SPIN REORIENTATION TRANSITIONS AND INTRINSIC DOMAIN NUCLEATION IN UNIAXIAL MAGNETS

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ABSTRACT — The nature of anisotropy-energy driven spin-reorientation transitions in uniaxial materials has been studied. A simple phenomenological model is developed to describe first and second order transitions for situations where the first two anisotropy constants vary linearly with temperature. The mechanism whereby first order transitions take place is studied and calculations made of the domain wall structure. It is shown that an intrinsic nucleation mechanism exists for 90° domain walls and that in multidomain samples the existence of domains always leads to the conversion of first order transitions to those of second order. It is shown that this analysis gives a satisfactory account of the spin reorientation transition in $Pr_2(Co_{0.8}Fe_{0.2})_{17}$.

1 – INTRODUCTION

A wide range of spin re-orientation transitions in uniaxial orthoferrites and metallic rare earth compounds (Belov et al. [1], Melville et al. [2]) take place because of the particular temperature dependence of their magnetocrystalline anisotropy constants. Transitions are from an axial ($\theta = 0$) phase to a planar phase ($\theta = \pi/2$) and in principle take place either continuously via two second order transitions through an intermediate easy cone situation if $K_2 > 0$, or as a single first order transition if $K_2 < 0$.

In such transitions the relevant term in the free energy is to second order in the anisotropy constants

$$F = K_1(T)\sin^2\theta + K_2(T)\sin^4\theta\,. \qquad (1)$$

The change in heat capacity at spin reorientation transitions with $K_2 > 0$ has been considered in a simple model with K_2 constant by Horner and Varma [3]. In the present work we extend their approach to more general situations and then examine the means by which spin reorientations take place. In particular we look at the role of domain walls in first order spin reorientation transitions in uniaxial systems.

2 – THERMODYNAMICS OF SPIN REORIENTATION TRANSITIONS

We examine first a simple illustrative model which, after Horner and Varma [3] considers K_2 to be constant and K_1 to be linear in temperature

$$K_1(T) = K_2(A + BT) \qquad (2)$$

where A and B are constante whose magnitude and sign are determined by the conditions $K_2 \gtrless 0$ and $dK_1/dT \gtrless 0$.

Fig. 1 shows the trajectories considered, with the arrows indicating direction of changing K_1 with increasing temperature. Substitution of (2) into (1) leads to the following results.

$K_2 > 0$:

H parallel to	Axis	Cone	Plane
Θ	0	$\sin^{-1}[(A + BT)/2]^{1/2}$	$\pi/2$
Entropy $S(\Theta)$	0	$\frac{1}{2} K_2B(A + BT)$	$-K_2B$
Heath Capacity $C(\Theta)$	0	$\frac{1}{2} K_2B^2T$	0

Thus for temperature increasing the total entropy change is always $\Delta S = |K_2B| = |dK_1/dT|$ and the heat capacity and entropy take the shape shown fig. 2a and 2b respectively.

$K_2 < 0$:

H parallel to	Axis	Plane
Θ	0	$\pi/2$
Entropy $S(\Theta)$	0	$-K_2B$
Heat capacity $C(\Theta)$	0	0

