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The magnetocaloric effect and spin reorientation transition in single-crystal $Er_2Fe_{14}Si_3$

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Abstract

The anisotropy of uniaxial ferrimagnetic $Er_2Fe_{14}Si_3$ subjected to heating successively changes from easy-cone to easy-axis and eventually to easy-plane. The anisotropy constants K_1 and K_2 evaluated by means of the Sucksmith–Thompson method have been used to establish the domain of existence of the first-order magnetization process observed in the single-crystal sample. The magnetocaloric effect (MCE) directly measured in the regions of easy-axis and easy-plane anisotropy was found to be -0.28 K and 0.2 K, respectively, with a field change of 1.2 T, provided that the field is perpendicular to the direction of easy magnetization. These values were satisfactorily compared with ones estimated via the thermodynamic model.

1. Introduction

$Er_2Fe_{14}Si_3$ is a ferrimagnetic ($T_C = 474$ K, $I_S = 9.6\ \mu_B$/f.u.) intermetallic compound possessing a hexagonal Th_2Ni_{17}-type crystal structure [1]. In the parent Er_2Fe_{17} compound the anisotropy constant of the Fe sublattice K_1(Fe) is negative and the anisotropy constant of the Er sublattice K_1(Er) is positive but smaller, so that the total anisotropy is of a planar type [2–4]. A partial substitution of Si for Fe leads to a decrease in the anisotropy of the Fe sublattice and results in a spin reorientation (SR) in $Er_2Fe_{14}Si_3$ [5] which occurs as two successive phase transitions [1]. Measurements of the magnetization of a single crystal have made it possible to determine the temperature dependences of the two anisotropy constants and the evolution of its easy-magnetization direction with temperature [1]. It was found that at low temperatures the magnetic moment is tilted off the *c*-axis with the angle decreasing with heating up to 50 K where cone-axis spin reorientation (SR2) occurs. The region with easy-axis anisotropy is followed by the region with easy-plane anisotropy. The first-order axis-plane spin reorientation (SR1) phase transition was observed at 116 K. Further investigations have shown that in the vicinity of this transition an external magnetic field may cause a flip of the magnetic moment usually referred to as a first-order magnetization process (FOMP) [6].

A number of thermodynamic models of anisotropic magnetic materials have been developed [7–10]. However, they are typically rather cumbersome and difficult to treat analytically. The situation may be different for $Er_2Fe_{14}Si_3$, having a spontaneous spin reorientation at elevated temperatures where the anisotropy constants of sixth and higher orders are small. In this case, the relevant model is simplified allowing explicit relationships for the magnetization and critical field for the FOMP to be obtained.

The considerable interest in the investigation of magnetic first-order phase transitions is related to the development of materials possessing an enhanced magnetocaloric effect. It has been understood that the release of latent heat of the field induced transition can give rise to a large MCE [11]. Although the change in entropy associated with spontaneous spin reorientation is rather modest [12], FOMP can be accompanied by other phenomena, such as large magnetostriction, contributing to the total MCE.

In the present paper a thermodynamic approach is used to calculate the magnetic phase diagram and to determine the domain of existence of FOMP. This allows us to estimate the MCE accompanying FOMP in $Er_2Fe_{14}Si_3$. The obtained results are satisfactorily compared with directly measured MCE in the vicinity of the spontaneous (SR1) spin reorientation phase transition.

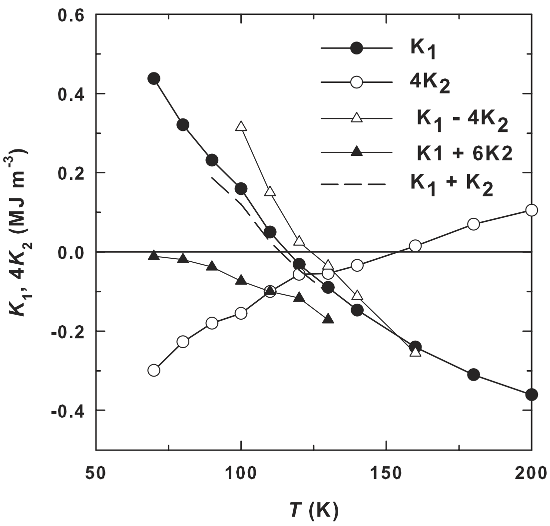

Figure 1. Temperature dependences of anisotropy constants.

