J. Phys. IV France **11** (2001)

Structural and magnetic investigations on Ni_2MnAl

Ll. Mañosa, A. Planes, Ch. Somsen[1], Ch. Fell[1] and M. Acet[1]

Departament d'Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Catalonia, Spain
[1] *Tieftemperaturphysik, Gerhard-Mercator Universität Duisburg, 47048 Duisburg, Germany*

Abstract. Ferromagnetic alloys undergoing thermoelastic martensitic transformations have recently become very attractive owing to the possibility of inducing giant deformations by rotating martensitic domains with an externally applied magnetic field. It is expected that ferromagnetic alloys with the Heusler structure may exhibit a strong magnetoelastic coupling resulting in potentially interesting magneto-mechanical properties. In this paper we present preliminary results on structural and magnetic studies on Ni_2MnAl. It is shown that in this material the magnetic properties strongly depend on the heat treatment, chiefly because of the difficulty in achieving a complete $L2_1$ order.

1. INTRODUCTION

The shape-memory effect occurring in a number of alloys is associated with the thermoelastic martensitic transformation and has proven to be of significant technological interest. Over the years, many devices have been developed which rely both on the one-way and the two-way shape memory effects. However, one of the major inconveniences that all these devices have is the slow response, which is inherent to the thermal control of the martensitic transformation. A possible way for circumventing such an inconvenience has recently been envisaged. The existence of ferromagnetic shape-memory alloys, for which a shape change is achieved by the application of a magnetic field, seems to open up the possibility of developing magnetic actuators [1].

Until now, the only system which has been shown to exhibit such an interesting property is Ni-Mn-Ga with compositions close to that of the Heusler compound Ni_2MnGa. These alloys possess an $L2_1$ structure that transforms martensitically on cooling. The magnetic coupling in both the parent and the product phase is ferromagnetic. In the martensitic phase, the combination of a relatively large magnetic anisotropy and a strong magnetoelastic coupling enables the rotation of martensite domains under the application of a magnetic field [2]. From the point of view of practical application however, this alloy has the drawback of being brittle.

The search for materials other than Ni-Mn-Ga which are potentially able to exhibit magnetic shape memory effect seems to be of capital importance. Good candidates are Ni-Mn-Al alloys. Already a number of investigations aimed at determining the properties of this alloy system [3-6] have been undertaken. However, the results reported differ considerably from one another. This appears to originate from the extreme sensitivity of the properties of this material to heat treatment, which varies amongst different groups.

Earlier X-ray diffraction studies have shown that above 1220 K the alloy Ni_2MnAl is in a disordered bcc phase (A2). Below this temperature the system undergoes a second order transformation into the B2 phase. Below about 1000 K there is another onset of a second order transformation into the $L2_1$ Heusler phase [7]. Before one can understand the properties of the martensitic transformation, for which the properties are very sensitive to composition, a thorough understanding of the physical properties of the stoichiometric composition is required. In this work we undertake a study of the structural and magnetic behavior of Ni-Mn-Al alloys and consider the as-prepared state and the state after quenching from 1373 K. We report on preliminary results on the magnetic behavior of the stoichiometric compound Ni_2MnAl.

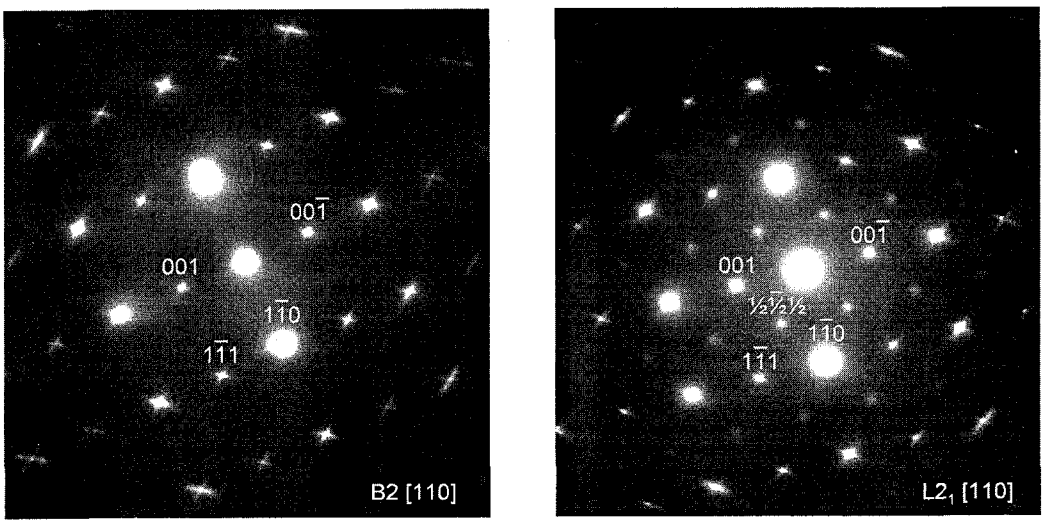
2. EXPERIMENT

The Ni_2AlMn sample was prepared by induction melting. EDX analysis gave an actual concentration of $Ni_{50.4}Mn_{24.7}Al_{24.9}$. Samples of appropriate sizes were cut from the resulting ingot for AC susceptibility χ_{ac} and

