Magnetic anomaly in Ni$_{51.5}$Fe$_{21.5}$Ga$_{27}$ single crystalline ferromagnetic shape memory alloy studied by ac impedance measurements

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A magnetic anomaly in the austenitic state of Ni$_{51.5}$Fe$_{21.5}$Ga$_{27}$ single crystalline ferromagnetic shape memory alloy has been studied by means of ac impedance measurements. A much stronger effect of the degree of atomic order on the temperature of this anomaly (as compared to the temperature of the martensitic and para-ferromagnetic transitions) has been found. It has been shown that apart from the previously reported slight variation in the saturation magnetization, the magnetic anomaly results in a nearly one order of magnitude change in the value of initial magnetic permeability. The anomaly is not revealed in the resistive impedance at low frequencies, pointing likely to its purely magnetic origin. © 2009 American Institute of Physics. [DOI: 10.1063/1.3106043]

I. INTRODUCTION

Shape memory alloys show a structural phase transition called thermoelastic martensitic transformation (MT). The MT is behind such peculiar effects present in these alloys as large reversible mechanical deformations (superelasticity) and the shape memory effect. Ferromagnetic shape memory alloys, in addition to previous properties, can exhibit large magnetic field induced strains in comparison with other ferromagnetic materials. These materials demonstrate a variety of additional features as magnetic anomalies, which, in the majority of cases, have been linked to premartensitic and/or intermartensitic transitions. Ni–Mn–Ga alloys present magnetic field induced deformations of up to 10%, but their brittleness is a reason to search alternatives, such as Ni–Fe–Ga systems. Murakami et al. studied Ni$_{51.5}$Fe$_{21.5}$Ga$_{27}$ with electron holography and Lorentz microscopy, and they reported a magnetic anomaly related to a change in the topology of magnetic domain structure. Sharma et al. reported a drop in magnetization and an elbow in resistivity of Ni$_{54}$Fe$_{19}$Ga$_{27}$ about 20 K before the MT on cooling. They proposed a premartensitic or intermartensitic transition as the mechanism behind this phenomenon. The aim of the present work was to clarify (i) whether or not the reported anomaly is associated with supposed premartensitic/intermartensitic phenomena and (ii) whether or not this structural rearrangement can be observed both in magnetic properties and resistivity. To this end, a Ni$_{51.5}$Fe$_{21.5}$Ga$_{27}$ alloy was used in which the para-ferromagnetic and MT temperatures are widely separated. This fact enabled us to obtain strong variations in MT, para-ferromagnetic transition, and magnetic anomaly temperatures by changing the degree of $L_2_1$ order through different thermal treatments but keeping a wide temperature range between the MT and the Curie temperature ($T_c$).

II. SAMPLE PREPARATION AND METHOD

Single crystals were grown by Bridgman method. Several bar-shaped samples $2 \times 1 \times 17$ mm$^3$ were spark cut with longitudinal axis in [100] direction and the two other perpendicular axes in $<110>$ directions.

Two basic heat treatments were used in order to obtain different degrees of atomic order. The samples were annealed at 1070 K for 15 min and then slowly cooled (SC) in air (SC samples) or water quenched (WQ) after annealing for 30 min at 970 K (WQ samples). The former treatment leads to a high degree of $L_2_1$ long range order, whereas the latter reduces it. WQ samples received afterward several consecutive annealings at 470 K to gradually increase the degree of $L_2_1$ order. Measurements of electric impedance were performed after each heat treatment/annealing.

When an alternating current (AC) flows in a sample, in the quasistatic limit of the classical model, the magnetic penetration depth or skin depth is given by

$$\delta = \sqrt{\frac{2\rho}{\omega\mu a}}$$

where $\rho$ is the resistivity, $\omega$ is the angular frequency of the electric current, and $\mu$ is the effective transverse magnetic permeability. From Maxwell equations, the electrical impedance $Z=R+iX$ (where $R$ is resistive impedance, in phase signal or real part, and $X$ is the inductive impedance, out of phase signal or imaginary part), for a cylindrical conductor of radius $a$ and direct current resistance $R_{dc}$, is given by

$$Z = R_{dc}ka J_0(ka) \frac{2J_1(ka)}{J_0(ka)^2},$$

where $k=(1+i)/\delta$ and $J_0$ are the Bessel functions of the first kind. From Eq. (2), in the low frequency limit ($a/\delta \ll 1$), the real and imaginary parts of $Z$ may be approximated as

$$R = R_{dc} \left[ 1 + \frac{1}{48} \left( \frac{a}{\delta} \right)^4 + \cdots \right],$$

$$X = \frac{R_{dc}a^2}{4} \left( \frac{a}{\delta} \right)^2 \left[ 1 + \frac{1}{24} \left( \frac{a}{\delta} \right)^4 + \cdots \right].$$

