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Ultrasonic Study of Structural Instabilities in Nickel Induced by Magnetic Fields

Ariel Moreno-Gobbi[a], *Daniel Moreno*[b]*, *Gabriel Zamir*[c]

[a]*Instituto de Física, Facultad de Ciencias, Iguá, 4225, Montevideo, Uruguay*
[b]*Israel Propulsion Physics Division, Soreq NRC, Yavne 81800, Israel*
[c]*Department of Physics, NRCN, P.O. Box 9001, Beer Sheva 84190, Israel*

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The ultrasonic phase velocity was measured on a high purity nickel single crystal with a bias magnetic field in cooling and heating runs over the interval of temperatures from approximately 100 to 325 K. An evident anomaly of the phase velocity was observed in both branches of the temperature cycle. The temperature of the anomaly in the heating run was always greater than that in the cooling run, indicating the presence of a hysteretic mechanism. The observed changes are attributed to dimensional alignment of the nickel single crystal twins which are able to distort the crystalline network. The temperature of the anomalies and its hysteretic behavior depend on the synergy between the direction and strength of the magnetic field, the direction of the ultrasonic wave propagation, the internal friction between the domains and the crystallographic orientation. The frictions between magnetic domains that do not contribute to the velocity anomaly produce a hysteretic loop. The process can be easily inhibited by disorientation of the magnetic field.

Keywords: *ultrasound, crystalline nickel, shape memory, magnetism*

1. Introduction

Active materials convert the thermal, electric or magnetic energy applied to them into mechanical energy. Special materials defined as "Shape Memory Alloys" (SMAs) display a thermally activated transformation, with the characteristic of large changes of dimensions. Because of their ability to return to their original shape and to modify their geometry, these materials have a wide range of technological applications.

"Ferromagnetic Shape Memory Alloys" (FSMAs) are the most interesting active materials, because of their rapid reaction speed and large dimensional changes. At certain temperatures, these materials produce dimensional changes when they are exposed to magnetic fields. The use of magnetic fields as a catalytic agent in this process enables these materials to respond a hundred times faster than thermally activated materials.

For instance: The NiMnGa intermetallic alloy has a martensitic and ferromagnetic phase stable below 273 K. In a previous study, the application of a 0.8 Tesla magnetic field parallel to [001] to this alloy induced a dimensional change in the same direction. The initial change (0.2%), observed in the preliminary experiments, was later improved to reach 10%[1,2]. These dimensional changes are attributed to the material's high magnetic anisotropy. The martensitic phase, which appears on this alloy at 265 K, has a twin microstructure and a prominent magnetic anisotropy. When a magnetic field is applied, the domains on both sides of the twin boundaries try to align themselves in the direction of the field. According to the authors, the energy necessary to produce domain rotations is higher than that necessary to move the twin boundaries; therefore the twin boundaries motion process can explain the dimensional change. Twin boundary domains oriented in the direction of the magnetic field will grow at the expense of those with different magnetic orientation[3].

As it is well known, Ni is a ferromagnetic FCC metal with a Curie temperature of 627 K, which presents a negative magnetostrictive coefficient. The magnetostriction in Ni has a saturation value smaller than $\Delta l/l \approx -40 \times 10^{-6}$ [4], from which a maximum relative variation of $\approx 0.004\%$ for the velocity can be expected for this metal by electrostriction.

Among the FCC materials, nickel is remarkable for its many uses in technologies with magnetic applications. Despite the fact that, as it cools, nickel does not produce the ferromagnetic and martensitic transformations observed in the FSMAs, the behaviour of nickel under applied magnetic fields is of great interest. Unlike NiMnGa, which has a tetragonal structure and forms twins during the martensitic transformation, the FCC structure of nickel tends to form stacking faults during solidification.