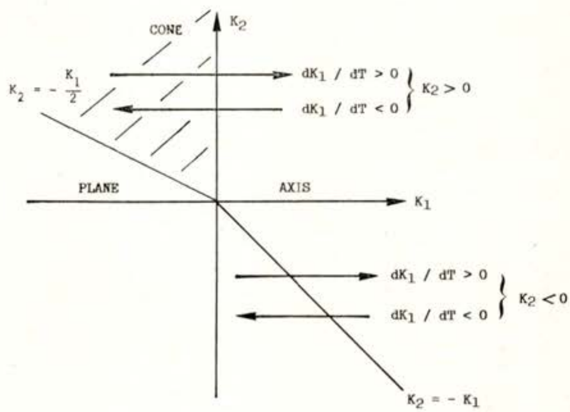

Fig. 1 — Spin reorientations in the K_2, K_1 plane

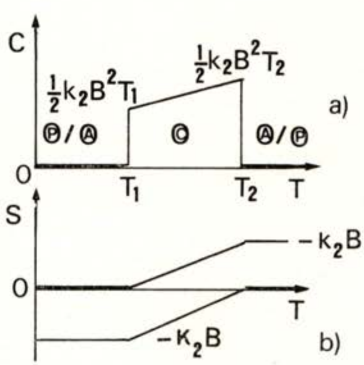

Fig. 2 — (a) Heat capacity for constant $K_2 > 0$, corresponding to $B > 0$ (plane stable for $T < T_1$) and $B < 0$ (axis for $T < T_1$)

(b) Entropy for constant $K_2 > 0$. Lower curve $B > 0$. Upper curve $B < 0$

In this case the transition from axis to place or vice versa takes place at $T = T_0$ with entropy increase $-K_2B = |dK_1/dT|$ and a positive singularity in the heat capacity. The heat capacity and entropy are as shown in Figs. 3a and 3b respectively.

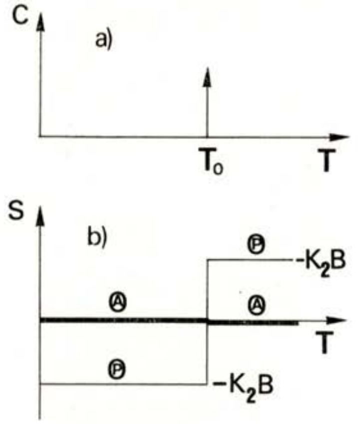

Fig. 3 — (a) Heat capacity for constant $K_2 < 0$, corresponding to $B > 0$ (plane stable at $T < T_0$) and $B < 0$ axis stable for $T < T_0$

(b) Entropy for constant $K_2 < 0$. Lower curve $B > 0$. Upper curve $B < 0$

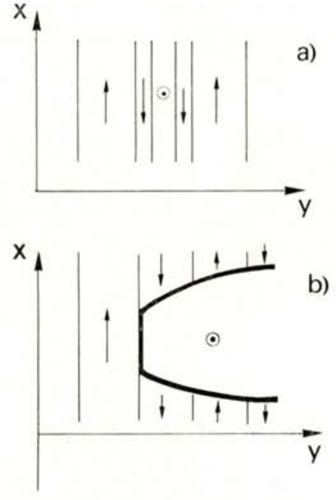

Fig. 4a, b — Schematic domain structures as T_0 is approached. The heavy lines correspond to $\pi/2$ domain walls

This illustrative model can readily be extended to the situation often observed experimentally where both K_1 and K_2 are temperature dependent. Thus we can write in general

$$\begin{aligned} K_1(T) &= \alpha + \beta T \\ K_2(T) &= \gamma + \varepsilon T \end{aligned} \qquad (3)$$

In this case for $K_2 > 0$ we have

H parallel to	Axis	Cone	Plane
Θ	0	$\sin^{-1}\left(\frac{-(\alpha+\beta T)}{2(\gamma+\ T)}\right)^{1/2}$	$\pi/2$
Entropy $S(\Theta)$	0	$\frac{1}{4}\ \frac{[2\alpha\beta\gamma + 2\beta^2\gamma T + \beta^2\ T^2\ -\alpha^2\varepsilon]}{(\gamma+\ T)^2}$	$-(\beta+\varepsilon)$
Heat Capacity $C(\Theta)$	0	$\frac{T(\alpha\varepsilon - \beta\gamma)^2}{2(\gamma+\varepsilon T)^3}$	0

where the easy cone region is defined by temperatures $T_1 = -\alpha/\beta$ and $T_2 = -(\alpha + 2\gamma)/(\beta + 2\varepsilon)$ corresponding to $\Theta = 0$ and $\Theta = \pi/2$ respectively.

For $K_2 < 0$ we have.