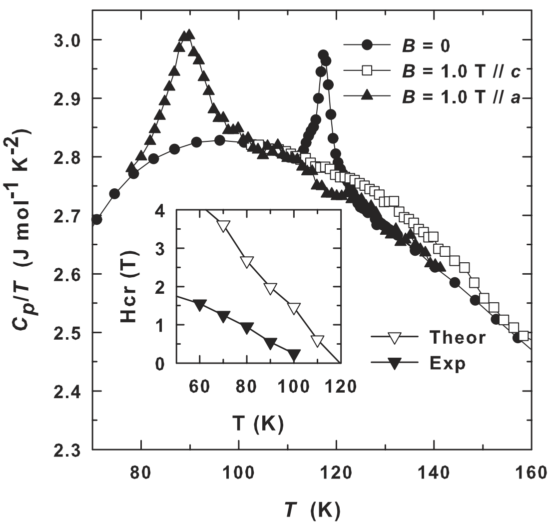

Figure 2. Heat capacity and critical field of FOMP.

2. Experimental details

A single crystal of $Er_2Fe_{14}Si_3$ was grown by the Czochralski method. Its crystal structure was determined by means of x-ray powder diffraction analysis, and was found to be hexagonal of the Th_2Ni_{17} type with lattice parameters $a = 840.9$ pm, $c = 823.2$ pm. The MCE was measured directly. The set-up is capable of continuous registration of the temperature change induced by the adiabatic field rise of 1.2 T. The rate of the field sweep was 0.5 T s^{-1}. The experimental error in determination of ΔT is 10%. A PPMS-9 was used for the measurement of the specific heat in the magnetic field.

3. Results and discussion

The magnetic phase diagram of the uniaxial ferromagnetic sample in the absence of an external field can be developed using the conventional relationship for the magneto-crystalline anisotropy energy

$$F = K_1 \sin^2\theta + K_2 \sin^4\theta. \tag{1}$$

The minimization of the functional (1) yields three different solutions [8]

$$\theta = 0 \qquad \theta = \frac{\pi}{2} \qquad \sin^2\theta = \frac{-K_1}{2K_2}$$

$$F = 0 \qquad F = K_1 + K_2 \qquad F = \frac{-K_1^2}{4K_2}$$

$$K_1 > 0 \qquad K_2 < -\frac{K_1}{2} \qquad K_1 < 0, \quad K_2 > -\frac{K_1}{2}.$$

This model implies that the evolution from easy-axis to easy-plane type anisotropy occurs through the first-order phase transition. The anisotropy constants of $Er_2Fe_{14}Si_3$ calculated earlier [1] by means of the Sucksmith–Thompson method [13] are presented in figure 1. It is clearly seen that in the vicinity of 116 K K_1 changes its sign from positive to negative on heating. According to the model (1) this should result in a phase transition from the easy-axis to the easy-plane state. The sharp peak at 116 K on the curve of the temperature dependence of heat capacity measured at zero field was attributed to this phase transformation (see figure 2). Explicit expressions for the entropy of both phases and the value of the entropy change ΔS associated with the spontaneous (SR1) phase transition are presented in table 1. Under adiabatic conditions this phase transformation would give rise to the temperature change

$$\Delta T = -\Delta S \frac{T}{C} = -0.36\ \text{(K)}. \tag{2}$$

The minus sign in equation (2) means that in this case the magnetic entropy change is compensated by the change in the lattice entropy.

