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Exchange interactions and magnetic properties of intermetallic compounds①

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Abstract: The temperature dependence of lattice parameters a and c of intermetallic compounds RMn_2Ge_2(R= La, Sm and Gd) were measured in the temperature range of 10－800 K by using the X-ray diffractometer. It is found that the high temperature magnetic transitions of Mn-subsystem in light rare earth compounds from paramagnetic to antiferromagnetic state accompany the negative magnetoelastic anomalies of lattice parameters c, where a does not change. This indicates that the antiferromagnetic component of intralayer Mn-Mn exchange coupling is correlated with lattice constant c. The low temperature first order ferromagnetism → antiferromagnetism transitions(or antiferromagnetism → ferromagnetism transition) of Mn-subsystem in $SmMn_2Ge_2$ and $GdMn_2Ge_2$ accompany the abruptly decrease(or increase) of lattice parameter a, and $\Delta a/a \approx 0.15\%$. This demonstrates that the interlayer Mn-Mn exchange interaction is very sensitive to the intralayer Mn-Mn distance. The critical value of lattice constant a_k, at which the interlayer Mn-Mn coupling changes its sign, is $4.044\,5 \times 10^{-10}$ m. Based on the molecular field model of exchange interaction the magnetic curves of $GdMn_2Ge_2$ single crystal at different temperatures were calculated and a good agreement with experimental data had gotten. The Gd-Gd, Gd-Mn, intralayer Mn-Mn and interlayer Mn-Mn exchange coupling parameters were estimated.

Key words: intermetallic compound; magnetic phase transition; exchange interaction
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1 INTRODUCTION

The intermetallic compounds RMn_2Ge_2 crystallize in the body-centered-tetragonal $ThCr_2Si_2$-type structure (space group is I4/mmm), which is consisted of R, Ge and Mn layers, stacked in the sequence R-Ge-Mn-Ge-R along the c-axis[1]. From the magnetic point of view, RMn_2Ge_2 compounds have two different magnetic subsystems: R- and Mn-subsystem. In RMn_2Ge_2, there are different kinds of exchange interactions. A number of research works[1] indicate that the intralayer Mn-Mn exchange interaction is the strongest and gives rise to the magnetic order temperature of RMn_2Ge_2 as high as 350－450 K, depending on R. The interlayer Mn-Mn and R-Mn exchange interactions have the same order but they are substantially less than the intralayer Mn-Mn exchange interaction. However, their interplay is reflected in the magnetic properties of magnetically ordered state. The smallest one is the R-R exchange interaction. Many studies[2-3] have shown that the interlayer Mn-Mn exchange interaction is very sensitive to the intralayer Mn-Mn distance, and consequently the lattice parameter a. When a is larger than a critical value a_k, the interlayer Mn-Mn exchange interaction is ferromagnetic, otherwise it is antiferromagnetic. For this reason, the Mn-sublattice in most of light rare earth compounds has ferromagnetic structure, and the intrinsic magnetic structure of Mn-sublattice in the compounds with heavy rare earth is antiferromagnetic. Recently, Venturini et al have extensively performed neutron diffraction study on RMn_2Ge_2[3-6]. Their studies indicate that in the light rare earth compounds the Mn magnetic structure of the same sublayer is not collinear ferromagnetic, and there is a large antiferromagnetic component perpendicular to the c-axis. Their investigations have also shown that the intralayer Mn-Mn exchange interaction is ferromagnetic for the intralayer Mn-Mn distance $d_{Mn\text{-}Mn}$ lower than 2.84×10^{-10} m and antiferromagnetic for $d_{Mn\text{-}Mn}$ greater than 2.89×10^{-10} m, whereas the mixed planes, where ferromagnetic and antiferromagnetic components coexist, are observed for intermediate distances. Just because of these peculiar properties of exchange interaction the RMn_2Ge_2 compounds display abundant magnetic properties.

