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Shifting martensite transformation temperatures of single crystalline $Fe_{72}Pd_{28}$ thin films by external magnetic fields

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The effect of an external magnetic field B on the martensite phase transformation temperature T_0 was studied for single crystalline $Fe_{72}Pd_{28}$ thin films. From in-plane and out-of-plane aligned magnetic field dependent resistance measurements under various fields up to 9 T, T_0 was determined. The relation between T_0 and B is explained quantitatively by the Clausius–Clapeyron equation. The calculated value of 0.62 K/T is close to the values of the linear fits of 0.79 K/T and 0.76 K/T obtained from measurements with B aligned in-plane and out-of-plane.

Keywords: Magnetic shape memory alloy; Resistance; Magnetism; Clausius–Clapeyron

Ferromagnetic shape memory alloys have attracted significant attention since the discovery of the ferromagnetic shape memory effect (FSME) in 1996 [1,2]. These materials are in principle capable to strain by several per cent when an external magnetic field is applied. The FSME in $Fe_{70}Pd_{30}$ is related to a thermo-elastic fcc to fct martensite phase transformation, which was studied extensively in the 1980s [3–7]. The biocompatibility is a significant advantage of $Fe_{70}Pd_{30}$ over the "conventional" magnetic shape memory alloy Ni_2MnGa paving the way for biomedical applications such as stents or pumps [8–11]. A lift-off process to release the $Fe_{70}Pd_{30}$ film from the MgO substrate and keep it chemically and structurally unchanged was recently demonstrated and is a key requirement for any application [12].

Magnetic properties are directly linked to the magnetic shape memory behavior of $Fe_{70}Pd_{30}$ especially the change of saturation magnetization which can be attributed to the phase transformation. The Zeeman energy difference between two martensite variants is given by the difference of magnetizations multiplied by the external magnetic field and is the physical basis for the force acting on a twin boundary [13]. Recently for $Fe_{70}Pd_{30}$ the effect of a magnetic field constraint on the formation of martensite variants was studied [14]. Here we study the shift of the martensite transformation temperature as a consequence of an externally applied magnetic field.

The sample used in this study was a 500 nm thick $Fe_{72}Pd_{28}$ film grown by electron beam evaporation on a 0.5 mm thick single crystalline MgO substrate in a UHV chamber with a base pressure better than 10^{-9} mbar [15,16]. TEM measurements revealed a cube-on-cube orientation relationship for the $Fe_{70}Pd_{30}$ austenite fcc phase to the cubic MgO substrate [16]. Resistance and VSM measurements were performed with a Quantum Design PPMS equipped with a 9 T magnet. SQUID measurements were performed with a Quantum Design MPS-XL7. For resistance measurements a direct current of 100 nA was applied through the outer contacts in a four point line configuration while the voltage drop was measured between the inner contacts.

The magnetic field strength was varied between 0 T and 9 T and applied in-plane (B parallel to $[0\,1\,0]_{fcc}$) and out-of-plane (B parallel to $[0\,0\,1]_{fcc}$). The change of resistance behaved fully reversible for several temperature cycles. Fig. 1 shows exemplarily two resistance measurements for magnetic field strengths of 0 T and 9 T applied out-of-plane. From the change of resistance the phase above 330 K is identified to be austenite fcc while for temperatures below 300 K the phase is martensite fct [17]. The magnetic field of 9 T shifts the resistance curve to higher

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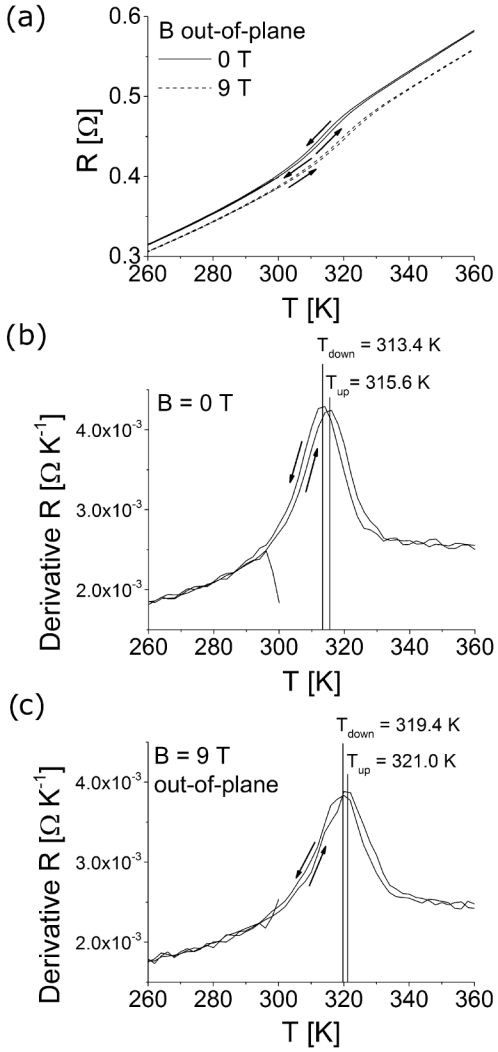

Figure 1. (a) Temperature dependent resistance measurements for heating and cooling of $Fe_{72}Pd_{28}$ without and with a magnetic field of 9 T, respectively, applied out-of-plane. (b) and (c) from the amplitudes of the derivatives of the curves shown in (a) the martensite transformation temperature T_0 is obtained by averaging the values for cooling T_{down} and heating T_{up}.

temperatures. In order to quantify the strength of shift of the martensite transformation temperature, the derivative of the resistance curves were evaluated which are shown in Fig. 1(b) and (c). Each derivative shows two maxima which can be attributed to the heating and cooling process of the sample. The appearance of two maxima is caused by the hysteresis behavior of the martensite transformation. By averaging T_{up} and T_{down} the martensite transformation temperature T_0 is obtained.