The free energy of a uniaxial ferromagnetic sample placed in the external field can be expressed as

$$F = K_1 \sin^2\theta + K_2 \sin^4\theta - \vec{M} \cdot \vec{H}. \tag{3}$$

Calculations presented in [9, 10] have shown that when $H \perp c$-axis FOMP takes place in the domain of the easy-axis anisotropy if

$$K_1 + K_2 > 0; \qquad K_1 + 6K_2 < 0 \tag{4}$$

and when $H \parallel c$-axis FOMP takes place in the domain of the easy-plane anisotropy if

$$K_1 + K_2 < 0; \qquad K_1 - 4K_2 > 0. \tag{5}$$

It is seen in figure 1 that the conditions (4) hold below a temperature of (SR1), but the conditions (5) hold only in the narrow region above this temperature. Therefore the magnetic field should give rise to FOMP in the domain of the easy-axis anisotropy below 116 K but at a temperature a few degrees higher than this only a reversible rotation of the magnetic moment is possible. Provided that $H \perp c$-axis the critical field of the FOMP is given by [9]

$$H_{CR} = \frac{2K_1 - 4|K_2|}{M_S}. \tag{6}$$

Table 1. Parameters for calculation of ΔS. S_a and S_p are the entropy of the easy-axis and easy-plane phases respectively, calculated as $S = -(\partial F/\partial T)$. Values of the temperature derivatives of K_1 and K_2 and value of C/T are taken at 116 K.

S_a	S_p	$\partial K_1/\partial T$ (MJ m^{-3} K^{-1})	$\partial K_2/\partial T$ (MJ m^{-3} K^{-1})	ΔS (MJ m^{-3} K^{-1})	C/T (MJ m^{-3} K^{-1})
0	$-(\partial K_1/\partial T) - (\partial K_2/\partial T)$	−0.0083	0.0011	0.0072	0.02

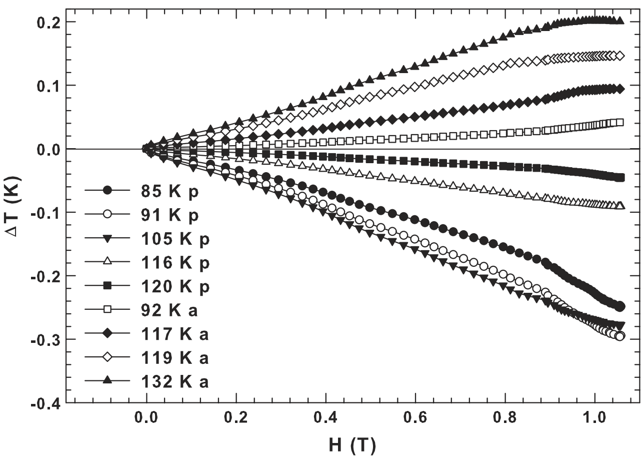

Figure 3. MCE directly measured for $H \perp c$ (p) and $H \parallel c$ (a).

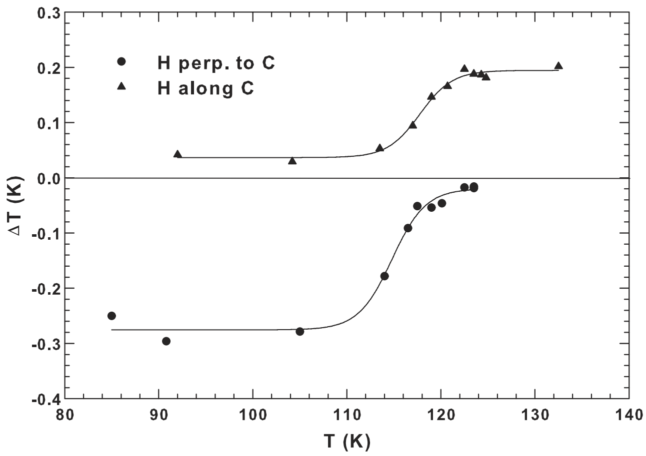

Figure 4. MCE directly measured for a field change of 1.2 T.

