

Magnetocrystalline anisotropy and spin reorientation transition of DyMn₆Sn₆ compound

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Abstract: The spin-reorientation transition of intermetallic compound DyMn₆Sn₆ was investigated by applying the molecular field theory. The temperature dependence of easy magnetization direction of compound and the magnetic moment directions of Dy and Mn ions were theoretically calculated and they have good agreement with the experimental data. In the framework of single ion model, the temperature dependence of magnetocrystalline anisotropic constants K_{1R} and K_{2R} of Dy ion were also calculated. The results show that the fourth-order crystal field parameter, B_4^0 , and the corresponding second-order magnetocrystalline anisotropic constant, K_{2R} , of Dy ion must be taken into account in order to explain the spin-reorientation transition satisfactorily. The competition between K_{2R} and K_{1R} plays a key role in the spin-reorientation transition of DyMn₆Sn₆.

Key words: rare earth-transition metal compound; spin-reorientation transition; magnetocrystalline anisotropy

1 Introduction

Recently, the rare earth-transition metal compounds RM₆X₆ (R=rare-earth elements, M=transition metal and X=Sn and Ge) have attracted much attention due to their abundant magnetic properties[1–15]. RMn₆Sn₆ with heavy rare earth element crystallizes into HfFe₆Ge₆-type structure (space group is P_6/mmm), which is composed of hexagonal R layers comprising Sn atoms and Mn Kagomé nets, stacked in the sequence -Mn-R-Mn-Mn-R-Mn- along the *c*-axis[1]. From the magnetic point of view, RMn₆Sn₆ have two different magnetic subsystems: R- and Mn-subsystems. Neutron diffraction studies and magnetic measurements[1–3] indicate that Mn- and R-subsystems simultaneous transfer from paramagnetic state into ferromagnetic state for compounds with Tb, Dy and Ho below Curie temperature T_C (where T_C =423, 393 and 376 K for Tb, Dy and Ho, respectively) due to the strong R-Mn exchange interaction. Mn-subsystem and R-subsystem are antiferromagnetically coupled with each other. When temperature drops to T_{SR} , spin reorientation transition

occurs in the compounds and the easy magnetization direction transfers from *c*-plane to *c*-axis. The spin reorientation temperatures T_{SR} are 330, 300 and 200 K for Tb, Dy and Ho compounds, respectively. For TbMn₆Sn₆, when temperature is below 250 K, the easy magnetization direction completely transfers to *c*-axis. While for DyMn₆Sn₆ and HoMn₆Sn₆, the directions do not completely transfer to *c*-axis. The angles of easy direction with *c*-axis are 45° for Dy at 220 K and 48° for Ho at 100 K and keep constants until 2 K. Many researches[2,4–5] show that the mechanism of spin reorientation transition is different for three compounds. The spin reorientation transition in TbMn₆Sn₆ comes from the competition of magnetocrystalline anisotropy energies of Tb- and Mn-subsystems. While for DyMn₆Sn₆ and HoMn₆Sn₆, the competition between the first- and the second-order magnetocrystalline anisotropy constants K_1 and K_2 plays a very important role (which means the fourth-order crystalline field parameter of rare earth ions cannot be ignored). In this paper, the mechanism of spin reorientation transition of DyMn₆Sn₆ compound was quantitatively investigated in the frame work of molecular field theory. The temperature depend-

ences of magnetocrystalline anisotropy constants of Dy ion were also calculated based on the single ion model.

2 Theoretical model

DyMn₆Sn₆ is composed of two magnetic subsystems: Dy- and Mn-subsystems. According to the molecular field theory, the Hamiltonians of Dy and Mn ions have the following forms:

$$\hat{H}_{\text{Dy}} = g_J \mu_B J \cdot (\mathbf{H}_{\text{ex,Dy}} + \mathbf{H}) + B_2^0 O_2^0 + B_4^0 O_4^0 \quad (1)$$

$$\hat{H}_{\text{Mn}} = g_S \mu_B \mathbf{S} \cdot (\mathbf{H}_{\text{ex,Mn}} + \mathbf{H}) + K_{1t} \sin^2 \theta_t \quad (2)$$

