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A phenomenological description of the first-order transition in the $Gd_5(Si_xGe_{1-x})_4$ $(0.24 < x < 0.5)$ alloys

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Abstract
With the help of the Landau–Devonshire theory, in this paper we produce a good phenomenological description of the first-order magnetocrystalline transition that occurs in the $Gd_5(Si_xGe_{1-x})_4$ $(0.24 < x < 0.5)$ alloys, and derive the magnetic phase diagram in a magnetic field versus temperature presentation. The description reproduces not only the field-induced magnetic transition and the temperature-induced transition, but also the magnetic hysteresis and the thermal hysteresis. Also, it gives the critical external field and the critical temperature for the magnetic hysteresis and the thermal hysteresis.

(Some figures in this article are in colour only in the electronic version)

The rare-earth $Gd_5(Si_xGe_{1-x})_4$ $(0.24 < x < 0.5)$ alloys, which display a giant magnetocaloric effect (GMCE), have recently taken on importance in view of their potential application in room temperature magnetic refrigeration [1–4]. The outstanding magnetocaloric features of these rare-earth compounds have prompted many experimental and theoretical investigations [5–12]. The experimental research has shown that these materials all undergo a first-order magnetocrystalline transition (FOMCT), and the GMCE is closely related to this FOMCT [8–10]. The FOMCT in these materials is a first-order magnetic transition (from ferromagnetic to paramagnetic) accompanied by a structural transition (from orthorhombic to monoclinic), which is similar to the first-order transition found recently in MnAsSb compounds [13], and has two important features. On the one hand, it behaves as a field-induced paramagnetic-to-ferromagnetic transition with the application of an external magnetic field, and displays a magnetic hysteresis. On the other hand, the Curie temperature at which the transition from

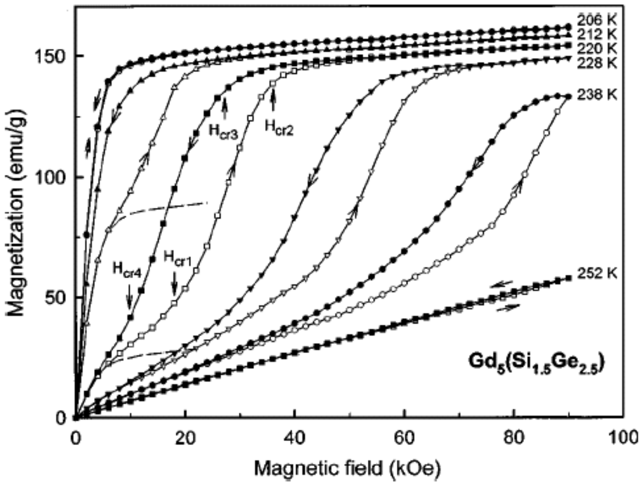

Figure 1. The magnetic field dependence of the magnetization of $Gd_5(Si_{1.5}Ge_{2.5})$ at various temperatures during magnetic field increase (open symbols) and decrease (filled symbols). The extrapolated behaviour of the magnetization at 212 and 220 K without the field-induced PM/FM transformation is shown by the dashed curves. Locations of critical magnetic fields are shown for an isotherm at 220 K [8].

the ferromagnetic/orthorhombic phase to the paramagnetic/monoclinic phase occurs exhibits a field-driven nature, and there is a thermal hysteresis. Therefore, a reasonable and accessible description of the FOMCT is strongly desired. This paper presents a phenomenological description of the FOMCT exhibited by these rare-earth Gd-based compounds.

It is well known that experimental results for the $Gd_5(Si_xGe_{1-x})_4$ ($0.24 < x < 0.5$) alloys can be roughly divided into two types. The first type consists of the measurements of their magnetic properties, such as the magnetization curves at different temperatures (i.e., M–H curves) and the M–T curves at different magnetic fields [1, 7, 8, 10]; e.g., see figure 1. In the field dependence of the magnetization, a typical feature is that the first-order magnetic transition can be induced by application of an external magnetic field, and also a large magnetic hysteresis is found on increasing and decreasing the field. In fact, it is clear that the GMCE is associated to a great extent with the rapid change of magnetization in this first-order field-induced transition. In the temperature dependence of the magnetization there is a similar feature, in which the temperature induces the first-order magnetic transition from the ferromagnetic to the paramagnetic state and a thermal hysteresis is found upon heating and cooling. Levin *et al* [8] showed that the magnetic hysteresis and the thermal hysteresis usually reach magnitudes of about 10 kOe magnetic field range and 10 K temperature range respectively. Additionally, the field-driven nature of the transition temperature is obvious. The other type comprises the experimental measurements of the crystal structures of the alloys. Although a detailed understanding of the crystallography of these alloys with various compositions or for different external magnetic fields or for different temperatures is being built up continuously, many researchers have shown that for the composition range $0.24 < x < 0.5$ the $Gd_5(Si_xGe_{1-x})_4$ alloys undergo a first-order structure transition from a monoclinic to an orthorhombic structure [8–10, 12] (e.g., see figure 2) which has not been fully explained so far.

