Magnetoelasticity and Magnetoresistance in Cu–Al–Mn Shape-Memory Alloys

Jordi Marcos, Antoni Planes, Lluís Mañosa, Amílcar Labarta, and Bart Jan Hattink

***Abstract*—This paper is aimed at studying the effect of a magnetic field on the martensitic transition of a Cu–Al–Mn shape-memory alloy. The martensitic transition has been studied through resistance measurements under applied magnetic fields ranging from 0 to 50 kOe. Negative magnetoresistance showing an almost linear dependence with the square of the magnetization has been observed. This magnetoresistive effect is associated with the existence of small ferromagnetic Mn-clusters. Its strength and thermal dependence is different in both phases. The martensitic transition temperature is slightly increased and its spread in temperature significantly reduced upon increasing the field. These results show the existence of magnetoelastic coupling, which favors the nucleation of those martensitic variants with the easy magnetization axis aligned with the field.**

***Index Terms*—Cu–Al–Mn, magnetoelasticity, magnetoresistance, martensitic transition.**

I. Introduction

SHAPE-MEMORY alloys are systems which can recover from large permanent deformations (in some cases larger than 10%) by just slightly increasing their temperature [1]. The physical mechanism behind this peculiar behavior is a martensitic transition (MT) from an ordered bcc (β-phase) toward a close-packed martensitic structure (M-phase). Indeed, these materials have become very attractive from a technological point of view since they can function as sensors as well as actuators.

During the last few years there has been a great deal of interest in the development of new magnetic alloys undergoing a martensitic transition in which the shape-memory effect can be induced at a constant temperature by means of an applied magnetic field. It has been shown that this is feasible when suitable magnetoelastic coupling exits, which produces motion of M/β or M/M interfaces due to the magnetic field [2]. Recently this has been verified to be the case in the Heusler Ni_2MnGa alloy where deformations of $\sim$6% have been induced by means a moderate magnetic field (below 10 kOe) [3]. In this system the induced deformation has been associated with the motion of twin-boundaries in the M-phase under the driving force of the Zeeman energy difference of twin-related domains arising from the strong magnetic anisotropy of the tetragonal M-phase.

The present paper is aimed at studying the effect of a magnetic field on the martensitic transition of a Cu–Al–Mn shape-memory alloy. In this material the MT occurs at intermediate compositions between the Cu_3Al and the Heusler Cu_2AlMn [4]. For these compositions the β-phase, which is only stable at high temperatures, is retained in a long-lived metastable state at low temperature by means of fast enough cooling. Two successive ordering transitions to the $B2$ and $L2_1$ structures take place during this cooling [5], [6]. On further cooling the MT takes place toward an $18R$ or $2H$ structure depending on composition [8]. The magnetic properties originate from localized magnetic moments at Mn-atoms [7]. In the $L2_1$ structure these Mn-atoms are mainly located on one of the four distinguishable sublattices. This ordering of the Mn-atoms enables ferromagnetism in the stoichiometric Heusler compound. In contrast, the systems of interest here display a spin-freezing process at a rather low temperature [9].

In this work, the MT has been studied through resistance and magnetization measurements under applied magnetic fields up to 50 kOe in a wide temperature range covering the MT. These measurements enable the effect of the magnetic field on the MT and the effect of the MT on the magnetoresistive properties of the system to be studied. While it is expected that magnetoresistive and magnetoelastic effects are weak in the studied nonstoichiometric material, their study may play a decisive role in understanding the behavior of ferromagnetic shape-memory materials.

The paper is organized as follows. In Section II we briefly describe the main characteristics of the samples used and the experimental set-up. The results presented in Section III are then discussed in Section IV.

II. Experimental

Measurements have been performed on a Cu–Al–Mn polycrystal (grain size $\sim$ 0.1 mm) prepared by melting pure elements. The nominal composition of the studied sample is Cu; 22.8 at% Al; 9.0 at% Mn. On cooling from the β-stability region, the two ordering transitions to the $B2$ and $L2_1$ structures take place at 849 K and 795 K respectively, and the nominal MT temperature T_M is 157 K. For the composition of our system the martensite is $18R$.