In FCC materials, the intrinsic energy of the stacking faults is defined as the energy necessary to change the disposition of the atomic planes from the typical ABCABC order found in the FCC structure, to the ABCBCA order, which is characteristic of an HCP structure. Near the fusion temperature, the Helmholtz free energy for these two structures differs by only 0.05%[5,6]. For that reason, we can expect to find large numbers of stacking faults in nickel[7].

The growth of magnetic domains in a material depends upon the magnetic field applied and the material's elastic and magnetic properties. The magnetic behaviour of a crystalline, ferromagnetic material depends upon its atomic structure and crystallographic orientation. In fact, the coercitivity and magnetic anisotropy of HCP structures are usually higher than that found in FCC structures[8,9]. Moreover, despite the fact that these crystalline structures are very similar, some calculations demonstrate that the elastic constants of FCC structures are 20% higher than those of HCP structures[10].

This research is a study of the change in ultrasonic behaviour with temperature of a high purity nickel single crystal exposed to a magnetic field. Special emphasis was placed on description of the

*e-mail: moreno@fisica.edu.uy

processes which link the crystallographic structure and orientation to the applied magnetic field.

2. Experimental Procedure

For the purposes of this investigation, electro-erosion was used to cut a high purity nickel single crystal sample into the shape of a cylindrical bar of circular section with a diameter of 10 mm and a height of 10 mm. After cutting, the sample was mechanically polished until a parallelism of 10^{-4} radians was attained between the opposing faces. This parallelism is indispensable for the accuracy of ultrasonic measurements.

Residual stresses induced by the polishing were eliminated from the sample surface by chemical polishing with a solution of 30 cc of nitric acid, 10 cc sulphuric acid, 10 cc phosphoric acid and 50 cc acetic acid, at a temperature of between 85 and 95 °C for approximately 15 seconds.

The ultrasonic wave velocity through the sample was measured using the conventional pulse-echo technique[11]. A MATEC ultrasonic system and one X-cut quartz transducer of 5 MHz fundamental frequency generated longitudinal ultrasonic waves. To match the acoustic impedance between the sample and the transducer, water-free oil with a low solidification temperature was used. For all the measurements, the wave propagation direction was coincident with the sample's crystallographic direction [001]. The time for the wave's round trip was determined by the pulse echo overlap technique (Papadakis) applied to the transit time due to diffraction[12]. Therefore, the phase velocity obtained for the ultrasonic waves was v = 2d/t, when d is the height of the sample. Measurements were taken at a frequency of 15 MHz, and the sample temperature was changed (in cooling and heating runs) within the range of temperatures between 150 and 350 K at a controlled rate of 1 K/min. During measurements, the sample was exposed to a constant magnetic field of approximately 0.3 Tesla. The lines of magnetic field and the trajectory of the ultrasonic wave were arranged alternatively to be parallel and perpendicular to each other.

3. Results

Figure 1 show the results for the ultrasonic phase velocity *vs.* temperature, when a bias magnetic field was applied to the sample, in a direction perpendicular to the ultrasonic path. Beginning in 330 K, the sample was cooled down until 120 K, and then heated up to 330 K in a closed temperature cycle. It is relevant to note that two evident anomalies are observed in the velocity at each branch of the cycle, being the one observed at higher temperatures the more pronounced. It is also noticeable that both anomalies show a hysteretic behaviour, and that the velocity is not completely recovered at 330K.

A_{C1} and A_{H1} indicate the high temperature anomalies in the cooling and in the heating run respectively. The change (A_{C1}) begins at 289 K and ends at 283 K. The corresponding change in the heating run (A_{H1}) starts at 301 K and ends at 307 K. In both cases the wave velocity presents an abrupt change of approximately 0.15%. The difference of 12 K observed between the anomalies in the cooling and the heating run indicates a hysteretic process. B_{C1} and B_{H1} respectively mark the anomalies observed at lower temperatures (Figure 1). This anomalies present a weaker change than the one observed at higher temperatures, with little variation in the velocity of 0.3 m/s over an interval of temperatures of 4 K (see inset of Figure 1). The beginning of the anomaly B_{C1} takes place at 257 K and it ends at 253 K. The anomaly B_{H1} begins at 273 K and ends at 279 K. The difference of 16 K between the anomalies in both branches indicates that this is also a hysteretic process.