Values of H_{CR} calculated for $Er_2Fe_{14}Si_3$ using the anisotropy constants from figure 1 are presented in the inset of figure 2 together with the experimental values of H_{CR} deduced from the isothermal magnetization curves [6]. The rise of the field $H \perp c$-axis causes a lowering of T_{SR1} and a respective shift of the peak position on the $C/T(T)$ curve is clearly seen in figure 2. A $C/T(T)$ curve measured in the field directed along the c-axis does not possess a sharp cusp displaying the absence of the FOMP above T_{SR1}. However, experimental values of the critical field are lower those predicted by the equation (6), demonstrating that a simple thermodynamic model represents observed phenomena adequately but does not give a reliable quantitative description of the system.

The MCE originating from the FOMP is given by equation (2). Since the magnetic entropy increases with tilting magnetization off the c-axis with the field, the lattice entropy should decrease, providing the conservation of the total value of the entropy. Therefore a negative adiabatic temperature change should appear. Field dependences of MCE measured directly at certain temperatures and temperature dependences of MCE measured for a field change of 1.2 T are presented in figures 3 and 4, respectively. According to figure 2 the critical field of the FOMP is less than 1.2 T in the range of temperatures from 80 to 116 K, therefore an external field is sufficient to accomplish the phase transition. Negative ΔT of −0.28 K was observed below T_{SR1} when $H \perp c$-axis. The difference between the experimental MCE and the estimated value (2) could be attributed to the minor positive contribution

$$\Delta T = -\int_{H_{CR}}^{H} \frac{T}{C}\left(\frac{\partial I}{\partial T}\right) \mathrm{d}h, \tag{7}$$

originating from the conventional magnetization of the ferromagnet in fields exceeding the H_{CR}.

Above T_{SR1} the MCE produced by the field $H \parallel c$-axis could be estimated using equation (3). The second term proportional to K_2 could be omitted since FOMP does not take place in this region and the contribution of the first term, proportional to K_1, dominates. An explicit relationship for the free energy takes the form

$$F = K_1 \sin^2\theta - I_S H \cos\theta. \tag{8}$$

I and I_S are the magnetization and the saturation magnetization, respectively

$$\cos\theta = \frac{I}{I_S}. \tag{9}$$

Minimization of (8) with respect to θ yields the $I(H)$ curve

$$\frac{I}{I_S} = -\frac{I_S H}{2K_1}. \tag{10}$$

Substituting $\cos\theta$ in (8) with the value from (10) and taking the temperature derivative under the constant H we obtain the entropy as a function of the field

$$S = -\frac{\partial K_1}{\partial T}\left[1 - \left(\frac{I_S H}{2K_1}\right)^2\right]. \tag{11}$$

According to (10) saturation magnetization is reached in the field

$$H_S = -\frac{2K_1}{I_S}. \tag{12}$$

Substitution of H_S into (11) yields entropy change for the field change of H_S

$$\Delta S = \frac{\partial K_1}{\partial T}.$$

Taking values of the temperature derivative and C/T from table 1 we get the respective MCE

$$\triangle T = -\triangle S \frac{T}{C} \approx 0.42 \text{ (K)}.$$

Since K_1 decreases with the temperature ΔS is negative and ΔT is positive. The MCE directly measured above T_{SR1} in the field $H \parallel c$-axis was also found to be positive (see figure 4), but its values are lower than the predicted ones.

4. Conclusion

A simple thermodynamic model of FOMP was utilized to calculate a magnetic phase diagram of uniaxial ferrimagnetic $Er_2Fe_{14}Si_3$. It was found that an easy-axis type of anisotropy exists below T_{SR1}. At 116 K first-order spontaneous spin reorientation phase transition occurs and above this temperature easy-plane anisotropy was observed. In the domain of the easy-axis anisotropy exposure to a field perpendicular to the c-axis gives rise to discontinuous rotation of the magnetization (FOMP). Meanwhile, in the region of easy-plane anisotropy FOMP is possible only in the narrow vicinity of T_{SR1}. Estimated values of MCE are satisfactorily compared with experimental ones. The MCE itself was found to be rather low, being about −0.28 K below and 0.2 K above T_{SR1} for a field change of 1.2 T. Nevertheless an explicit relationship between MCE and the magnetic parameters of the sample obtained in the paper could be useful for further investigations.

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