Based on the experimental results mentioned above, a phenomenological description of the first-order magnetocrystalline transition exhibited by the $Gd_5(Si_xGe_{1-x})_4$ ($0.24 < x < 0.5$) alloys can be presented as follows.

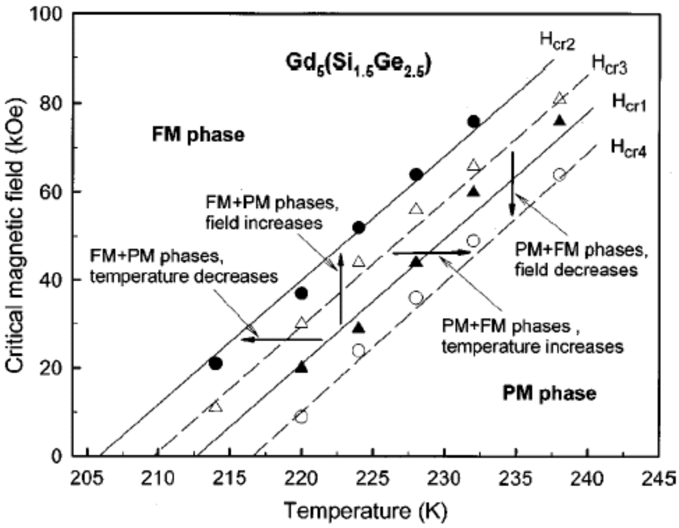

Figure 2. Critical magnetic fields determined from the magnetization of $Gd_5(Si_{1.5}Ge_{2.5})$ during isothermal increase (H_{cr1}, H_{cr2}) and reduction (H_{cr3}, H_{cr4}) of the magnetic field. Two ranges where the ferromagnetic and paramagnetic phases coexist are shown [8].

Usually, all these rare-earth Gd-based compounds have a sandwich crystalline structure, which is constituted by the layers of the Gd atoms and the layers of the other atoms in accordance with a certain sequence [10, 11]. The intra-layer and inter-layer exchange interactions in these compounds have the definitive influence upon the magnetic structure and magnetic transition in these materials. And in the layer of Gd atoms the exchange interaction between Gd atoms is of utmost importance, and it determines to a large extent the magnetic ordering temperature. In addition, these $Gd_5(Si_xGe_{1-x})_4$ alloys have their particularities. One is that for the single element Gd, when the temperature approaches the Curie point, the direction of the magnetic moment of the Gd atom will be rapidly turned from the c-plane to the c-axis, which indicates that the strong coupling near the transition point is of importance and will greatly influence the crystalline and magnetic structures of the material. Another is that the Ge and Si atoms show explicit sensitivities of the energy band to temperature and other conditions. Therefore, while alloying Gd with Ge and Si there are strong and diverse magnetocrystalline correlations in $Gd_5(Si_xGe_{1-x})_4$. With the application of a magnetic field or a change of temperature, the correlations will lead to competition between intra-layer and inter-layer interactions or between intra-atom and inter-atom interactions, and change in the magnetic and crystalline structures of the materials; this will result in a first-order magnetocrystalline transition in these rare-earth Gd-based compounds.

Because the correlative interactions involved in these compounds are strong and very complex, the Landau–Devonshire theory [14] is adopted to describe the transition in these compounds phenomenologically. The Landau–Devonshire theory is a revised version of the Landau theory, and it may be used to explain first-order transitions, such as the martensitic transformation in a shape-memory alloy. According to the Landau–Devonshire theory, the magnetization M is taken as the ordering parameter, so the free energy of the system can be written as a function of M (the ordering parameter), T (the temperature), and B (the external magnetic field), i.e.

$$\Phi(M, T, B) = \Phi_0(T) + \alpha(T - T_0)M^2 - \beta M^4 + \gamma M^6 - \delta MB. \qquad (1)$$

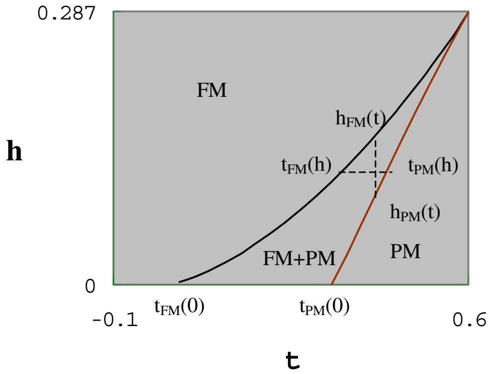

Figure 3. The magnetic phase diagram, presented as magnetic field versus temperature.