In this paper we have studied the lattice constant dependence of exchange interactions in RMn_2Ge_2(R= La, Sm and Gd) compounds by using the X-ray diffractometry. Based on the molecular field model of exchange interaction, we calculate the magnetization curves of $GdMn_2Ge_2$ single crystal with the field along the different

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crystallographic axes at different temperatures by taking into account of the lattice constant dependence of interlayer Mn-Mn exchange interaction.

2 EXPERIMENTAL AND RESULTS

The polycrystalline samples of RMn_2Ge_2 (R= La, Sm and Gd) were prepared by induction melting the constituent elements in a water-cooled crucible under argon atmosphere. Melting was repeated several times in order to ensure homogeneity. Then ingots were sealed in a quartz tube for further annealing at 750 ℃ for one week. The quality of the samples was verified by X-ray diffraction, and the samples were found to be single phase.

The temperature dependence of lattice constants of RMn_2Ge_2(R= La, Sm and Gd) was measured in the temperature range of 10 ~ 800 K by using X-ray diffractometry. The X-ray diffraction was carried out on the Geigerflex diffractometer with Fe K_α radiation.

Fig. 1 shows the temperature dependence of lattice parameters a and c of $LaMn_2Ge_2$. According to the magnetic measurements[7], the $LaMn_2Ge_2$ orders ferromagnetically at temperature T_c = 310 K. Recently, neutron diffraction studies[3] have shown the Curie temperature T_c is not the transition temperature of paramagnetism → ferromagnetism. Above T_c, $LaMn_2Ge_2$ has some kind of antiferromagnetic structure; at higher temperature, $T_N \approx$ 413K, $LaMn_2Ge_2$ becomes magnetic disordered. Our measurement confirms the existence of high temperature antiferromagnetic structure. It can be seen from Fig. 1 that the spontaneous magnetic transitions at T_N accompanies the negative magnetoelastic anomaly of lattice parameter c, where transition at T_c accompanies the negative magnetoelastic anomaly of lattice parameter a.

The temperature dependence of lattice parameters a and c of $SmMn_2Ge_2$ are depicted in Fig. 2. Magnetic measurements show[1,2] that, when T_c= 341 K, the Mn-subsystem in $SmMn_2Ge_2$ orders ferromagnetically. When temperature decreases to T_{t1}= 150 K, the Mn-subsystem undergoes first order magnetic transition from ferromagnetic to antiferromagnetic state due to the thermal contraction, which causes the interlayer Mn-Mn exchange interaction change its sign. As the temperature continues to reduce, the Mn-sublattice reentrants into the ferromagnetic state at T_{t2}= 100 K. At the same time the Sm-sublattice becomes ferromagnetically ordered and ferromagnetically coupled with the Mn-sublattice. As in the case of $LaMn_2Ge_2$, above T_c, $SmMn_2Ge_2$ also has some kind of antiferromagnetic structure, and the transition into the paramagnetic state occurs in higher temperature T_N= 385 K[8]. It can be seen from Fig. 2 that the a —T and c —T curves display a series of anomalies with reduction of temperature. The high temperature paramagnetism → antiferromagnetism transition at T_N and antiferromagnetism → ferromagnetism at T_c of Mn-sublattice accompany the magnetoelastic anomalies of c and a, respectively. The low temperature first order ferromagnetism → antiferromagnetism transition at T_{t1} (= 150 K) accompanies the abruptly decrease of a, where the first order transition at T_{t2} accompanies the abruptly increase of a. At these first order transition points the lattice constant c does not change.

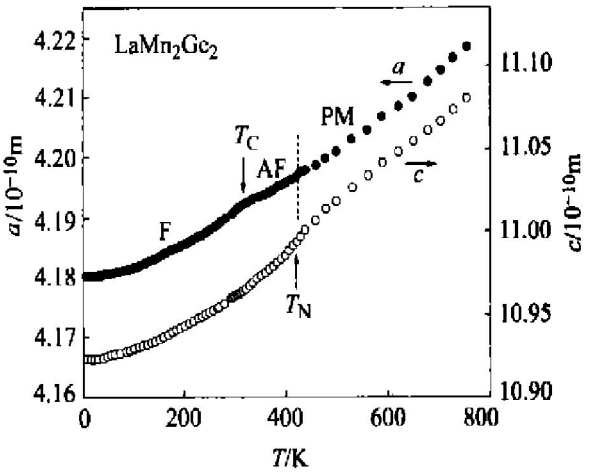

Fig. 1 Temperature dependence of lattice parameters a and c of intermetallic compound $LaMn_2Ge_2$