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our samples were not cylindrical, Eqs. in magnetic permeability with temperature were expected to be produced by variations in frequency, the changes in the imaginary part of the signal may be written at low frequencies as

\[ \begin{align*}
X &= \frac{1}{4\pi} \left[ \frac{1}{\delta} \right]^2 - \frac{1}{384} \left( \frac{1}{\delta} \right)^6 + \cdots , \\
\end{align*} \tag{4} \]

respectively. As the exponents of \( \delta \) increase rapidly in the series, only the first term will be considered. Using Eq. (1), Eq. (4) may be written at low frequencies as

\[ X = \frac{\omega \mu}{8 \pi} = \omega L, \tag{5} \]

where \( L \) is the inductance of a wire of length \( L = \mu l / 8 \pi \). As our samples were not cylindrical, Eqs. (3) and (4) were basically used to perform a qualitative estimation. For a fixed frequency, the changes in the imaginary part of the signal with temperature were expected to be produced by variations in magnetic permeability [Eq. (5)]. The in phase component of impedance at low frequencies tends to represent the dc resistance. At elevated frequencies, it is also affected by the variation in permeability [Eq. (3)] since the depth of the skin effect \( \delta \) depends on \( \omega \mu \) [Eq. (1)].

\[ R \text{ and } X \text{ were measured by four probe method by means of an EG&G 5204 lock-in amplifier for frequencies between 21.7 and 6800 Hz. Before starting the measurements, the samples were heated at } \sim 40 \text{ K above the } T_c \text{ in order to adjust the imaginary part (out of phase signal) to zero.} \]

III. RESULTS AND DISCUSSION

In Fig. 1 the data on \( R \) and \( X \) are shown as a function of temperature for an ordered SC sample at 68.6 Hz. The real part of impedance [Fig. 1(a)] exhibits two important effects: a small change in the slope at around 350 K and a notable increase in the resistance around 150 K during cooling, followed by a fully reversible decrease around 160 K during heating. The first effect does not demonstrate temperature hysteresis, and it corresponds to the para-ferromagnetic transition. The strong variation in resistance accompanied by temperature hysteresis is due to the MT.

The imaginary part of \( Z \) is plotted in Fig. 1(b). The main features are as follows.

(i) An extremely sharp peak at about 350 K, very close to \( T_c \). This peak is identified as a Hopkinson peak.

(ii) In the range of \( \sim 350-240 \text{ K} \), \( X \) decreases during cooling. There is thermal hysteresis between cooling and heating curves over the temperature range of 350–285 K. In the range of approximately 330–310 K, the variation in \( X \) is the strongest. This feature is similar to the drop reported by Majumdar et al. in ac susceptibility measurements of Ni_{54}Fe_{19}Ga_{27}.

(iii) Between 230 K and the MT, \( X \) remains almost temperature-independent.

(iv) Contrary to the real part [Fig. 1(a)], the imaginary part of the impedance decreases during the transition from parent to martensitic phase due to the lower permeability in the latter.

(v) Lastly, in the martensite phase, \( X \) increases on cooling.

Figure 2 shows the derivative of \( R \), \( dR/dT \), on cooling at 21.7 Hz. According to Eq. (3), \( R \) at low frequency tends to represent the direct current resistance \( R_{dc} \). \( dR/dT \) clearly shows the direct MT start \( (M_t) \) and finish \( (M_f) \) temperatures, as well as \( T_c \). On the contrary, no effect is detected in the resistance \( R_{dc} \) between \( M_t \) and \( T_c \).

In Fig. 3, results of the measurements at 68.6 Hz for a WQ sample are shown. This sample is characterized by an initial low degree of \( L2_1 \) atomic order and its consecutive increase after the series of annealings at 470 K.

Data of \( R \) [Fig. 3(a)] show that as the atomic order increases with the annealing time, the resistance decreases, as should be expected. The MT is also notably shifted to lower temperatures with increasing long range ordering, as has been observed in Ref. 15.

In Fig. 3(b), data of \( X \) are shown. From this figure, several salient features of the para-ferromagnetic transition can be distinguished.

(i) This transition after water quenching is more diffuse...
than in the case of SC sample in the sense that the imaginary part rises much more gradually over a wider range of temperatures [see Fig. 1(b) and the curve for 0 ks in Fig. 3(b)]. Its temperature range is reduced with the increase in atomic ordering as a result of consecutive annealings. This tendency is consistent with the observation of a sharp para-ferromagnetic transition in the sample with high degree of atomic ordering [SC sample, Fig. 1(b)].

(ii) $T_m^c$ is increased by atomic order. This means that the temperature range of the ferromagnetic parent phase broadens with the rise in atomic order.

(iii) Near $T_m^c$, there is a peak whose height increases with the degree of atomic ordering: for 0 ks of annealing it is not visible, but for 95.4 ks, the peak is well defined. As mentioned above, it is identified as a Hopkinson peak. For the samples with 95.4 ks of annealing, the temperature of this peak is very close to $T_m^c$.