DC susceptibility χ_{dc} measurements. For transmission electron microscopy (TEM), 3 mm diameter and 250 μm thick samples with were prepared by electrochemical etching using an acid solution [8]. The experiments were carried out on samples that were simply left to cool to room temperature after melting (as-prepared) and on samples that were quenched to 0 °C after having been annealed at 1100 °C (1373 K) for three days within the A2 phase. In the temperature range $300\,K \leq T \leq 900\,K$ the χ_{dc} was measured with a vibrating sample magnetometer. The measurements below room temperature were carried out using a SQUID magnetometer. χ_{ac} was measured in the temperature range $80\,K \leq T \leq 300\,K$ in a field of 25 Oe with a frequency of 666 Hz. The specific heat measurements were carried out using a modulated differential scanning calorimeter in the temperature range $200\,K \leq T \leq 350\,K$.

3. RESULTS

3.1 Electron microscopy



(a) (b)

Figure 1. Electron diffraction patterns of (a) the B2 and (b) the $L2_1$ phase of Ni_2MnAl of the [110] zone. The indices in B2-phase notation refer to the spots underneath.

The results of the TEM observations are given with the electron diffraction images in figure 1a and figure 1b for the sample in the state quenched from 1373 K within the A2 stability range and in the as-prepared state respectively. Both patterns relate to the [110] zone. The image in figure 1a is characteristic of the B2 phase indicating that the A2 phase is not retained with the quenching rate used in this experiment. However, from this figure alone one cannot exclude the possibility of some amount of coexisting A2 phase. The presence of an $L2_1$ phase is not observable in this image. The sample in the as-prepared state gives the image in figure 2b which is characteristic of the $L2_1$ phase observed in Heusler alloys. However, the possibility of a coexisting B2 phase cannot be excluded. The streaking of the spots in both figures are eventually observed as crosses when moved to the outer parts of the images. Such streaking has also been observed in Ni-Mn-Al samples with slightly different compositions [3], and also in other Ni-based shape-memory alloys [7]. This has been ascribed to the existence of modulated structures (tweed-pattern) associated with a premartensitic state in the cubic phase at temperatures well above the nominal martensitic transition temperature. Although the stoichiometric alloy does not undergo a martensitic transformation, its composition lies close to the transformation boundary so that the origin of such streaking can be due to similar causes.

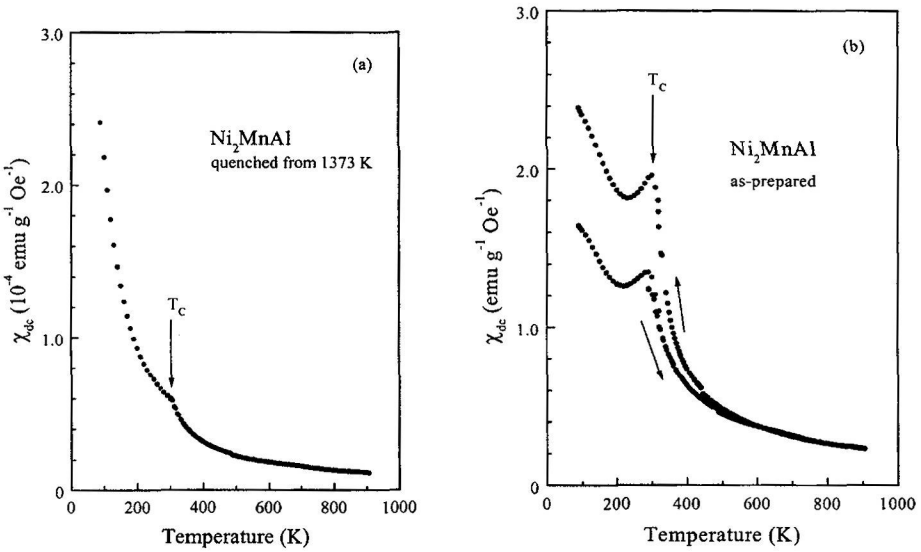


Figure 2. $\chi_{dc}(T)$ of Ni_2MnAl in the (a) quenched and (b) as prepared states. The arrows in part (b) indicate the temperature change direction.