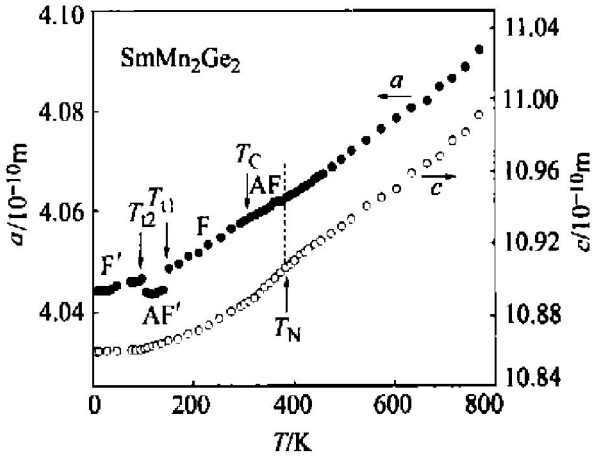

Fig. 2 Temperature dependence of lattice parameters a and c of intermetallic compound $SmMn_2Ge_2$

Fig. 3 presents the temperature dependence of lattice parameters a and c of compound $GdMn_2Ge_2$. In accordance with Refs. [9, 10] the Mn-subsystem in this compound becomes antiferromagnetically ordered at T_N= 365 K. At T_t= 97 K the Mn-subsystem undergoes the first order magnetic phase transition from antiferromagnetic to the ferromagnetic state; at the same time the Gd-sublattice becomes ferromagnetically ordered and antiferromag-

netically couples with Mn-sublattice. It can be seen from Fig. 3 that the transition from paramagnetic to antiferromagnetic phase at T_N accompanies the negative magnetoelastic anomaly of lattice constant a. The first order antiferromagnetic to ferromagnetic state of Mn-subsystem at T_t accompanies the sudden increase of a, where c does not change.

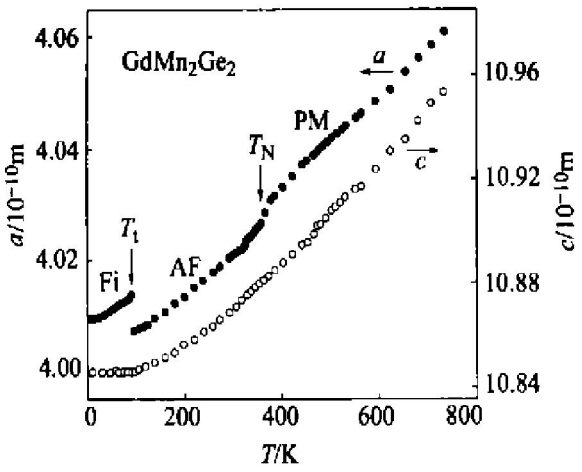

Fig. 3 Temperature dependence of lattice parameters a and c of intermetallic compound $GdMn_2Ge_2$

