveal that a martensitic phase transformation is taking place.

Figure 6 shows a plot of the susceptibility versus temperature, where several interesting characteristics can be seen: First, a hysteresis is observed from ≈ 4 to 200K. This is, to our knowledge, the first time when a feature directly related to the martensitic transition of this alloy is seen clearly. Previously reported studies [4, 6], with less precision and resolution, have found the same behavior. The second thing to notice is found in the 330–200K region: first, a temperature independent behavior from high temperatures down to about 255K and then

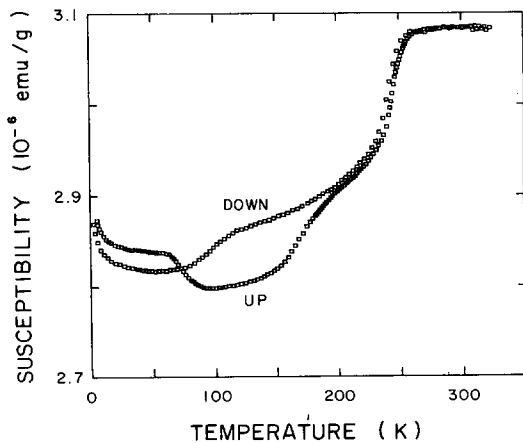


FIG. 6. Magnetic susceptibility as a function of temperature.

a steep decrease until an 8% lower value is reached at 200K.

The observed temperature behavior is related to Pauli susceptibility, which, in general, can be separated into two terms, one that depends on temperature and another that does not. The equation that accounts for this behavior is given by [8]:

$$\chi_P = \chi_O + \chi(T).$$

The first term can be written as $\mu_B^2 D(E_F)$, where μ_B is the Bohr magneton, and $D(E_F)$ is the density of electronic states at the Fermi level. The second term, however, is only important at high temperatures, when $kT \gg E_F$, and it is of no concern in this work.

It is interesting to point out that an opening of a gap at the Fermi surface will drastically decrease the electronic density of states; if this is the case, Pauli's susceptibility should show a sharp variation. Therefore, the observed changes in our measurements below 255K must be related with a kind of condensation that reduces the total energy of the system. This gap opening could be due to the nesting of a small portion of the Fermi surface, as a result of a strengthening of the electron-phonon interaction at the transition temperature of 255K; this, in turn, couples part of the Brillouin zone with a possible formation of a charge density wave (CDW). Actually, according to our measurements, only around 8% of the total Fermi surface has been nested in accordance with the increase of the resistivity.

CONCLUSIONS

The resistivity and calorimetric measurements indicate that at around 255K, a structural transition associated with a diminishing of the number of charge carriers is taking place. The behavior of the Mössbauer parameters as a function of temperature indicates that there is, indeed, a broad premartensitic transition that starts before this transition manifests itself in the resistivity and calorimetric characteristics. The small values of δQ during the temperature interval from 250 to 13K indicate that the struc-

tural deformations probably correspond to a rhombohedral, rather than to a tetragonal, distortion, as has been reported [9]. No real evidence of a martensitic transition can be extracted from the δQ values. The temperature dependence of the IS can be understood in terms of changes in screening effects due to the variation in the electronic density of states when a CDW is formed. This is confirmed by the way in which the magnetic susceptibility changes with temperature, which, on the other hand, clearly shows a hysteresis in the 13–200K range. To our knowledge, this is the first clear evidence that a martensitic transformation is taking place in this system. In short, all our measurements indicate the formation of a CDW responsible for the premartensitic R-phase formation.

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