3.2 DC susceptibility and the magnetization

The temperature dependence of χ_{dc} for the quenched and annealed samples are shown in figure 2a and 2b respectively. χ_{dc} of the quenched sample, which is essentially in the B2 phase, decreases with increasing temperature and at a critical magnetic transition temperature $T_C \simeq 300$ K the curve exhibits an abrupt change of slope before resuming to decrease progressively. The features in the temperature dependence of χ_{dc} of the as prepared sample shown in figure 2b are somewhat different. On increasing temperature χ_{dc} initially decreases and then passes through a maximum at T_C where the magnetic transition is seen to be more pronounced than in the quenched state. χ_{dc} then resumes decreasing on further increasing the temperature.

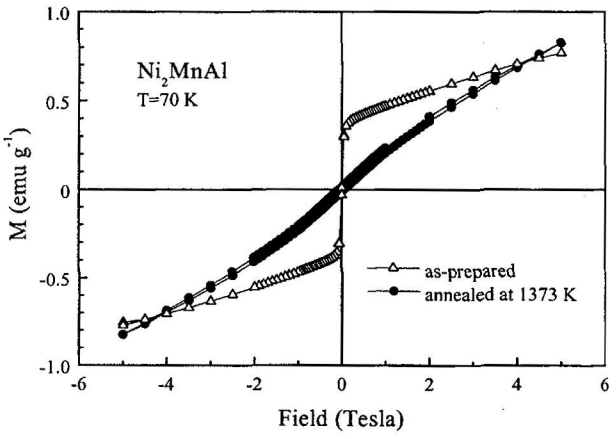


Figure 3. The field dependence of the magnetization of the quenched and as-prepared samples at 70 K.

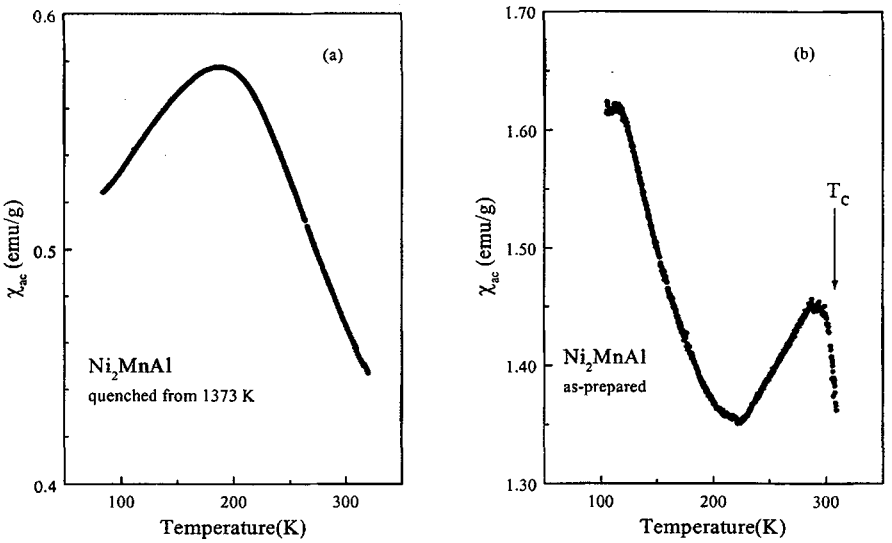


Figure 4. The temperature dependence of the real part of the ac susceptibility for the (a) annealed and (b) as-prepared sample.

In the process of heating above 600K diffusion effects become effective and any frozen-in B2 entity in the as-prepared sample begins to decompose leaving its presence to the more stable $L2_1$ phase. On recooling from 900K the decomposition progresses back down to 600K. This portion of the measurement lasts about 12 hours. The new state, which is still a B2-$L2_1$ mixture but with more $L2_1$ components than the as-prepared state exhibits a larger susceptibility with the essential features remaining similar to the heating curve.

The field dependence of the magnetization up to 6T is shown in figure 3. Neither the magnetization of the as-prepared nor the annealed sample approaches saturation at high fields. The magnetization of the annealed sample deviates from linearity, but changes smoothly in the measured field range. The as-prepared sample exhibits a fast reversal of the magnetization at small fields indicating to the presence of ferromagnetic components.

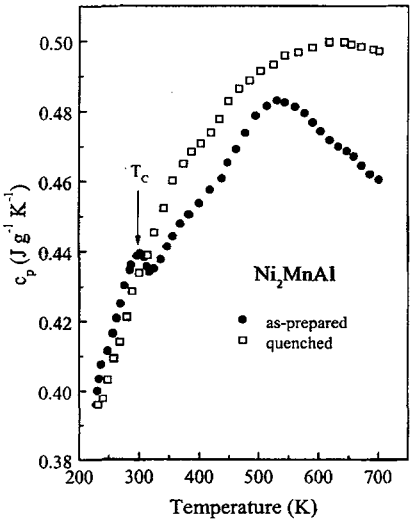


Figure 5. The temperature dependence of the specific heat of Ni$_2$MnAl in the two sample preparation states.