3 DISCUSSION

As stated in the introduction, the Mn magnetic structure of the same sublayer in the light rare earth compounds at $T > T_c$ is not collinear ferromagnetic, and there is a large antiferromagnetic component perpendicular to the c-axis. In the temperature range of $T_c < T < T_N$, the Mn magnetic structure of the same sublayer is antiferromagnetic and the magnetic moment is perpendicular to the c-axis[3, 4]. It can be seen from temperature dependence of lattice parameters a and c of $LaMn_2Ge_2$ and $SmMn_2Ge_2$ (Fig. 1 and Fig. 2) that the paramagnetism → antiferromagnetism transition at T_N accompanies the negative magnetoelastic anomaly of lattice constant c, where a almost does not change. This indicated that the antiferromagnetic component of intralayer Mn-Mn exchange interaction is correlated with lattice constant c. The low temperature first order magnetic transition of Mn-subsystem in $SmMn_2Ge_2$ and $GdMn_2Ge_2$ from ferromagnetic to antiferromagnetic state(or from antiferromagnetic to ferromagnetic state) accompanies the abrupt reduction(or increment) of constant a, where c does no change(Fig. 2 and Fig. 3). These results are in agreement with Ref. [2], confirming that the interlayer Mn-Mn exchange interaction is very sensitive to the intralayer Mn-Mn distance, as this first order transition is related with the change of interlayer Mn-Mn coupling from ferromagnetic to antiferromagnetic. The critical lattice constant value a_k estimated from our experimental result is $4.044\,5 \times 10^{-10}$ m. The change of lattice constant $\Delta a/a$ caused by the first order ferromagnetism → antiferromagnetism in Mn-sublattice is about 0.15%.

In Ref. [11], we have demonstrated that the lattice constant dependence of interlayer Mn-Mn exchange interaction has strong influence on the magnetic properties of polycrystalline Gd_xLa_{1-x}-Mn_2Ge_2 system. In the following we will see, in order to describe the magnetic properties of $GdMn_2Ge_2$ single crystal, it is also necessary to take into account of the lattice parameter dependence, and consequently, the temperature dependence of interlayer Mn-Mn exchange coupling.

According to the molecular field approximation of exchange interaction, the molecular fields, acting on the Gd and Mn ions, can be written as follows:

$$H_{ex,\,Gd} = \lambda_{Gd\text{-}Gd} M_{Gd} + \lambda_{Gd\text{-}Mn} M_{Mn1} + \lambda_{Gd\text{-}Mn} M_{Mn2}$$
$$H_{ex,\,Mni} = \lambda_{Gd\text{-}Mn} M_{Gd} + \lambda_{Mn\text{-}Mn} M_{Mnj} + \lambda_{Mn\text{-}Mn} M_{Mni}$$
$$(i = 1,\ 2;\ j = 2,\ 1) \qquad (1)$$

where $\lambda_{Gd\text{-}Gd}$, $\lambda_{Gd\text{-}Mn}$, $\lambda_{Mn\text{-}Mn}$ and $\lambda_{Mn\text{-}Mn}$ represent the coefficients of molecular field of Gd-Gd, Gd-Mn interlayer Mn-Mn and intralayer Mn-Mn exchange interactions. M_{Gd} and M_{Mn} are the thermal average of magnetization of Gd- and Mn-subsystem, respectively. $M_{Mn1} = M_{Mn2}$.

The Hamiltonians of Gd and Mn ions have the following form:

$$\hat{H}_{Gd} = g_J \mu_B \hat{J} \cdot (H_{ex,\,Gd} + H)$$
$$\hat{H}_{Mni} = g_s \mu_B \hat{S}_i \cdot (H_{ex,\,Mni} + H) \quad (i = 1,\ 2) \qquad (2)$$

where g_J, g_s represent the g-factor of Gd and Mn, $\hat{J}$ and $\hat{S}$ are the total angular momentum operator of Gd ion and the spin angular momentum operator of Mn ion. H is the magnetic field.

The free energy of system can be given as follows:

$$G = -k_B T \ln Z_{Gd} - k_B T \sum_i^{1,2} \ln Z_{Mni} + \frac{1}{2} M_{Gd} \cdot H_{ex,\,Gd} + \frac{1}{2} \sum_i^{1,2} M_{Mni} \cdot H_{ex,\,Mni} + \sum_i^{1,2} K \sin^2 \theta_i \qquad (3)$$

where k_B is Boltzman constant, K and θ_i are magnetic anisotropy constant of Mn ion and the angle between M_{Mni} and c-axis, respectively. Z_{Gd}, Z_{Mni} are partition functions of Gd and Mn ions:

$$Z_{Gd} = Tr(-\hat{H}_{Gd}/k_B T),$$
$$Z_{Mni} = Tr(-\hat{H}_{Mni}/k_B T) \quad (i = 1,\ 2)$$

From the stable equilibrium condition, we can get the magnitude of thermal average M_{Gd} and M_{Mni} as well as their directions respect to the c-axis, consequently, decide the magnetic structure and the temperature and field dependence of magnetization.