Without magnetic field the transformation temperature was $T_0(B = 0\,\mathrm{T}) = 314.5\,\mathrm{K}$. Its shift due to an external magnetic field was calculated according $\Delta T_0(B) = T_0(B) - 314.5\,\mathrm{K}$ and is plotted in Fig. 2. For the in-plane direction ΔT_0 lies on a straight line with a slope of $(0.79 \pm 0.03)\,\mathrm{K/T}$. For the out-of-plane-direction only the straight part of the curve from 4.0 T to 9.0 T was fitted linearly and gave a value of $(0.76 \pm 0.03)\,\mathrm{K/T}$. From the derivative of resistance shown in Fig. 1(b) and (c) one also sees that the width of the hysteresis of around 2 K is much smaller than the transformation region of around 30 K.

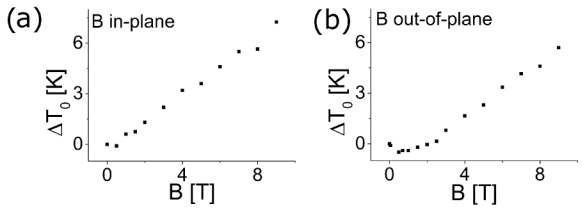

Figure 2. The shift of the transformation temperature ΔT_0 is plotted against the magnetic field B. When B is applied in-plane the relation between ΔT_0 and B is linear while for the out-of-plane direction a linear relationship is present above a field strength of around 2 T. Below this value the martensite transformation temperature is shifted to lower temperatures.

Thus $M_f \approx A_s$ and $M_s \approx A_f$ which denote the austenite and martensite start and finish temperatures.

The austenite to martensite transformation is a first order transformation with latent heat H [18]. Thus the shift of the martensite transformation temperature can be explained by the Clausius–Clapeyron equation [19,20]: $dT_0/dB = -\Delta M/\Delta S$. ΔM is the difference of magnetization between the martensite and austenite phase while ΔS denotes the change of entropy of the phase transformation. Under the assumption that ΔS is not affected by the magnetic field one can in principle calculate ΔT_0 by integrating ΔM along B. Resistivity measurements without external magnetic fields (Fig. 1) reveal that around 330 K the austenite starts to transform to martensite. At 300 K the transformation to martensite is accomplished. This width of transformation region of 30 K is too large to integrate the difference of magnetization curves along B according to the Clausius–Clapeyron equation (Fig. 3). The reason is that the magnetization curves are not solely affected by the phase transformation instead thermal effects play a significant role, viz. the saturation magnetization increases with decreasing temperature. Only phase transformation related changes of the saturation magnetization have an impact on the shift of the phase transformation temperature under magnetic fields.

In order to obtain the change of saturation magnetization ΔM_s which can solely be attributed to the phase transformation and is free of temperature effects, temperature dependent in-plane VSM measurements were performed. A magnetic field of 5 T was applied during the measurement in order to make sure the saturation magnetization is

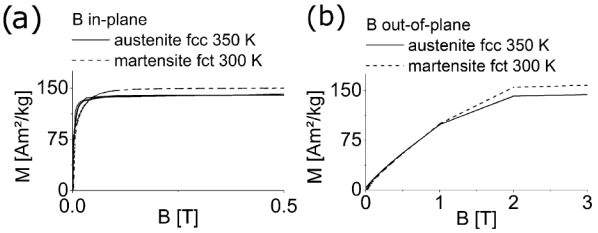

Figure 3. (a) In-plane and (b) out-of-plane SQUID magnetization curves for the fcc and fct phases. For low magnetic fields the magnetization of the austenite phase is larger than the magnetization of the martensite phase. This relation turns for higher fields. Curves for heating and cooling are shown but are indistinguishable. Due to the shape anisotropy which favors in-plane magnetization, the saturation magnetization for the out-of-plane direction is reached at higher external magnetic fields compared to the in-plane direction.