Rectangular-shaped samples (around $12 \times 4 \times 0.5\,\mathrm{mm}^3$) were cut from cylindrically-shaped ingots. The samples were annealed for 900 s at 1073 K, quenched in a mixture of ice and water, and aged at room temperature for several days. For

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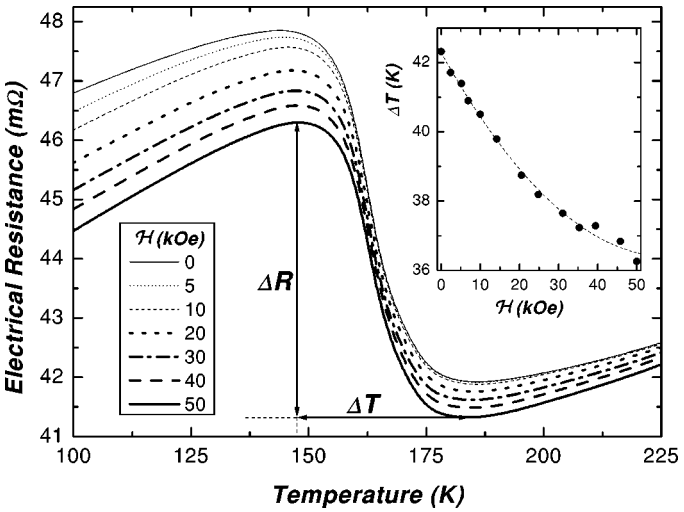

Fig. 1. R versus T curves across the martensitic transition at different values of the magnetic field $\mathcal{H}$, showing the change of electrical resistance ΔR and the spread in temperatures (ΔT) at the transition. The inset shows ΔT as a function of $\mathcal{H}$.

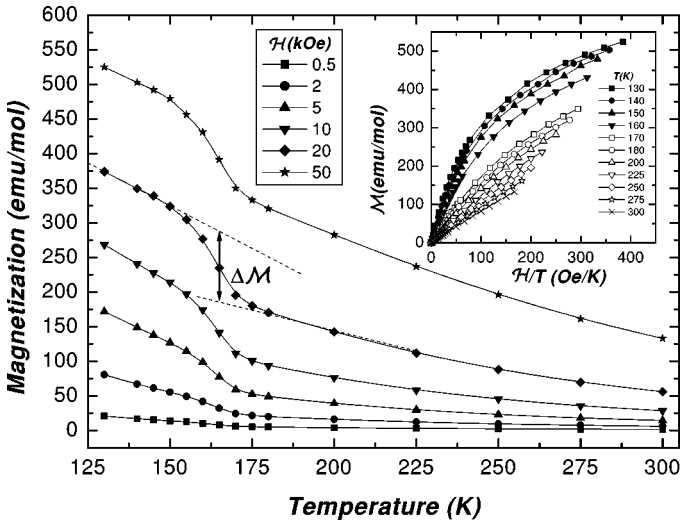

Fig. 2. Magnetization versus temperature at different values of the field showing the change of magnetization $\Delta\mathcal{M}$ at the transition. The inset shows $\mathcal{M}$ as a function of $\mathcal{H}/\mathcal{T}$.