H parralel to	Axis	Plane
Θ	0	$\pi/2$
Entropy $S(\Theta)$	0	$-(\varepsilon+\beta)$
Heat capacity $C(\Theta)$	0	0

The form of the entropy and heat capacity is exactly as in Figs. 3a and 3b but with $-K_2B$ replaced by $-(\varepsilon+\beta)$.

3 – DOMAIN NUCLEATION NEAR SPIN REORIENTATION TRANSITIONS

The discussion above does not attempt to address the problem of how the thermodynamically stable state at the end of a transition is reached.

We consider this question now and concentrate on the $K_2 < 0$ case where thermodynamics predicts a first order reorientation at $T = T_0$. In a multidomain sample the situation is complicated by the existence in each phase of a part of the specimen (the domain wall) with spins whose angles differ from the easy direction for the phase considered ($\Theta = 0$ or $\pi/2$). These domain walls act as nuclei for the formation of the new phase since at all temperatures they contain spins whose direction corresponds to that of the currently unstable phase.

This point has already been noted by Belov et al. [1] in considering antiferromagnetic to weak ferromagnetic phase transitions in orthoferrites, by Mitsek et al. [5] and Baryakhtar et al. [6] for uniaxial antiferromagnets and by Belov et al. [1] for spin-flip transitions in cubic ferrimagnets. We present here a detailed shape analysis for 180° domain walls in a uniaxial material when a first order phase transition in which $K_1 + K_2 = 0$ ($K_2 < 0$) is approached.

We can write the total free energy of a single domain wall as

$$F = \int_{-\alpha}^{\alpha} \left[A \left(\frac{d\Theta}{dy} \right)^2 + K_1 \sin^2\Theta + K_2 \sin^4\Theta \right] dy$$

where A is the exchange constant and y is a position coordinate across the wall. The corresponding Euler equation is [7].

$$A \frac{d}{d\Theta} \left(\frac{d\Theta}{dy} \right)^2 + 2K_1 \sin\Theta \cos\Theta + 4K_2 \sin^3\Theta \cos\Theta = 0$$

Thus with y measured from the wall centre we have (for 180° walls)

$$y_{\pi}(\Theta) = \int_{\pi/2}^{\Theta} [(K_1/A) \sin^2\Theta + (K_2/A) \sin^4\Theta]^{-1/2} \, d\Theta \qquad (4)$$

Integration of (4) yield.

$$y_{\pi}(\Theta) = \sqrt{A/K_1} \log \tan\left(\tan^{-1}\left(\sqrt{1+K} \tan \Theta\right)/2\right) \qquad (4a)$$

with inverse relation

$$\Theta_{\pi}(y) = \tan^{-1}\left[\tan\left(2 \tan^{-1} \exp\left(\sqrt{\frac{K_1}{A}}\, y\right)\right)/(1+K)\right] \qquad (4b)$$

where $K = K_2/K_1$.

The domain wall thickness is given according to the usual approximation [7]

$$\delta_{\pi} \simeq \pi \left(\delta y/\delta\Theta\right)_{\Theta = \pi/2} \quad \text{as} \quad \delta_{\pi} \simeq \pi \sqrt{\frac{A}{K_1 + K_2}} \qquad (5)$$

It is instructive to consider the approach to a spin reorientation transition with $K_2 < 0$ as K_1 decreases from a large positive value to the point where the transition takes place and $K_1(T_0) = -K_2(T_0)$. For $K_1 > -2K_2$ the axial phase has a minimum energy and the planar phase is a maximum and the sample will exist as a set of 180° domains parallel to the c axis. At a temperature T_1 where $K_1(T_1) = -2K_2(T_1)$ the planar direction also becomes an energy minimum, but not an absolute minimum. This will produce initially a tendency to pin the 180° domain wall at its centre. However as the point. $K_1(T_0) = -K_2(T_0)$ is approached it becomes more and more favourable for spins to lie in this metastable energy direction. This process is aided by the associated lowering of exchange energy which alignment brings. Thus the spins existing in the $\pi/2$ direction act as a nucleus for the creation of two or more 90° domain walls,. In terms of equation (5) the 180° domain wall width tends to infinity. This will lead to domain structures of the type schematically illustrated in Figs. 4a and 4b.