where g_J and g_S represent the g -factors of Dy and Mn ions; J and S are the total angular momentum operator of Dy ion and spin momentum operator of Mn ion, respectively; μ_B is Bohr momentum; B_2^0 and B_4^0 describe the crystalline field parameters of Dy³⁺; O_2^0 and O_4^0 are Stevens operators; K_{1t} is magnetocrystalline anisotropy constant of Mn ion and θ_t is the angle of Mn ion magnetic moment with respect to c -axis; $\mathbf{H}$ is external magnetic field; the molecular fields acting on the Dy and Mn ions are $\mathbf{H}_{\text{ex,Dy}}$ and $\mathbf{H}_{\text{ex,Mn}}$, which can be written as

$$\mathbf{H}_{\text{ex,Dy}} = \lambda_{\text{Dy-Dy}} \langle \boldsymbol{\mu}_{\text{Dy}} \rangle + 6\lambda_{\text{Dy-Mn}} \langle \boldsymbol{\mu}_{\text{Mn}} \rangle \quad (3)$$

$$\mathbf{H}_{\text{ex,Mn}} = \lambda_{\text{Mn-Mn}} \langle \boldsymbol{\mu}_{\text{Mn}} \rangle + \lambda_{\text{Dy-Mn}} \langle \boldsymbol{\mu}_{\text{Dy}} \rangle \quad (4)$$

$\lambda_{\text{Dy-Dy}}$, $\lambda_{\text{Dy-Mn}}$ and $\lambda_{\text{Mn-Mn}}$ represent the molecular field constants of Dy-Dy, Dy-Mn and Mn-Mn exchange interaction, respectively. $\langle \boldsymbol{\mu}_{\text{Dy}} \rangle$ and $\langle \boldsymbol{\mu}_{\text{Mn}} \rangle$ are the thermal average of magnetization of Dy- and Mn-subsystems, respectively.

The free energy of system can be given as

$$F = -k_B T \ln Z_{\text{Dy}} - 6k_B T \ln Z_{\text{Mn}} + \frac{1}{2} \langle \boldsymbol{\mu}_{\text{Dy}} \rangle \cdot \mathbf{H}_{\text{ex,Dy}} + 3 \langle \boldsymbol{\mu}_{\text{Mn}} \rangle \cdot \mathbf{H}_{\text{ex,Mn}} \quad (5)$$

where k_B is Boltzmann constant; Z_{Dy} and Z_{Mn} are partition functions of Dy and Mn ions, respectively.

$$Z_{\text{Dy}} = \text{Tr}[\exp(-\hat{H}_{\text{Dy}}/k_B T)],$$

$$Z_{\text{Mn}} = \text{Tr}[\exp(-\hat{H}_{\text{Mn}}/k_B T)] \quad (6)$$

From the stable equilibrium condition the magnitude of $\langle \boldsymbol{\mu}_{\text{Mn}} \rangle$ and $\langle \boldsymbol{\mu}_{\text{Dy}} \rangle$, as well as their direction with respect to the c -axis can be evaluated. Consequently, the magnetic structure and the temperature

and field dependence of magnetization of compounds can be determined.

3 Results and discussion

In our calculation the values of Dy and Mn magnetic moments at 4.2 K are taken to be $10\mu_B$ and $2.21\mu_B$, respectively[2]. By fitting the experimental data in Ref.[2], including the spin reorientation temperature and thermal magnetization curves, the other magnetic parameters are estimated as follows: $\lambda_{\text{Mn-Mn}}=162.3T/\mu_B$, $\lambda_{\text{Dy-Mn}}=-5.8T/\mu_B$, $\lambda_{\text{Dy-Dy}}=2.1T/\mu_B$, $B_2^0=-0.25$ K, $B_4^0=0.003$ K, $K_{1t}=-1.5$ K/Mn (valued at $T=4.2$ K).