In Figure 1, the B_{C1}-B_{H1} anomalies are in fact the magnetized material's response. This is shown in Figure 2, which displays the measurements carried out without an externally applied field.

In Figure 2 we observe only one anomaly in the velocity, similar to those observed in Figure 1 in the same temperature interval (253-279 K). The temperature of this anomaly corresponds to B_{C1}-B_{H1} in Figure 1, and by this reason we indicated as B_{C2} and B_{H2}. B_{C2} begins at 257 K and ends at 254 K, and B_{H2} begins at 273 K and ends at 276 K.

To study the effects of the orientation of the magnetic field with respect to the direction of wave propagation, the bias magnetic field was applied to the sample in a direction parallel to the ultrasonic

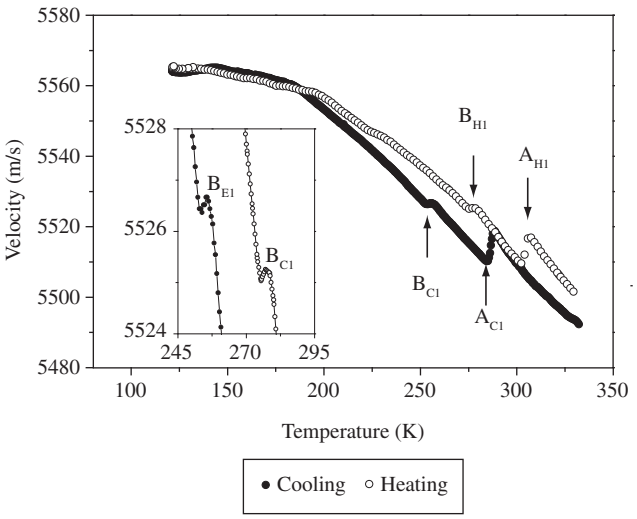

Figure 1. Phase velocity vs. temperature in single crystal nickel with the external magnetic field perpendicular to the trajectory of the ultrasonic wave. A_{C1} and A_{H1} respectively, mark the higher temperature anomaly in the cooling and the heating run respectively, and B_{C1} and B_{H1} mark the lower temperature anomaly in the cooling and the heating run respectively. Inset: amplification of the region of anomalies B.

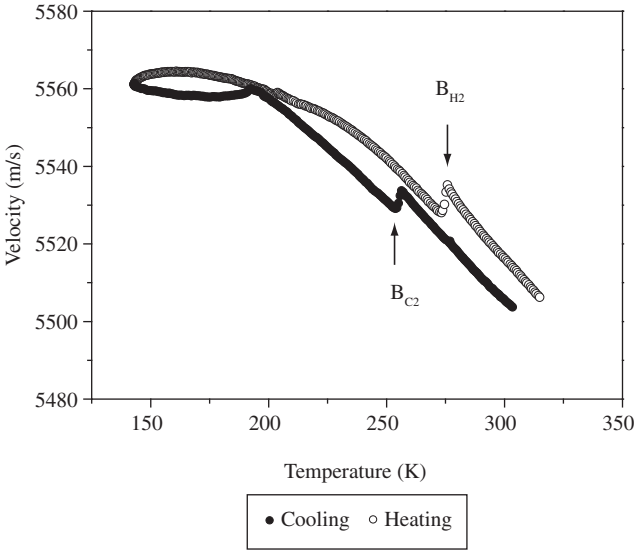

Figure 2. Phase velocity vs. temperature in single crystal nickel, in the presence of the remaining magnetic field. B_{C2} and B_{H2} respectively indicate the cooling and the heating runs of the lower temperature anomalies observed in Figure 1.

