PECULIARITIES OF THE MAGNETOCALORIC EFFECT IN THE VICINITY OF THE FERROMAGNETIC-ANTIFERROMAGNETIC TRANSITION IN AN IRON-RHODIUM ALLOY

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ABSTRACT

We have investigated the large magnetocaloric effect (MCE) in a $Fe_{50.4}Rh_{49.6}$ alloy subjected to a slowly cycled magnetic field of up to 1.8 T in magnitude over a range of temperatures, 250 K < T < 350 K. Our measurements showed that the MCE associated with the first order ferromagnetic/antiferromagnetic phase transition in this material was asymmetric with respect to whether the transition took place by heating the material from temperatures below the transition or by cooling it from above. We have explained these peculiarities using ab-initio density functional theory-based disordered local moment theory calculations.

Keywords: Magnetocalorics; magnetic refrigeration, iron-rhodium alloys.
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1. INTRODUCTION

Conventional nearly equiatomic, stoichiometric Fe-Rh alloys are unusual in that they undergo a first order ferromagnetic (FM)-antiferromagnetic (AFM) transition close to room temperature [1–5]. These alloys exhibit a giant magnetocaloric effect (MCE) which has led to a proposal [6] for their use in magnetic refrigerators. Further discussion about the creation of a magnetic refrigerator which exploits such a 1st order FM/AFM transition has also been published [6,7]. Another promising area of application for these alloys is in heat-assisted magnetic recording (HAMR) [8–10] in high density magnetic storage technology. There is also some scope for their use in medical applications [11]. In this paper we report on some subtleties of the MCE associated with the first-order transition in this intriguing material.

2. THEORETICAL CONSIDERATION

We used the ab-initio disordered local moment theory [12,13] to describe the MCE properties of Fe-Rh alloys as reported in [13,14]. In the calculations we specified a Fe-Rh alloy for a composition close to the stoichiometric, perfectly ordered CsCl-type (B2) phase as Fe(100-x)Rh(x) – Rh(100-y)Fe(y) where both x and y are small percentages. The proportion of iron in the material c = (100-x+y)/2 and the long-range order parameter S = 1-y/100. For the $Fe_{50.4}Rh_{49.6}$ sample, which we studied experimentally, we used values c=50.4 and y=1.5 which were consistent with the experimental characterization data. For a specific composition, c, y, the free energy of the alloy is given by the expression [13]

$$F(c,y,H,T) = U(c,y,m_f,m_a) - T\left(S_{mag}(m_f,m_a,T) + S_{latt}(T)\right) - H\,m_f \qquad (1)$$

where U is the internal magnetic energy, S_{mag} the magnetic entropy, S_{latt} the lattice vibration entropy [14] and H the magnitude of applied magnetic field. m_f is the ferromagnetic order parameter (proportional to the overall magnetization) and m_a the anti-ferromagnetic order parameter. For complete AFM order m_a = 1, m_f = 0, for complete FM order, m_a = 0, m_f = 1 and in the high temperature paramagnetic state both are zero. From ab-initio calculations for several c and y values [13] we found an explicit expression for the internal energy, $U(c,y,m_f,m_a)$, in terms of m_f and m_a as reported in [14]. The values of the ferro- and antiferromagnetic order

parameters, m_f and m_a, were taken from where the free energy of Eq.(1) was minimized. We used this model to analyse the experimental results reported in this paper.

3. EXPERIMENTAL TECHNIQUE

We performed direct magnetocaloric effect (MCE) measurements using a MagEq MMS 801 (AMT&C LLC) system which has been described elsewhere [14–16]. As with all magnetic materials which undergo a 1st order phase transition, Fe-Rh alloys demonstrate temperature hysteresis in their magnetization [3,17,18]. Consequently, for further insight into the magnetocaloric properties of Fe-Rh, direct measurements of the magnetization of our $Fe_{50.4}Rh_{49.6}$ sample were performed by both heating and cooling through the phase transition. On heating there was a 'direct' AFM-FM transition and on cooling there was a 'reverse' FM-AFM transition. The AFM-FM transition was observed after having first slowly cooled the sample to 240 K. This value was chosen after several preliminary measurements and was checked to be a temperature at which the sample was fully in the AFM state. In a similar vein the sample was initially warmed to 350 K to be in the fully FM state for measurements of the 'reverse' FM-AFM transition. All measurements of field induced adiabatic temperature changes were performed uniformly with a 2 K/minute heating or cooling rate to exclude significant temperature fluctuations and to start the measurements from as stable a state as possible.

4. RESULTS AND DISCUSSION

Fig.1(a) shows the results of direct adiabatic temperature change, $\Delta T(T)$, measurements in the bulk $Fe_{50.4}Rh_{49.6}$ sample taken on both routes through the phase transition. Those taken on heating the sample (red open circles) have already been presented in Fig.3 of [14]. It is noticeable that the route through the phase transition had a significant influence on both the temperature of the maximum MCE value and the MCE value itself. In the present work we have defined the magnetic phase transition temperature as the temperature at which the MCE reached its maximum value [19,20]. We found different phase transition temperature values, T_{tr}, of 323.5 K and 319 K for the AFM-FM and FM-AFM transformations respectively. The maximum MCE value, obtained by cooling from the FM state, was -5K, whereas the comparable value obtained on heating from the AFM state, was -7.5 K. Also it is worth noting that the $\Delta T(T)$ associated with 'reverse' transition had significant values over a temperature range which had half the extent of that associated with the 'direct' one. Evidently the hysteresis of the magnetocaloric properties accompanying the 1st order phase transition in the Fe-Rh sample appeared to be influenced directly by the overall magnetization.