It is possible to study this process by calculating the domain wall structure as a function of K_2/K_1 using equation (4b). The results are shown in Fig. 5 where the calculation has been made at 300 points across the wall. It can be seen that as T_0 is

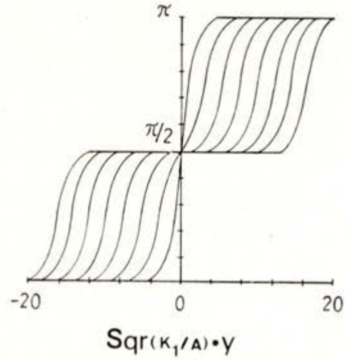

Fig. 5 — Variation of spin direction in a 180° domain wall as K_2/K_1 changes from 0 to close to -1. K_2/K_1 values: (a) 0; (b) $-(1-10^{-1})$; (c) $-(1-10^{-2})$; (d) $-(1-10^{-3})$; (e) $-(1-10^{-4})$; (f) $-(1-10^{-5})$; (g) $-(1-10^{-6}$; (h) $-(1-10^{-7})$

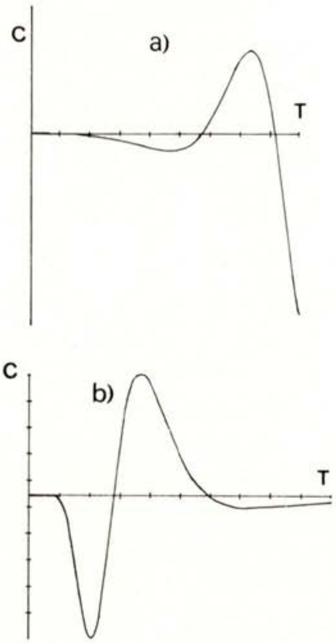

Fig. 6 — Heat capacity variation predicited for $Pr_2\,(Co_{.8}\,Fe_{.2})_{17}$ by equation (8) using

$$\text{(a)}\quad \Theta\,(T) = \frac{\pi}{2}\left[\,1 - \left(\frac{T - T_1}{\Delta T}\right)^3\,\right] \text{ and}$$

$$\text{(b)}\quad \Theta\,(T) = \frac{\pi}{2}\,\left[\,1 - \exp\text{-}(\,T - T_1\,)^{-2}\,\right]$$

approached the 180° domain wall splits into two 90° domain walls leading to what are effectively metastable 90° domains. Thus there is a coexistence of easy axis and easy plane domains before T_0 is reached. The same effect is present in the transition from easy plane to easy axis. A complete picture of the sample domain structure is not easy to obtain, but it is clear that the result of the process described above is to produce a *continuous* change from easy axis to easy plane magnetisation and vice versa. This change will occupy a small temperature range on either side of T_0. Thus over a small temperature range as T_0 is approached a large number of 90° domain walls will exist and therefore a significant number of spins will be lying in non-symmetry directions. This large number of domain walls should manifest itself as an increase in ultrasonic attenuation.

Our conclusion therefore is that in multidomain samples the domain structure converts first order reorientation transitions to continuous transitions. The same conclusion can be made in the case of first order magnetisation processes [8], [2] where spin reorientations associated with anisotropic effects are produced by the application of external magnitic fields.

4 — HEAT CAPACITY AT T_0 IN A MULTIDOMAIN SAMPLE

Recently [4] we have reportend measurements on the heat capacity of $Pr_2(Co_{0.8}Fe_{0.2})_{17}$. This uniaxial material [2] has $K_2 < 0$ and undergoes a spin reorientation transition from easy plane to easy axis as temperature is increased through $T_0 = 188$ K. The phase transition, as seen in the heat capacity, occupies an interval of 2.5 K and is predominantly negative going with a final sharp positive going peak.