Figure 3(b) shows also a magnetic anomaly in $X$ within the temperature domain of the ferromagnetic parent phase, consisting of a maximum followed by a fast drop on cooling, between the Hopkinson peak and MT. On further cooling, below the magnetic anomaly temperature, $X$ drops again at the MT. When increasing the order with successive annealings, the magnetic anomaly is strongly shifted to higher temperatures, the shift being higher than those of the MT and $T_m^c$ after 95.4 ks of annealing. It is remarkable that the value of the maximum is higher for the intermediate times of annealing. The behavior of the SC sample [Fig. 1(b)] at 350–270 K can be seen as a limiting case of the observed evolution of the magnetic anomaly for WQ sample [Fig. 3(b)] when atomic order grows. It is worthy to note, comparing the ratio of $R$ and $X$ in Figs. 3(a) and 3(b) with the ratio given by Eqs. (3) and (4), that the condition $a/\delta \leq 1$ is fulfilled for a given frequency of $f=68.6$ Hz. Therefore, Eq. (5) is applicable to evaluate magnetic permeability values from the temperature dependence of $X$.

The magnetic anomaly studied in the present work is thought to be the same anomaly as reported previously.\(^5,7\) The difference in the temperature ranges can be attributed to atomic ordering and different compositions. So, in reference to this magnetic anomaly, conclusions are as follows.

(i) It is not an intermartensitic transition, contrary to the hypothesis of Sharma et al.\(^7\) Using an alloy with widely separated $M_s$ and $T_m^c$ and varying the temperature of the anomaly by heat treatments allow us to clearly identify the positions of that anomaly and MT. Comparing Figs. 3(a) and 3(b), it is clearly visible that the increase in resistivity during MT is situated at much lower temperatures than the sharp drop related to the magnetic anomaly.

(ii) It does not seem to be a premartensitic transition related to the MT, as suggested before,\(^7\) because the MT is shifted to lower temperatures and the magnetic anomaly to higher ones with the increase in atomic ordering, just as the $T_m^c$ does.

(iii) Its origin is likely related to magnetic phenomena: first, the $T_m^c$ rises and the magnetic anomaly also shifts to higher temperatures when atomic ordering increases; second, the anomaly can be discerned neither in differential scanning calorimetry (DSC) runs\(^19\) nor in the real part of the ac impedance at low frequencies (which means that it does not have any effect on the direct current resistivity $\rho$). Therefore, no structural transition can be distinguished within the resolution of the used experimental techniques. On the other hand, one cannot discard a possible role of fine structural rearrangements, such as recently reported formation of long range elastic strain fields\(^20\) not revealed by present experiments.

It is notable that the para-ferromagnetic transition is diffuse in samples with low degree of long range order, as seen in Fig. 3(b) in comparison with Fig. 1(b). This broadening of the transition is unlikely the effect of composition variations since the temperature of annealing (470 K) is not high enough for long range diffusion in our crystals; there is no degradation of the MT even for 10 Ms of aging at 520 K.\(^21\) The size of antiphase domains has been found to be very small (at the order of 10–30 nm) in disordered Ni$_{51}$Ga$_{27}$Fe$_{22}$ alloy,\(^14\) thus producing a high density of antiphase boundaries. The latter are efficient pinners for the magnetic domain walls.\(^22\) Thus, high density of obstacles for the motion of
magnetic domain walls probably can explain broadening of the para-ferromagnetic transition in samples with low degree of long range order.

Figure 4 illustrates the effect of frequency on the imaginary part of the impedance \(X\) for a SC sample: temperature spectra on cooling at different frequencies (21.7, 68.6, 686, 2170, and 6860 Hz), with the plots at low frequencies of 21.7 and 68.6 Hz in the inset.

As mentioned earlier, comparison of the absolute values of \(X\) and \(R\) shows that the condition \(a/\delta \ll 1\) is fulfilled for the frequency of 68.6 Hz. Therefore, Eq. (4) is transformed into Eq. (5), and temperature dependence of \(X\) just reflects the temperature dependence of the permeability. On the other hand, provided \(a/\delta \ll 1\), the frequency dependence of \(X\) should be linear with the slope yielding the absolute value of permeability [Eq. (5)]. Figure 5(a) shows the cross-section of data in Fig. 4 up to 686 Hz (higher studied frequencies do not properly satisfy the condition \(a/\delta \ll 1\) for our full experimental temperature range) at different temperatures between 100 and 340 K. In the same way, Fig. 5(b) shows a cross-section from the data of the sample annealed for 9 ks after water quenching (in Fig. 3(b), data at 68.6 Hz are shown) at temperatures between 120 and 310 K. Those temperatures were chosen to check the behavior in the different zones of the \(X\) temperature spectra. As expected, \(X\) demonstrates linear dependence with the frequency when \(a/\delta \ll 1\). Although our samples were not of cylindrical geometry, as required by Eq. (5), we believe that this equation can be used for estimation of the effect of temperature on \(\mu\) since the data for different temperatures are obtained for the same sample. The values of permeability obtained from the slopes of the \(X\) frequency dependences [see Eq. (5)] are given in Table I for the SC sample and the sample which has been annealed for 9 ks after water quenching. The permeability in the ferromagnetic martensite is the lowest but is of the same order as that in the low permeability zone in the ferromagnetic parent phase below the magnetic anomaly temperature. On the other hand, permeability values are one order of magnitude higher

<table>
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<tr>
<th>(T) (K)</th>
<th>(\mu/\mu_0)</th>
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netic anomaly is detected at temperatures well above the MT, and therefore, it forms the low-temperature limit of a permeability window.

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