3.3 AC susceptibility

Figures 4a and 4b show the temperature dependence of the real part of χ_{ac} for the samples under the two preparation conditions. The features in these two figures are also quite different. In the quenched state of the sample χ_{ac} first increases with increasing temperature and goes through a maximum, after which it decreases continuously. There is no indication of a magnetic transition around 300K. On the other hand χ_{ac} of the as-prepared sample first decreases with increasing temperature and goes through a minimum around 220 K. χ_{ac} then increases and subsequently drops rapidly as T_C is approached.

3.4 Specific heat

The temperature dependence of the specific heat c_p for both sample states is shown in figure 5. c_p of the quenched sample increases steadily with increasing temperature up to about 600K above which diffusion effects become

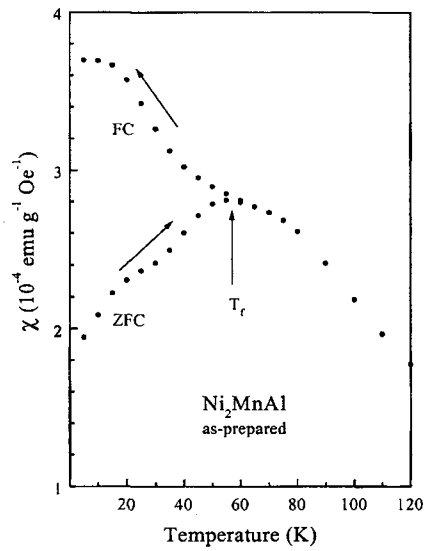


Figure 6. The presence of a difference in the FC and ZFC susceptibilities showing the spin-glass nature of the as-prepared Ni_2MnAl sample at low temperatures.

effective, by which the $L2_1$ phase begins to stabilize and the measurements are no longer in equilibrium, as also observed in the χ_{dc} data in figure 2. c_p of the as-prepared sample on the other hand shows a feature around 300K which corresponds to T_C observed in the magnetic measurements.

4. DISCUSSION

The measured parameters in the present work show that the features pertaining to the magnetic transition observed in the data of the $L2_1$ phase strongly fade, and they are practically nonexistent in the B2 phase. Although the B2 phase appears not to be responsible for the magnetic ordering effects, the value of χ_{dc} is still comparable to that of the $L2_1$ phase.

The occurrence of magnetic ordering in the $L2_1$ phase is in good agreement with earlier investigations [5,6,10]. Earlier neutron diffraction experiments at 4 K[10] had given evidence for antiferromagnetic ordering. Antiferromagnetic components no doubt exist due to the occurrence of a spin-glass-like frustrated state at low temperatures, as seen by the difference of the magnetic susceptibilities in the field-cooled (FC) and zero-field-cooled (ZFC) states in figure 6. On the other hand, the occurrence of ferromagnetic components, required for the presence of the spin glass state, is evidenced in the magnetization curve in figure 3. Presently, it is not possible to give a clear description of the nature of magnetic ordering occurring just below T_C. A sample prepared wholly in the $L2_1$ phase is required for such a study.

Acknowledgments

This work was partially supported by DGESIC (Spain) and DAAD (Germany).

References

1. K. Ullakko, J.K. Huang, C. Kantner, R.C. O'Handley, V. V. Kokorin, Appl. Phys. Lett. **69**, 1966 (1996).
2. Ll. Mañosa, A. Planes, Adv. in Solid State Phys. 2000 (in press), and references therein.
3. R. Kainuma, H. Nakano, K. Ishida, Metall. and Mater. Trans. **27A**, 4513 (1996).
4. Y. Sutou, I. Ohnuma, R. Kainuma, K. Ishida, Metall. and Mater. Trans. **29A**, 222 (1998).
5. F. Gejima, Y. Sutou, R. Kainuma, K. Ishida, Metall. and Mater. Trans. **30A**, 2721 (1999).
6. S. Morito, T. Kakeshita, K. Hirata, K. Otsuka, Acta Met. **46**, 5377 (1998).
7. J. Soltys, phys. stat. sol. (a) **66**, 485 (1981).
8. D. B. Williams and C. B. Carter, *Transmission Electron Microscopy I*, (Plenum, New York 1996) p. 158.
9. S.M. Shapiro, B.X. Yang, Y. Noda, L.E. Tanner, D. Schryvers, Phys. Rev. B **44**, 9301 (1991).
10. K. R. A. Ziebeck and P. J. Webster, J. Phys. F **5**, 1756 (1975).