Here α, β, γ, δ, and T_0 are the parameters for the particular material. On introducing the following dimensionless quantities:

$$f = \frac{\gamma^2}{\beta^3}\Phi, \qquad t = \frac{\alpha\gamma}{\beta^2}(T - T_0), \qquad \eta = \sqrt{\frac{\gamma}{\beta}}M, \qquad h = \frac{\delta}{\beta}\left(\frac{\gamma}{\beta}\right)^{3/2} B,$$

equation (1) can be written as

$$f(\eta, h, t) = f_0 + t\eta^2 - \eta^4 + \eta^6 - h\eta. \tag{2}$$

From the equilibrium condition

$$\left(\frac{\partial f(\eta, h, t)}{\partial \eta}\right)_{h,t} = 0 \tag{3}$$

the ordering parameter η as a function of h and t can be determined from

$$h = 2t\eta - 4\eta^3 + 6\eta^5. \tag{4}$$

The h–t magnetic phase diagram based on the above equation can be obtained as follows. Firstly, according to the single-root condition for η in the equation for $(\partial h/\partial \eta)_t = 0$, the critical magnetic field h_c and the critical temperature t_c (with the transition no longer taking place) can be respectively given as follows:

$$h_c = 16\sqrt{5}/125 \qquad \text{and} \qquad t_c = 3/5. \tag{5}$$

(Incidentally, the same results can be obtained from the single-root condition for η in the equation for $(\partial t/\partial \eta)_h = 0$.) Secondly, from the equation for $(\partial t/\partial \eta)_h = 0$ one has the critical lower- and upper-limit temperatures for the coexistence of paramagnetic and ferromagnetic states in zero magnetic field, i.e.

$$t_{FM}(0) = 0 \qquad \text{and} \qquad t_{PM}(0) = 1/3. \tag{6}$$

Similarly, the critical lower- and upper-limit temperatures for the coexistence of paramagnetic and ferromagnetic states in a certain magnetic field h $(0 < h < h_c)$, $t_{FM}(h)$ and $t_{PM}(h)$, can be obtained respectively. Consequently the h–t magnetic phase diagram can be plotted as in figure 3, in which FM, PM, and FM + PM indicate the ferromagnetic state, paramagnetic state, and coexistence of ferromagnetic and paramagnetic states, and $h_{PM}(t)$ and $h_{FM}(t)$ indicate the critical lower- and upper-limit magnetic fields for the coexistence of paramagnetic and ferromagnetic states at temperature t, respectively. It may be noted that there is an obvious difference between the theoretical phase diagram (figure 3) and the experimental one (figure 2).

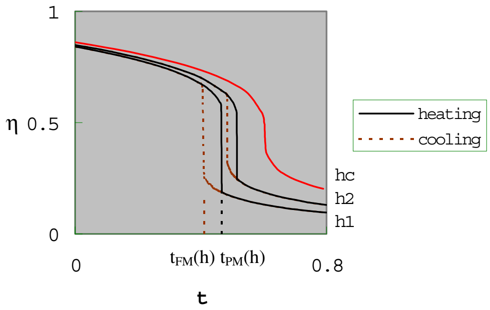

Figure 4. The temperature dependence of the order parameter ($h_1 = 0.15$ and $h_2 = 0.2$), according to the Landau–Devonshire theory.

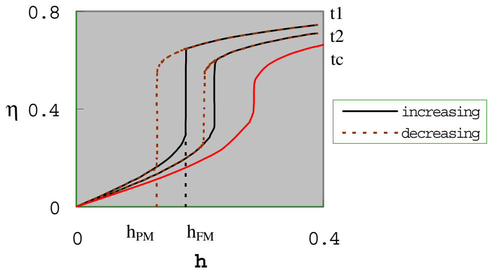

Figure 5. The field dependence of the order parameter ($t_1 = 0.45$ and $t_2 = 0.52$), according to the Landau–Devonshire theory.

In fact, this mainly arises because the experimental phase diagram is plotted for a smaller range of temperature or magnetic field. From figure 1 it can be seen that when temperature increases to a large value (in fact, it does not need to be very large), the hysteresis will disappear. It has been shown experimentally that there is a critical temperature and that the two critical lines in the phase diagram will not be parallel over a large range of temperature. Therefore the theoretical phase diagram is in agreement with the experimental one to a large extent.

From the h–t magnetic phase diagram, the η–t curve for a certain h and the η–h curve for a certain t can be obtained. Figures 4 and 5 show the theoretically calculated results, including the temperature dependence (the η–t curve) and the field dependence (the η–h curve).