As above mentioned the interlayer Mn-Mn exchange coupling is very sensitive to the intralayer Mn-Mn dis-

tance. Brabers et al[12] studied the temperature dependence of interlayer Mn-Mn exchange interaction of compound YMn_2Ge_2 by using the high magnetic field measurement. Their studies indicate that the λ_{Mn-Mn} can be expressed as

$$\lambda_{Mn-Mn} = \alpha - \beta\omega(T) \quad (4)$$

where α is the λ_{Mn-Mn} value at $T = 0$ K and β is a parameter. $\omega(T)$ represents the departure with temperature of the unit-cell volume from the equilibrium value at $T = 0$ K. We suppose that the temperature and the lattice parameter dependence of λ_{Mn-Mn} in $GdMn_2Ge_2$ are the same as that in YMn_2Ge_2.

In our calculation, we use the values of Gd and Mn magnetic moment as equal to 7 μ_B and 1.8 μ_B at $T = 4.2$ K[13]. The other parameters are evaluated by fitting a series of experimental data of $GdMn_2Ge_2$ single crystal (the experimental data include the magnetic transition temperatures, magnetization curves along the crystallographic axes at different temperatures and temperature dependences of magnetization). They are as follows $\lambda_{Mn-Mn} = 245$ T/μ_Bf.u., $\lambda_{Mn-Mn} = 10.9$ T/μ_Bf.u., $\lambda_{Gd-Mn} = 8.4$ T/μ_Bf.u., $\lambda_{Gd-Gd} = 0.97$ T/μ_Bf.u. and $K = 6.4$ Tμ_B/Mn.

Fig. 4 shows the calculated magnetization curves at $T = 77$ K and 4.2 K with the magnetic field perpendicular to the c-axis and the corresponding experimental data

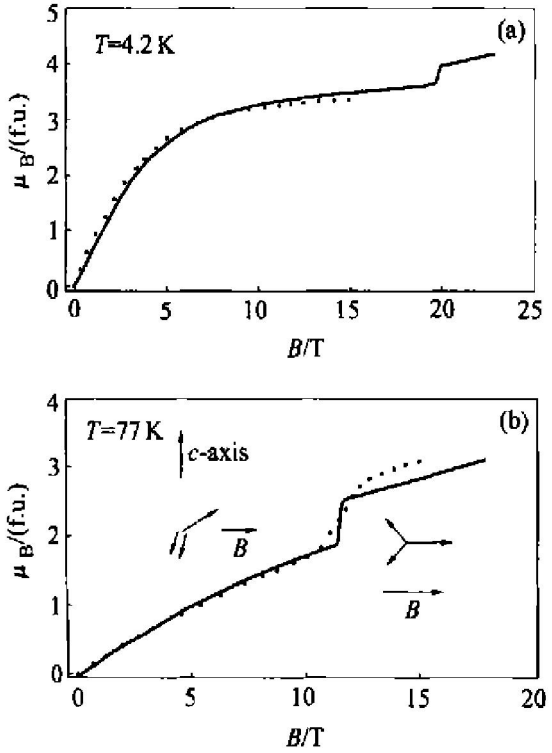

Fig. 4 Magnetic curves of $GdMn_2Ge_2$ single crystal for magnetic field perpendicular to c-axis at 4.2 K(a) and 77 K(b).
(Lines are calculated curves, points represent experimental data(taken from Ref. [10]))