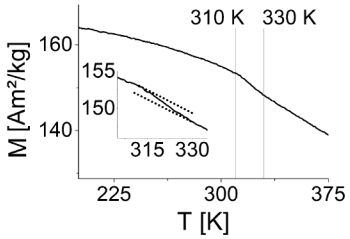

Figure 4. Temperature dependent in-plane magnetization measurement under a magnetic field of 5 T shows an increase of saturation magnetization for the martensite phase due to the phase transformation. The inset shows the tangential method used to calculate the phase transformation related change of saturation magnetization $\Delta M_s = 1.1\ \mathrm{Am^2/kg}$.

measured. At this field strength the in-plane saturation magnetization is reached by far as shown in Fig. 3(a). The change of saturation magnetization due to phase transformation is obtained by the tangent method. At 310 K and 330 K the slopes of the $M(T)$ curves shown in Fig. 4 are equal $-0.203\ \mathrm{Am^2/(kg\ K)}$. We calculate the saturation magnetization for the fct phase at 330 K for the case of no phase transformation and subtract the saturation magnetization of the austenite phase at 330 K: $\Delta M_s = M_{fct}(330\ \mathrm{K}) - M_{fcc}(330\ \mathrm{K}) = (153.4\ \mathrm{Am^2\ kg} - 0.203\ \mathrm{Am^2/(kgK)} \cdot 20\ \mathrm{K}) - 148.2\ \mathrm{Am^2/kg} = 1.1\ \mathrm{Am^2/kg} = 1.1\ \mathrm{Am^2/kg}$ is the increase of saturation magnetization of the martensite compared to the austenite.

For high magnetic fields the change of ΔT_0 can be explained by the change of saturation magnetizations between the two phases – a linear behavior of ΔT_0 against B is expected. Taking ΔM_s and ΔS and using the Clausius–Clapeyron equation the relation between T_0 and B is calculated to be 0.62 K/T which is close to the values of the linear fits of the measured data of (0.79 ± 0.03) K/T and (0.76 ± 0.03) K/T for the in-plane and out-of-plane direction, respectively. Deviations between the calculated and the measured values can be explained by (i) the negative magnetoresistance (NMR) and (ii) the latent heat. (i) Usually the NMR shifts down the resistance curve parallely to nearly parallely. Additionally the NMR effect is phase dependent. For these two reasons the NMR is capable to shift the position of the maxima of the derivative curves. This may cause deviations from the $T_0(B)$ behavior expected from the Clausius–Clapeyron equation. (ii) We used the latent heat $H = -0.53\ \mathrm{J/g}$ of the fcc–fct phase transformation for a polycrystal at around 300 K to calculate $\Delta S = H/T = -1.77\ \mathrm{J/(kg\ K)}$ [18]. Due to open surfaces and grain boundaries, thin films and polycrystals have an increased surface to volume ratio in common when compared with bulk single crystals. These open surfaces are expected to increase the energy of the martensite structure and thus reduce the latent heat. Indeed the latent heat of a bulk single crystal is -1.2 J/g and thus around half as large as the value of -0.53 J/g for the polycrystal [18,21]. In fact, the heat of transformation for a single crystalline $Fe_{70}Pd_{30}$ thin film on MgO has never been measured. Thus understanding $H = -0.53\ \mathrm{J/g}$ as a guiding value one can explain the difference between calculated and measured data.

Deviations from the linear behavior of ΔT_0 are expected when the magneto-crystalline anisotropy plays a role. For small magnetic field strengths the magneto-crystalline anisotropy influences the magnetization behavior and thus for small magnetic fields a non-linear dependence between ΔT_0 and B is expected. In the case of the martensite fct phase of $Fe_{70}Pd_{30}$ the two long axis are the easy axis of magnetization while the short axis is the hard axis [21]. Since the linear raise of $\Delta T_0(B)$ is independent of the field strength for the in-plane direction one can conclude that for this direction the magneto-crystalline anisotropy of the martensite fct phase does not affect ΔM and thus does not play a role. However temperature dependent magnetization curves shown in Fig. 3 a) reveal an increased magnetization of the austenite compared to the martensite for $B < 0.07$ T. Probably this increase is caused by differences of the magneto-crystalline anisotropy between the phases. A negative shift of ΔT_0 is expected. Since the field strength of 0.07 T is very small no negative shift of ΔT_0 is observed in Fig. 2(a). The situation is different for a magnetic field applied out-of-plane. Negative values of ΔT_0 can be found for magnetic fields applied out-of-plane which are smaller than 2.0 T. The effect is small but clearly visible. In this case the martensite transformation temperature shifts to lower temperatures. This behavior is caused by a higher magnetization of the austenite compared to the martensite phase which can be seen in Fig. 3(b) for magnetic fields smaller than around 0.72 T. The martensite phase shows variants which have their easy and hard magnetization axis out-of-plane. This multivariant state configuration of the martensite phase is more difficult to magnetize along the out-of-plane direction compared to the austenite phase and thus the austenite phase is favored for $B < 2.0$ T.

In summary the change of the martensite transformation temperature ΔT_0 due to an external applied magnetic field B aligned in-plane and out-of-plane was studied. The shift of the transformation temperature was explained by the Clausius–Clapeyron equation. To calculate the effect of B on ΔT_0 the change of saturation magnetization between the martensite and the austenite phase was determined. For the out-of-plane direction negative values of ΔT_0 were observed for small magnetic fields in contrast to the in-plane direction. The negative values of ΔT_0 are a result of the magneto-crystalline anisotropy of the multivariant martensite phase.

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