Fig.1 shows the theoretically calculated temperature dependences of easy magnetization direction of DyMn₆Sn₆ and the angles of Dy and Mn magnetic moments with respect to the c -axis. When temperature is above 300 K, as seen from Fig.1, the easy magnetization direction lies in the c -plane. The angles of Dy and Mn

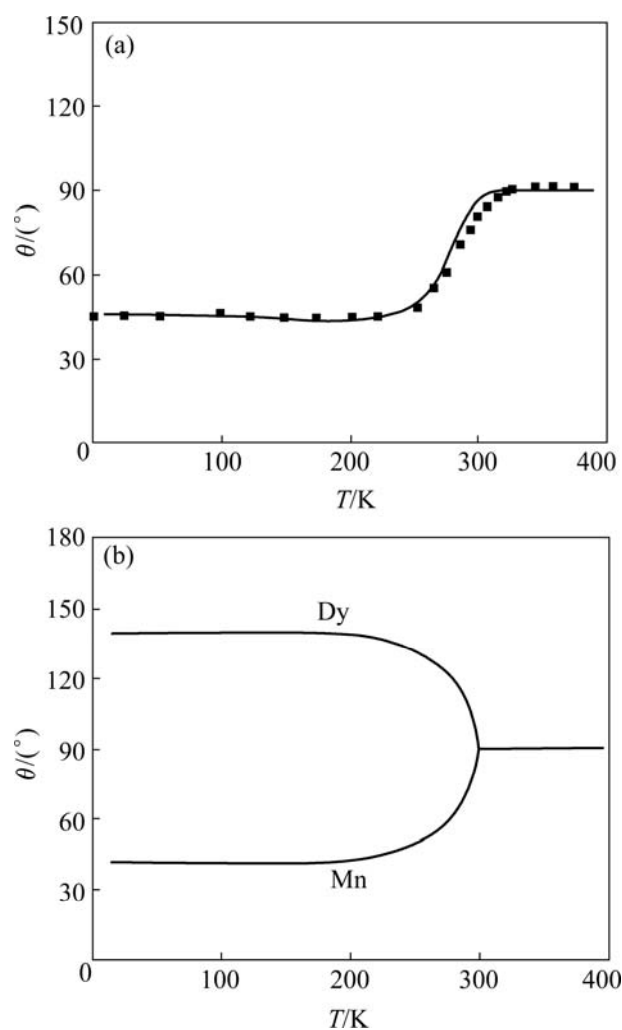


Fig.1 Temperature dependence of easy magnetization direction of DyMn₆Sn₆ (a) and angles of Dy and Mn magnetic moments with respect to c -axis (b) (Solid lines are theoretically calculated curves, dots denote experimental data)

magnetic moments are all equal to 90° . At $T=300$ K the spin reorientation transition occurs and the easy direction begins to turn to c -axis. As temperature reaches 220 K the angle between the easy direction and c -axis is 45° and keeps this value down to 2 K. During the process of spin reorientation the Dy and Mn magnetic moments keep antiparallel. The calculated results are in good agreement with neutron diffraction data[2].

There are many reasons that can lead to the spin reorientation transition. The competition between the magnetocrystalline anisotropy energies of two magnetic subsystems or the competition among the different order magnetic anisotropy constants in the same subsystem may all give rise to the change of easy magnetization direction. The estimated magnetocrystalline anisotropy constant K_{1t} of Mn-subsystem has negative value, which indicates that its easy magnetization direction lies in the c -plane. Neutron diffraction study also confirms that the easy direction of Mn-subsystem is in the c -plane[2]. The crystal field parameter B_2^0 acting on Dy^{+3} is negative (corresponding A_2^0 is positive), which favors the easy magnetization direction of Dy-sublattice along the c -axis. Investigations in Refs.[2, 4] showed the spin reorientation transition of $TbMn_6Sn_6$ can be described in the frame work of competition between the magnetocrystalline anisotropy energies of Tb- and Mn-subsystems. For $DyMn_6Sn_6$ and $HoMn_6Sn_6$, however, the competition between the first-order and the second-order magnetocrystalline anisotropy constants K_1 and K_2 play an important role in the process of spin reorientation[5–6]. In fact, the estimated B_2^0 is relatively small compared with other rare earth-transitional metal compounds (corresponding A_2^0 equals to $126 K \cdot a_0^{-2}$, while A_2^0 of $R_2Fe_{14}B$ is as large as $983 K \cdot a_0^{-2}$ [2]), which indicates that the higher order crystal field parameter cannot be neglected. Our calculations also show that B_4^0 plays a very important role in the spin reorientation transition in $DyMn_6Sn_6$. Furthermore, below 220 K, the easy magnetization direction of $DyMn_6Sn_6$ is in cone plane. This requests that K_1 and K_2 must satisfy the condition: $0 < -K_1 < 2K_2$. Therefore K_2 must be taken into account in order to explain the spin reorientation transition of $DyMn_6Sn_6$, which mainly comes from the fourth-order crystal field parameter, B_4^0 , of Dy ion.