In the spirit of the discussion in section above we construct a simple model of this transition as being associated with an effectively *continuous* variation of the average magnetisation vector from $\Theta = \pi/2$ to $\Theta = 0$ as temperature is increased through this small temperature interval. Thus we can assign an average free energy

$$F(\Theta) = K_1 \sin^2\Theta + K_2 \sin^4\Theta \qquad (6)$$

and an entropy

$$S(\Theta) = -[(dK_1/dT + dK_2/dT \sin^2\Theta) \sin^2\Theta + (K_1 + 2K_2 \sin^2\Theta) \frac{d \sin^2\Theta}{dT}] \quad (7)$$

and a heat capacity

$$C(\Theta) = -T [(K_1 + K_2 \sin^2\Theta) (2 \cos 2\Theta (d\Theta/dT)^2 + \sin 2\Theta (d^2\Theta/dT^2)) + 2 (dK_1/dT + \sin^2\Theta\, dK_2/dT) \sin 2\Theta (d\Theta/dT) + 2 (dK_2/dT) \sin^2\Theta \sin 2\Theta (d\Theta/dT) + 2K_2 \sin^2 2\Theta (d\Theta/dT)^2] \quad (8)$$

These expressions differ from those for the $K_2 > 0$ case since there is no direct connection between Θ and K_1, K_2 as in the easy cone situation.

From (6) and (7) the changes in entropy and heat capacity at the transition as temperature increases are

$$\Delta S = \left(\frac{dK_1}{dT} + \frac{dK_2}{dT} \right) \text{ and } \Delta C = 0$$

as in section 2 above. However the variation with temperature during the transition is interesting.

For $Pr_2 (Co_{0.8} Fe_{0.2})_{17}$ dK_1/dT and dK_2/dT are both positive [4] so that the first term in (7) will produce a monotonic increase from $-(dK_1/dT + dK_2/dT)$ to zero as Θ changes from $\pi/2$ to 0. In the second term, $d\sin^2\Theta/dT$ is always negative while $(K_1 + K_2 \sin^2\Theta)$ varies from $(K_1 + K_2)$ (> 0) to K_1 (> 0). Thus the overall contribution of this term to the entropy is an initially negative going shape followed by a positive peak and a return to zero.

The negative contribution to the entropy arises always from the K_2 component of the second term which is associated with the forcing of the spins into the metastable energy minimum corresponding to $\Theta = 0$. This is mediated by the domain wall nucleation process discussed in section 3 above. This negative contribution to entropy will lead therefore to the negative heat capacity peak observed experimentally.

The precise form of the heat capacity as a function of temperature predicted by equation (8) depends critically on the temperature variation of the average spin orientation Θ (T). This is not known but it is possible to speculate in view of the mechanism suggested above that it will vary initially rather slowly with a rapid acceleration as T_0 is approached. In Fig. 6, we plot the form predicted by equation (8) using the experimental anisotropy data [2, 4]

$$\text{for: (a)} \quad \Theta(T) = \pi/2 \left[1 - \left(\frac{T - T_1}{\Delta T} \right)^3 \right] \text{ and}$$

$$\text{(b)} \quad \Theta(T) = \pi/2 \; [1 - \exp(-1/(T - T_1)^2)],$$

where $\Delta T = 2.5$ K and $T_1 = 183.2$ K is the point where Θ departs from $\Theta = \pi/2$. It can be seen that both of these functions lead to the negative and positive peaks observed experimentally. It is unlikely however that any simple analytical function of this type will describe Θ (T) accurately. The indications from our own fitting attempts is that the variation Θ (T) which describes this particular data is most likely sigmoidal. This is a function which begins and ends slowly, but contains a rapid central variation. Such a form is also likely from the physics of the above model since 90° wall nucleation is initially gradual as T_0 is approached, but will only be complete asympotically.

5 – CONCLUSIONS

It has been shown that for spin reorientations in uniaxial materials with $K_2 > 0$ the heat capacity variation in the easy cone region can take a variety of shapes, depending in detail on the temperature dependence of the anisotropy constants. For $K_2 < 0$, the presence of domains changes first order spin reorientation transitions into those of second order with 90° domain walls nucleating at the centre of 180° walls.

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