path. At this instance, before measurements were taken, the remaining magnetization was eliminated by heating the sample above the Curie temperature (631 K). The phase velocity vs. temperature plot for the sample with the magnetic field parallel to the wave propagation direction is given in Figure 3. C_{C3} and C_{H3}, indicate the anomalies at the cooling and the heating run respectively. C_{C3} begin at 269 K and end at 265 K, while C_{H3} begin at 299 K and end at 303 K. In both cases the transition is manifested by a change of phase velocity of approximately 0.12%. The difference of 30 K observed between the anomalies in both branches indicates a considerable hysteretic process.

4. Discussion

The anomalies in the ultrasonic phase velocity and their hysteretic behaviour, observed when a bias magnetic field was applied in the high purity single crystal nickel, can be explained by a shape deformation of the sample. It is important to note that even if the anomalies were observed at different temperatures they are caused by the same mechanism. This is clear when the anomalies are observed at the same temperature. It is easy to check that the anomaly marked B_{C1}-B_{H1} in Figure 1 and the anomaly marked B_{C2}-B_{H2} in Figure 2 happen at exactly the same temperature. In Figure 1, the anomaly marked B_{C1}-B_{H1} is almost suppressed by the applied magnetic field. On the contrary, in Figure 2 the same anomaly marked B_{C2}-B_{H2} is induced by the remaining magnetic field. As we can see in the data, the temperature of the anomaly changes when the magnetic field is modified from external to remaining or from perpendicular to parallel.

Two different processes can induce a sample deformation exposed to a magnetic field: magnetostriction and Ferromagnetic Shape Memory.

Magnetic transformations in metals and alloys by magnetostriction are accompanied by stress conditions due to the appearance of domain boundaries that induce a volume change. However, for the observed anomalies, the magnetostrictive effect is objectionable. Our measurements indicate an anomaly of phase velocity between 0.12 and 0.15% that can be explained only if this effect induces a volume change of the same order of magnitude. Unfortunately, the magnetostrictive effect in pure nickel is only in the order of microstrains ($\Delta l/l \approx -40\times10^{-6}$ [4]). Then, even if this effect contributes to the anomaly, it is negligible.

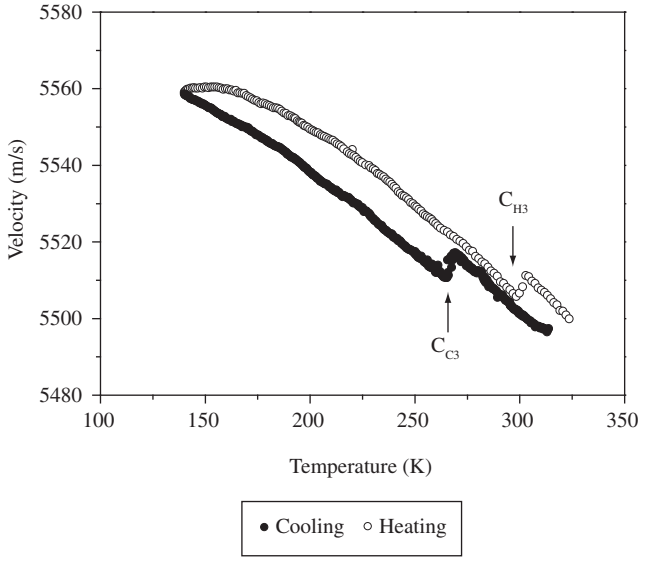

Figure 3. Phase velocity vs. temperature in demagnetized single crystal nickel with the external magnetic field parallel to the wave propagation direction. C_{C3} and C_{H3} respectively indicate the cooling and the heating run of the observed anomalies.