In order to explain the spin reorientation transition of $DyMn_6Sn_6$ quantitatively, we calculated the temperature dependence of magnetocrystalline anisotropy constants of Mn- and Dy-subsystems in the frame work of single ion model. We consider the magnetocrystalline anisotropy constant of Mn-subsystem follows the Akulov-Zener law: $K_i(T) \propto M(T)^3$. In

accordance with single ion model, the magnetocrystalline anisotropy coefficients of rare-earth sublattice can be written as follows:

$$K_2^0(0) = 2J_2B_2^0, \quad K_4^0(0) = 8J_4B_4^0 \quad (7)$$

where $J_2 = J(J-1/2)$, $J_4 = J_2(J-1)(J-3/2)$.

The temperature dependence of $K_n^m(T)$ is as

$$K_n^m(T) = K_n^m(0) I_{n+1/2} \left[L^{-1} \left(\frac{M(T)}{M(0)} \right) \right] \quad (8)$$

where $I_{n+1/2}$ is hyperbolic Bessel function and L is Langevin function.

The magnetocrystalline anisotropy constants K_{1R} and K_{2R} of rare earth subsystem can be calculated from the following formula:

$$K_{1R} = -\frac{1}{2}(3K_2^0 + 10K_4^0), \quad K_{2R} = \frac{35}{8}K_4^0 \quad (9)$$

Fig.2 shows the theoretically calculated temperature dependence of K_{1R} and K_{2R} of Dy-subsystem. It can be seen from Fig.2 that K_{2R} keeps positive in the whole temperature range of magnetically ordered state, which indicates that K_{2R} favors the easy magnetization direction of Dy-subsystem directed along the c -axis. In contrast, K_{1R} changes its sign from positive to negative with the decrease of temperature. In high temperature range K_{1R} favors the magnetic moment of Ho^{+3} along the c -axis. Below 145 K, K_{1R} becomes negative and makes for magnetic moment of Ho^{+3} perpendicular to the c -axis. The total magnetocrystalline anisotropy constants of $DyMn_6Sn_6$ are $K_1 = K_{1R} + 6K_{1t}$, $K_2 = K_{2R}$. In the whole temperature range of magnetically ordered state, K_1 is always negative and K_2 keeps positive.

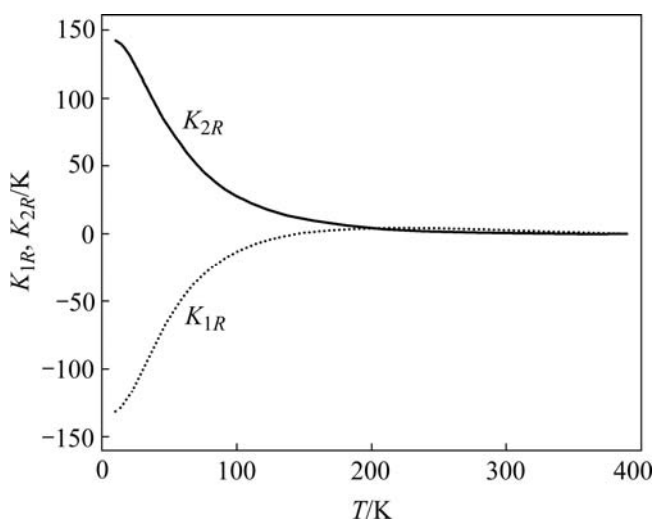


Fig.2 Theoretically calculated temperature dependence of K_{1R} and K_{2R}

Our theoretical calculations (Fig.1(b)) and neutron diffraction data[2] all show that the magnetic moments of Dy and Mn ions are always antiparallel in the whole magnetically ordered state. In this case, the free energy correlated to the spin reorientation transition only includes the magnetic anisotropic energy:

$$E_{\text{an}} = K_1 \sin^2 \theta + K_2 \sin^4 \theta \quad (10)$$

where θ is the angle of the easy magnetization direction of DyMn_6Sn_6 with respect to the c -axis. The directions of magnetic moments of Dy and Mn ions and the easy magnetization direction of compounds can be decided from equilibrium condition. There are three states: 1) $\theta_1=\pi/2$ corresponding the c -plane easy magnetization direction; 2) $\theta_2=0$ indicating the c -axis easy magnetization direction; 3) $\sin^2\theta_3=-K_1/2K_2$ and $\sin^2\theta_3\leq 1$ representing the easy magnetization cone. The free energies corresponding the three solutions are $E_1=K_1+K_2$, $E_2=0$ and $E_3=-K_1^2/4K_2$, respectively. By comparing the values of the three energies we can decide which state is the stablest one. Fig.3 displays the temperature dependences of E_1 , E_2 and E_3 . As shown in Fig.3, in high temperature range E_1 is the smallest one, which indicates that the easy magnetization direction is in c -plane. When temperature is below T_{SR} of 300 K, E_3 becomes the smallest one, showing the spin-reorientation transition occurs and the easy magnetization direction begins to transfer to the c -axis (when $T>T_{\text{SR}}$, $\sin^2\theta_3=-K_1/(2K_2)>1$, therefore θ_3 is not the solution). At $T=2$ K, $\sin^2\theta_3=0.513$, $\theta_3=45^\circ$. In the whole temperature range of magnetically ordered state E_2 is not the smallest energy. This means that the easy magnetization direction does not completely transfer to the c -axis. The calculated θ_3 and spin reorientation temperature T_{SR} are in good agreement with neutron diffraction results[2].

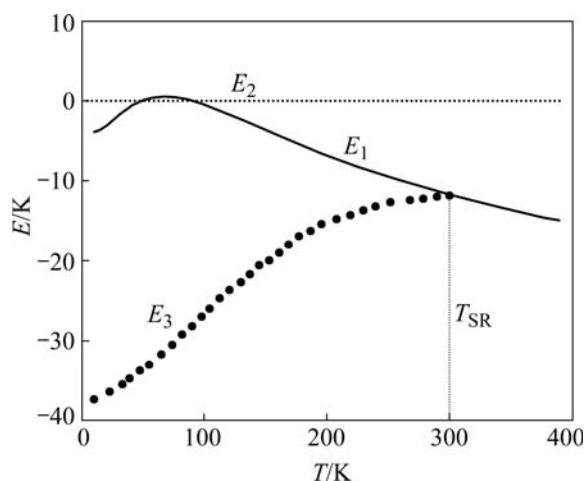


Fig.3 Temperature dependences of free energies E_1 , E_2 and E_3

4 Conclusions

1) The magnetic parameters of DyMn_6Sn_6 were estimated in the framework of molecular field model by fitting the different kinds of experimental data. The temperature dependence of magnetocrystalline anisotropy constants K_{1R} and K_{2R} of Dy ion was calculated. It is shown that the K_{2R} keeps positive in the whole magnetically ordered temperature range, which indicates that K_{2R} favors the magnetic moment of Dy ion directed along the c -axis. On the contrary, K_{1R} changes its sign from positive to negative at $T=145$ K. Above 145 K, K_{1R} is positive and makes for the magnetic moment of Dy ion directed along the c -axis, and below this temperature it favors the moment direction of Dy ion lying in the c -plane. The fourth order crystal field B_4^0 makes great contribution to the magnetocrystalline anisotropy energy. The total magnetocrystalline anisotropy constant K_1 is always negative and K_2 keeps positive in the whole temperature range of magnetically ordered state.

2) The spin reorientation of TbMn_6Sn_6 comes from the competition of magnetocrystalline anisotropies of Tb- and Mn-subsystems. For DyMn_6Sn_6 , however, in order to describe the spin reorientation transition satisfactorily, the fourth-order crystal field parameter B_4^0 (corresponding to the second-order magnetocrystalline anisotropy constant K_{2R}) must be taken into account, which plays the key role in the low temperature range. In compound DyMn_6Sn_6 the magnetocrystalline anisotropy energies of Dy- and Mn-subsystems also compete with each other, but the competition between K_{2R} with K_{1R} and K_{1t} are the main cause of spin reorientation in compound DyMn_6Sn_6 .

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