In our recent paper [14] the effect of irreversibility of the sample's temperature to its initial value, when the sample was subjected to a cycled external magnetic field at a sequence of increasing temperatures through the AFM-FM transition, was shown (Fig. 3 in [14]). We explained this effect in the framework of the ab-initio disordered local moment density functional theory (DLM-DFT) mentioned above [13]. Here we present new results of $\Delta T(H)$ measurements for the FM-AFM transition taken while cooling the same sample from the fully FM state. Figs. 1(b)-(d) show the measured $\Delta T(H)$ dependences: (c) at T_{tr} (319 K) where the MCE reached its maximum, (b) below T_{tr} (312.1 K) and (d) above T_{tr} (321.1 K), at which a MCE was still observed. We present the results at two different temperatures in the vicinity of the phase transition in order to reveal the comparable behavior of the MCE field dependences in both dominating AFM and FM phases below and above the phase transition temperature, respectively. A similar hysteresis to what was observed on heating through the AFM-FM transition was found as the field was varied (FWHM of about 1 T).

There was a noticeable absence of the 'irreversibility' effect of the type found in the earlier $\Delta T(H)$ measurements which were obtained on heating the same sample from the AFM state [14]. In the case of cooling from the FM state after a full magnetic field cycle we found the difference between the initial temperature and that after a complete cycle to be zero, $T_{FIN} - T_{INIT} = 0$.

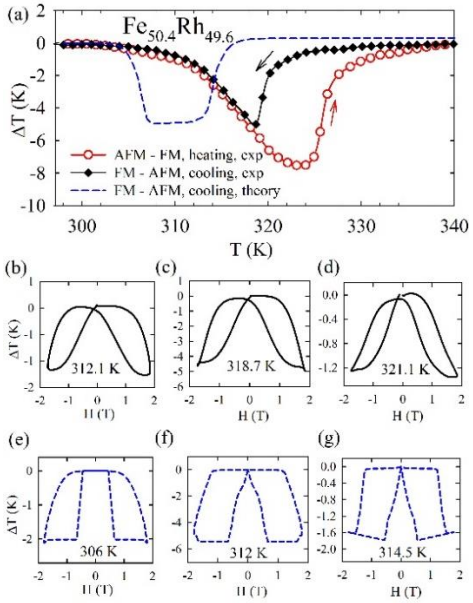

Fig. 1. (a) Experimental $\Delta T(T)$ values for $Fe_{50.4}Rh_{49.6}$ in a magnetic field 1.8T measured through the AFM-FM transition on heating (red open circles) and through the FM-AFM transition on cooling (black filled diamonds). Theoretical (blue dashed line) $\Delta T(T)$ values calculated for the system cooled through the FM-AFM transition are also shown. The experimental $\Delta T(H)$ values for one full cycle of the magnetic field while cooling the sample from the FM phase to specific temperatures are shown for (b) 312.1 K, (c) 318.7 K and (d) 321.1 K. The theoretical $\Delta T(H)$ calculations for one full cycle of the magnetic field while cooling from the FM phase to specific temperatures are shown for (e) 306 K, (f) 312 K and (g) 314. K. The black and red arrows in (a) indicate the direction in which the temperature was changed at a rate of 1 T/s.

In order to model the irreversibility in the AFM/FM heating ΔT(H) measurements in [14] we had invoked a simple mechanism. We assumed that for these measurements there was a weak, long-ranged, dynamic, magnetic response effect in play with a slow time variation so that equilibrium thermodynamics could be applied at every time step, t_i. The extents of ferromagnetic or anti-ferromagnetic order, $m_f(t_i)$ and $m_a(t_i)$, were averaged over compositional variations and ΔT for each value of the cycling magnetic field $H(t_i)$ was found. This dynamic effect led to an extra effective magnetic field, H_{eff} proportional to $m_f(t_{i-1})$, being added to the external field $H(t_i)$. This extra field incorporated into our model successfully reproduced the irreversibility feature. We have used the same model here to simulate the cooling results but with the one key difference that for each temperature we constructed the extra effective magnetic field at the first time step, t_0, from initial values of m_f, $m_f(t_0)$, taken from the FM state from where the sample was cooled (350K) instead of $m_f(t_0) = 0$ (suited for the AFM state), which was the case for the heating calculations. In both sets of calculations 20 time steps were allowed to ensue before the field-cycling was started.

The results are shown in Figs. 1(a), (e)-(g). Fig. 1(a) (blue dashed line) shows the theoretical ΔT(T) values for cooling. ΔT(T) for heating was presented in [14]. As in experiment the non-symmetric character stemming from the 1st order transition in Fe-Rh was evident and the cooling results had a smaller maximum than that of the results obtained for the heating scenario. In line with experiment we found $T_{FIN} - T_{INIT} = 0$ for this case. Figs. 1(e)-(g) show the cooling ΔT(H) values for one full cycle at three temperatures: (b) below the temperature where ΔT(H) had its maximum value (306K), (c) at this point (312K) and (d) above it (314.5K) where it is clear that $T_{FIN} - T_{INIT} = 0$.

5. CONCLUSIONS

Direct MCE temperature and field measurements in $Fe_{50,4}Rh_{49,6}$ alloy have been carried out and analysed in terms of a theoretical model. We have found a heating/cooling asymmetry of its magnetocaloric properties in the vicinity of the FM/AFM first order transition. This was demonstrated by the presence of an 'irreversibility' of the sample's temperature to its initial value during a full cycle of the magnetic field on heating which was absent in the analogous cooling measurement.

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