As it was already mentioned, magnetic fields induce large deformations in FSMAs. At low temperatures these alloys, such as Ni-Mn-Al, Ni-Fe-Ga and Co-Ni-Al[13], which contain different quantities of nickel, produced martensitic transformations characterized by twins. The dimensional change process occurring in these alloys involves the movement of the twin boundary of the martensite in the direction that allows a greater alignment of the domains with respect to the applied magnetic field[3].

In spite of the similarity of the experimental parameters (temperature and magnetic field) and the results (anomaly of phase velocity in our experiment and change of shape in FSMAs), we can't conclude that the effect observed in the nickel is caused by the same process that takes place in FSMAs. More precisely, pure nickel doesn't have martensitic transformations.

However, the anomalies in the ultrasonic phase velocity and its hysteretic behaviour can be explained similarly if the twins are already present in the nickel single crystal before we start the experiments. In other words, while FSMAs forms twins by martensitic transformation during the experiment, pure nickel needs to have the twins before the experiment starts. Given that the variation of the energy caused by the difference in orientation is minimal[5,6], during the solidification and growth of the nickel single crystal the stacking faults formed will rarely disappear. During the single crystal growth the undercooling in the [001] direction at the liquid/solid interface was controlled at approximately 60 K. In the [111] direction the temperature profile was less controlled and larger supercoolings are probable. In this case the formation of high density of stacking faults, typically formed in fast solidifications, is more likely. It is already known that twins can growth by stacking fault or fault packets[14,15]. Moreover, the energy of stacking fault is related to the energy of twin boundaries. Then, under energetically favourable conditions, the staking fault formations in nickel can lead the twin formation. Moreover, it is predicted that the twin concentration for a given material should increase with increasing grain size[16]. Then, because we use a single crystal, there is a possibility of a higher concentration of twins in the received nickel. In such a case we can speculate that the observed changes of phase velocity are the result of dimensional alignment induced by a reorientation of the magnetic domains in the twins formed from the stacking faults. It is also observed that in the cooling run the ultrasonic phase velocity diminishes in the chosen experimental configuration. The easy magnetization axis in Ni is [111] and the propagation of the ultrasonic wave is [100]. Therefore a component of this magnetization must increase the length of the ultrasonic path in the nickel single crystal.

It is clear that even if the anomalies have the same origin they occur at different temperature if the nature (external or remaining) and/or direction of the magnetic field are changed. The interaction between the magnetic moments of the matrix and the twins has certain anisotropy and needs to induce the necessary force, which is able to distort the crystalline network. Thus, we can suppose that at a certain temperature below the Curie temperature, a competition between the orientation strength of the magnetic domains, the miss of orientation strength originated in the mechanical energy (derived from the interaction of magnetic domains with the stress field of the ultrasonic wave) and the thermal energy, reaches a critical value, at which the alignment process is produced. We can therefore conjecture that the temperature of the anomalies in the ultrasonic phase velocity depends on the synergy between the direction and the strength of the

magnetic field, the direction of the ultrasonic wave propagation and the crystallographic orientation.

At a certain temperature we have the competition of four energies: the magnetic energy (W_H), the magnetoelastic energy (W_{ME}), the thermal energy (W_T) and the friction energy (W_{FR}).

W_H is originated from the interaction between the magnetic momentum of the domains and the applied magnetic field, which is negative.

W_{ME} is originated from the interaction between the magnetic field and the ultrasonic wave, and produce an alternation of the direction magnetic domains. It is a possibility that at a certain temperature these alternations contribute either to the alignment of the domains (during the cooling) or to randomizing it (during the heating).

W_T is the thermal energy.

W_{FR} represents the energy necessary to overcome the friction between the domains boundaries and it is always opposite to the process of alignment.

At high temperatures $W_H + W_{ME} + W_T + W_{FR} > 0$ and the magnetic domains remain not aligned. When $W_H + W_{ME} + W_T + W_{FR} \leq 0$ the alignment process begins, and this condition is reached, for a given magnetic field, at certain critical temperature T_{cr}.