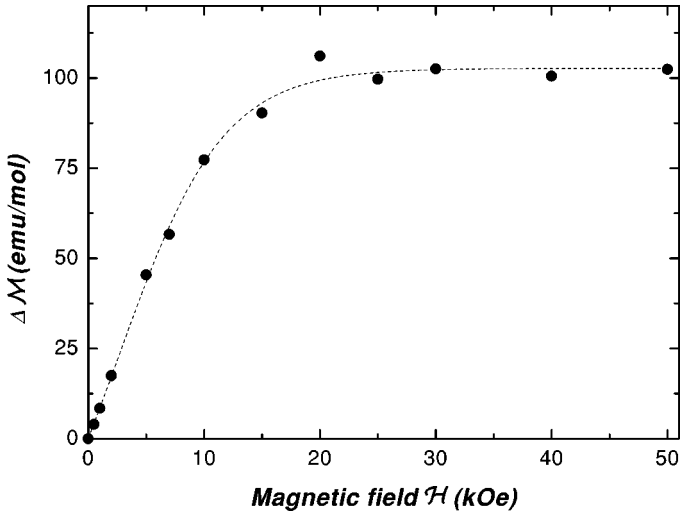

Fig. 3. Magnetization change at the martensitic transition as a function of the magnetic field.

electrical resistance measurements they were polished down to a thickness below 0.05 mm. These measurements were carried out in the range from 5 to 300 K using an ac four-probe method. Magnetization measurements were performed in a SQUID magnetometer. In the two experiments a superconducting magnet enables the application of fields up to 5T.

III. Results

Experiments were carried out by first cooling the sample down to 10 K and then increasing the temperature at 5 K steps. The electrical resistance R was measured during isothermal runs in which the field $\mathcal{H}$ was slowly varied from 0 to 50 kOe. From these measurements the change of R with temperature (T) across the MT can be obtained for different values of $\mathcal{H}$. Results are depicted in Fig. 1. This method provides R vs. T curves with the same shape as those obtained by directly measuring R vs. T under continuous heating at different constant values of $\mathcal{H}$. However, the latter can yield slightly different values for the transition temperature due to uncontrollable metastability effects occurring during thermal cycling through the MT [10].

A number of interesting features are seen from Fig. 1. There is a large decrease of electrical resistance ΔR on heating in the range between 150 K and 175 K where the MT takes place. The spread in temperature of the transition can be quantified by the temperature difference ΔT between the maximum and the minimum of the R vs. T curves. Interestingly, ΔT is significantly reduced upon increasing the magnetic field. This is shown in the inset of Fig. 1. Since the change of R with T provides a very good description of the corresponding evolution of the transformed fraction, it is clear that some magnetostructural coupling exists which is responsible for such an effect. Moreover, the inflexion point of the R vs. T curves shows a small but systematic dependence on $\mathcal{H}$. We have evaluated this dependence to be $\sim$5 mK/kOe.

A second feature regards the larger decrease of R with H in the M-phase. This leads to a reduction of ΔR as the field is increased which is a clear evidence of a magnetoresistive effect which seems to be different in the high and low temperature phases.

In order to further clarify the magnetic response of Cu–Al–Mn, we have carried out magnetization measurements over a wide range of temperatures from below to above the MT. Magnetization $\mathcal{M}$ versus $\mathcal{H}/\mathcal{T}$ curves are depicted in the inset of Fig. 2. Although no hysteresis of the magnetization is detected, it is clear from the figure that these curves do not scale with $\mathcal{H}/\mathcal{T}$. This excludes the simple superparamagnetic behavior of the ferromagnetic Mn-clusters, which indicates the existence of magnetic interactions among them. This finding is consistent with previous results reported in [11] for similar systems and also with the spin blocking observed at low temperature [9]. Fig. 2 also shows the temperature dependence of the magnetization measured at given values of $\mathcal{H}$. These curves show a significant (see Fig. 2) jump at the martensitic transition. The magnetization change $\Delta\mathcal{M}$ corresponding to this jump is plotted as a function of $\mathcal{H}$ in Fig. 3. Interestingly,