(taken from Ref. [10]). It is obvious that a metamagnetic transition occurs in $GdMn_2Ge_2$ when field exceeds a critical value. In accordance with the magnetic studies[9, 10], when $T < T_t = 97$ K, $GdMn_2Ge_2$ is ferromagnet (Fi). Gd- and Mn-subsystem have collinear ferromagnetic structure and antiferromagnetically couple to each other, and the magnetizations of two subsystems are all along the c-axis. When $T > T_t$, the Gd-subsystem becomes magnetic disordered and the Mn-subsystem transforms into collinear antiferromagnetic state(AF), and its magnetic moments is directed to the c-axis. Our theoretical analysis and numerous calculation have shown that, when $T = 77$ K and $H \perp c$, under the action of magnetic field, the ferromagnetic structure Fi first deforms, but the Mn-subsystem keeps the ferromagnetic structure. As field increases up to a critical value, $GdMn_2Ge_2$ transforms from Fi into the non-collinear triangular magnetic structure T' with a first order magnetic transition; at the same time the magnetic moments of Gd abruptly turn to the magnetic field direction(as shown Fig. 4(b)). Theory predicts that this kind of field-induced first order transition also occurs at higher field when $T = 4.2$ K. The calculated field dependence of magnetization and the corresponding experimental curves(taken from Ref. [10]) of $GdMn_2Ge_2$ with field parallel to the c-axis at $T = 290$ K are presented in Fig. 5. When $T > T_t$, as above mentioned, the Mn-subsystem has collinear antiferromagnetic structure. Numerous calculation show that the external field induces the spin-flip transition in Mn-subsystem from antiferromagnetic to ferromagnetic state(Fig. 5); at the same time, the Gd-sublattice becomes ferromagnetic ordered due to the Gd-Mn exchange interaction. From Fig. 4 and Fig. 5, it can be seen that, by taking into account of lattice parameter

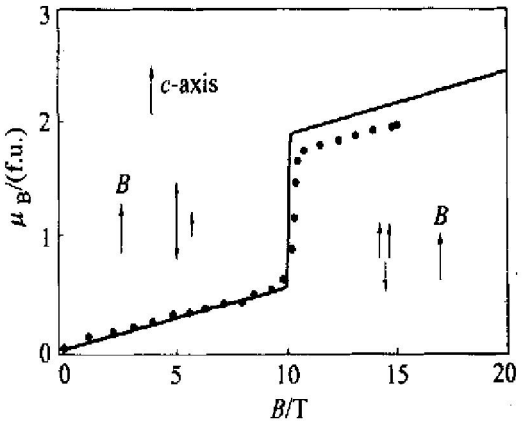

Fig. 5 Magnetic curves of $GdMn_2Ge_2$ single crystal for magnetic field parallel to c-axis at 290 K
(Lines are calculated curve, points represent experimental data (taken from Ref. [10]))

dependence and consequently the temperature dependence of interlayer Mn-Mn coupling, theoretical calculations well describe the magnetic curves at different temperature and the field-induced first order magnetic transition of $GdMn_2Ge_2$ single crystal.

4 CONCLUSIONS

The temperature dependence of the lattice parameters a and c of intermetallic compounds RMn_2Ge_2 (R= La, Sm and Gd) are measured by using the X-ray diffractometer. The study first shows that the high temperature magnetic transitions from the paramagnetic to antiferromagnetic state in Mn-subsystem in RMn_2Ge_2 with light rare earth elements accompany the negative magnetoelastic anomaly of lattice parameter c, where a does not change. This indicates that the antiferromagnetic component of intralayer Mn-Mn exchange coupling is correlated with c. The low temperature first order ferromagnetism $\rightarrow$ antiferromagnetism transition in Mn-sublattice accompanies the abruptly decrease (or increase) of lattice parameter a, confirming that interlayer Mn-Mn exchange interaction is very sensitive to a. The magnetization curves of $GdMn_2Ge_2$ single crystal in different temperatures with field parallel and perpendicular to the c-axis are calculated in the molecular field model of exchange interaction by taking into account of the temperature and lattice parameter dependence of interlayer Mn-Mn exchange coupling. Theoretical analysis and calculation show that, when $T < T_t$, $H \perp c$, the field-induced first order magnetic transition is the transition from ferromagnetic to non-collinear triangular magnetic structure. When $T > T_t$ and $H \parallel c$, the external magnetic field makes the Mn-subsystem transform from the antiferromagnetic to ferromagnetic state with a first order magnetic transition.

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