The relative orientation of the ultrasonic path can contribute favorably or unfavorably to the domain orientation, depending on its orientation relative to the magnetic field, which tries to align the magnetic domains. In other words, the effect of W_{ME} is dependent on whether the external field is parallel or perpendicular to the ultrasonic wave. If $v \perp H$ the ultrasonic wave hardly advances through the material, producing a large alternation of the direction of the magnetic domains and causing their alignment. On the other hand, if $v \parallel H$ the ultrasonic wave easily advances through the material producing a small alternation of the direction of magnetic domains and having a smaller effect on inducing their alignment. Moreover, W_{ME} depends on the strength of the magnetic field. Then, W_{ME} (remained) $< W_{ME}$ (applied). On this basis, we can expect that T_{cr} (remained) $< T_{cr}(\parallel) < T_{cr}(\perp)$.

At low temperatures $W_H + W_{ME} + W_T + W_{FR} < 0$ and the magnetic domains remain aligned. In the heating run, when $W_H + W_{ME} + W_T + W_{FR} \geq 0$ the misalignment start. This condition is reached, for a given magnetic field and experimental configuration, at certain critical temperature T_{cr}.

As it was presented in the results, for the same experimental configuration, the observed anomalies in the ultrasonic phase velocity in the cooling run and in the heating run happen at different temperatures. Evidently this hysteretic behaviour is the result of friction between the magnetic domains that always opposes to the process. Moreover in the parallel configuration this gap in temperature is almost twice than that in the perpendicular configuration. Then, other factor affects the T_{cr}. In addition to the friction between the magnetic domains, the temperature of the anomaly is influenced by the experimental configuration. In the $v \perp H$ experimental configuration the big alternation helps randomization and a smaller temperature gap is expected. In opposition, in the $v \parallel H$ experimental configuration the small alternation less induces the randomization and a bigger temperature gap is expected. Then, the difference in the temperature gap between alignment and randomization of the domains depend on the internal friction between the domains and the experimental configuration.

As we observed in Figures 1, 2 and 3 the ultrasonic velocity after heating is always higher than that measured before beginning the cooling showing a hysteretic curve characterized by an open cycle. This lag on the recuperation of velocity at the end of the temperature cycle can be attributed to the friction between magnetic domains that do not participate in the velocity anomaly. Higher temperatures (not available with our cryogenic system) would be necessary in order to obtain a closed cycle of the hysteresis curve.

Furthermore, it is important to mention that whereas the first observation was fortuitous, as soon as the configuration was changed to an arbitrary crystallographic orientation with respect to the magnetic field the effect was not observed anymore. This shows that the process can be easily inhibited. Inhibition of the process indicates that the force of magnetic origin must be properly orientated in order to induce the reorientation of the magnetic domains in the twins. Evidently, an additional, more comprehensive study of the transitions is still necessary in order to verify our hypothesis and enable better understanding of the processes.

5. Conclusions

The cooling and heating of a high purity nickel single crystal with oriented bias magnetic fields produced an abrupt change in ultrasonic phase velocity. We speculate that the observed changes are the result of dimensional alignment of the nickel single crystal twins induced by a reorientation of the magnetic domains which is able to distort the crystalline network. These twins, we believe, are already present in the nickel single crystal before we start the experiments, formed (under energetically favourable conditions) from the stacking faults. In these conditions the temperature of the anomalies and the hysteretic behaviour of the ultrasonic phase velocity depend on the synergy between the direction and strength of the magnetic field, the direction of the ultrasonic wave propagation, the internal friction between the domains and the crystallographic orientation. The process can be easily inhibited by miss orientation of the magnetic field. The open cycle observed in the cooling-heating run curve can be attributed to the friction between magnetic domains that do not contribute to the velocity anomaly. Evidently, further more comprehensive studies of the transitions will be necessary in order to verify our hypothesis and enable a better understanding of the processes.

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