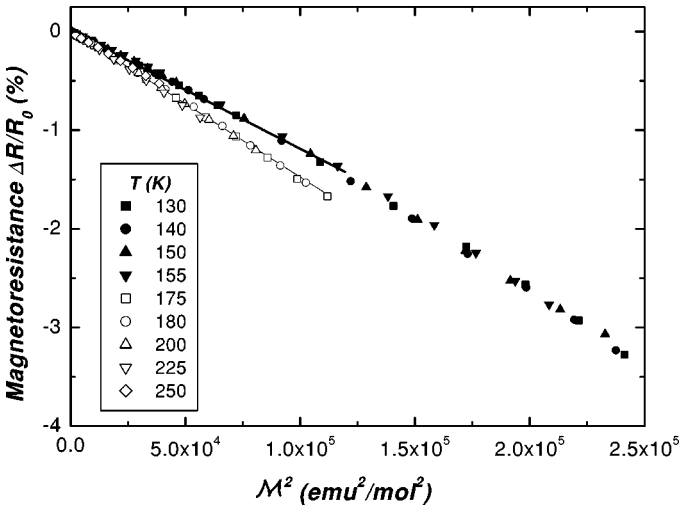

Fig. 4. Magnetoresistance as a function of the square of the magnetization. Solid symbols correspond to M-phase curves. Open symbols correspond to β-phase curves.

$\Delta\mathcal{M}$ saturates for values for which $\mathcal{M}$ is far from being saturated. This fact enables a change of magnetization at the MT of $\sim$100 emu/mol to be evaluated.

IV. Discussion

In this paper, the effect of a magnetic field on the properties of a Cu–Mn–Al alloy were studied. Magnetoresistive effects have been observed in bulk polycrystalline samples. Similar R vs. $\mathcal{H}$ behavior has recently been reported for melt-spun ribbons of composition close to that of the alloy studied in the present work [12]. The magnetoresistance, defined as the relative change of resistance with the application of a magnetic field at constant temperature, $MR = [R(T, \mathcal{H}) - R(T, \mathcal{H} = 0)]/R(T, \mathcal{H} = 0)$, is negative and scales with $\mathcal{M}^2$ as shown in Fig. 4. The scaling curve is different below and above the MT. These magnetoresistive effects are typical of granular magnetic solids where magnetoresistance mainly originates from the spin-dependent scattering of conduction electrons at ferromagnetic clusters embedded in a metallic nonmagnetic matrix [13].

In the studied alloy, the formation of ferromagnetic clusters is due to a tendency of the Mn-atoms to increase the number of third-order neighbors of the same species in the bcc-lattice. This leads to a nonhomogeneous distribution of Mn-atoms within one of the four distinguishable fcc-sublattices of the $L2_1$ structure.

The change of magnetization $\Delta\mathcal{M}$ at the MT is of the same order of magnitude as that measured for the ferromagnetic Heusler Ni_2MnGa [14]. Taking into account the Clausius–Clapeyron equation, the change of the martensitic transition with the magnetic field is expected to be given by:

$$\delta = \frac{T_M(\mathcal{H}) - T_M(\mathcal{H} = 0)}{\Delta\mathcal{H}} = -\frac{\Delta\mathcal{M}}{\Delta S}, \qquad (1)$$

where ΔS is the entropy change at the transition. Taking $\Delta S \simeq -1.4$ J/kmol [8] we obtain $\delta \simeq 7$ mK/kOe. This value is in good agreement with the observed change of the inflection point of the R vs. T curves with $\mathcal{H}$. Moreover, this value of δ is considerably smaller than the one reported ($\sim$0.1 K/kOe) for ferrous martensitic alloys [15].

The most significant effect of the magnetic field on the MT is the reduction of the temperature range over which the transition spreads. The physical mechanism behind this field-induced change of the transition path lies in the fact that in the vicinity of magnetic clusters, the magnetic field breaks the degeneracy of the M-phase by favoring the nucleation of those martensitic variants with magnetization easy-axis in the direction of the field. In Cu–Al–Mn, orthorhombic martensitic variants with the c-axis oriented along $\mathcal{H}$ are expected to have maximum nucleation probability. This effect seems to occur mainly during the first and last stages of the transformation.

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