Figure 4 shows the situation for heating or cooling in a certain field (h). When temperature is below $t_{FM}(h)$, the alloy has an orthorhombic structure with a ferromagnetic ordering. When temperature reaches $t_{FM}(h)$, the ferromagnetic/orthorhombic alloy begins to undergo a first-order magnetocrystalline transition—a structural transition from orthorhombic to monoclinic structure accompanied simultaneously by a magnetic transition from the ferromagnetic to the paramagnetic state, and then enters an *intermediate state* in which the two phases (paramagnetic/monoclinic and ferromagnetic/orthorhombic) coexist. With heating, the amount of higher-temperature phase (paramagnetic) in the intermediate state increases and the amount of lower-temperature phase (ferromagnetic) decreases. At $t_{PM}(h)$ the alloy has become transformed totally to a paramagnetic/monoclinic state. And the situation for cooling can be described in a similar way, but usually there is a thermal hysteresis.

Figure 5 shows the situation for increasing and decreasing magnetic field for a certain temperature (t). When the temperature is below $t_{FM}(0)$ the alloy in zero magnetic field is orthorhombic and ferromagnetic, so its magnetic behaviour in a magnetic field should be the usual magnetization of a soft-magnetic material. From figure 1 it can be seen that the experimental curve (say, the curve at 206 K in [8]) is just a typical magnetization curve for soft-magnetic material. The situation for decreasing magnetic field is same, and there is no magnetic hysteresis.

When the temperature is above $t_{PM}(0)$ the alloy in zero field lies in a monoclinic paramagnetic state. When the magnetic field is less than h_{PM} the alloy has a monoclinic structure with a paramagnetic ordering. On increasing the field to h_{PM} the paramagnetic/monoclinic alloy begins to undergo a first-order magnetocrystalline transition induced by the magnetic field, and then enters an intermediate state in which the two magnetocrystalline phases coexist. With increasing external field the ferromagnetic order increases and the paramagnetic order decreases in the intermediate-state range. Finally, when h_{FM} is reached the alloy has transformed totally into the ferromagnetic/orthorhombic state. And the situation is similar for decreasing magnetic field, but there is usually a magnetic hysteresis.

When the temperature is between $t_{FM}(0)$ and $t_{PM}(0)$, the alloy in zero magnetic field lies in the coexistence region of two different magnetic orderings. For the monoclinic ferromagnetic fraction, its magnetic behaviour in an external magnetic field is also the above-described usual behaviour of a soft-magnetic material. For the monoclinic paramagnetic fraction, however, the behaviour indicates a first-order transition (a field-induced transition with the application of a magnetic field). In this way, the total magnetization of the alloy is the weighted sum of the above soft-magnetic and Landau–Devonshire magnetizations, and the weighting is dependent on the temperature t (between $t_{FM}(0)$ and $t_{PM}(0)$). Therefore, the combination of the ferromagnetic fraction (the soft-magnetic magnetization) and the paramagnetic fraction (the Landau–Devonshire magnetization) results in the typical step-like magnetization of the alloy.

It is obvious that both the field-driven nature of the transition temperature (shown in figure 4) and the field-induced property (shown in figure 5) for the first-order magnetocrystalline transition can be described well. The thermal hysteresis and the magnetic hysteresis are also explicitly shown in figures 4 and 5. Usually, the temperature range of the thermal hysteresis and the magnetic field range of the magnetic hysteresis are determined by the difference of t_{PM} and t_{FM} and that of h_{FM} and h_{PM}. And it is noted that the critical values h_c and t_c correspond to the upper-limit values of the hysteresis behaviours; that is to say, when $h > (16\sqrt{5})/125$ and $t > 3/5$ there is no thermal hysteresis and no magnetic hysteresis respectively.

In addition, this reasonable explanation of the first-order magnetocrystalline transition reveals an interesting fact. Although the details and mechanisms of this FOMCT in these rare-earth compounds and the martensitic transformation in the shape-memory alloys are different, the descriptions of these two transitions are same. This shows that they belong in the same universality class of transitions. And it also indicates that the Landau theory is very general and comprehensive.

To summarize, with the help of the Landau–Devonshire theory this paper develops a good description of the first-order magnetocrystalline transition exhibited by the $Gd_5(Si_xGe_{1-x})_4$ $(0.24 < x < 0.5)$ compounds. It reproduces not only the field-induced magnetic transition and the field-driven transition temperature, but also the magnetic hysteresis and the thermal hysteresis. And it gives the critical external field and the critical temperature for the thermal hysteresis and the magnetic hysteresis. Of course, the description presented in this paper is merely a phenomenological one, and the physical mechanism of the first-order magnetocrystalline transition as well as the strong correlations in these compounds need to be studied and confirmed by further experiment and theoretical investigation.

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