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LETTER TO THE EDITOR

Correlation between crystal structure and magnetic properties of $Gd_5(Si_xGe_{1-x})_4$ compounds

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Abstract. Based upon the reported crystal structure data of $Gd_5(Si_xGe_{1-x})_4$ compounds, a possible correlation between the crystal structure and magnetic properties of the compounds is explored. An almost linear dependence of the ferromagnetic ordering temperature on a M–M (M = Si, Ge or a mixture of Si and Ge) bond length is derived within a first approximation. It is argued that the mechanism of the ferromagnetic coupling in the Gd_5Si_4-based ($x > 0.5$) and Gd_5Ge_4-based ($x \leqslant 0.2$) solid solutions is the same as that in the intermediate phase $Gd_5(Si_xGe_{1-x})_4$ ($0.24 \leqslant x \leqslant 0.5$), i.e. the ferromagnetic Gd–(Gd, M)–Gd blocks couple with each other via an M_2 layer, regardless of their crystal structures at room temperature. The M–M bond length in the M_2 layer is a crucial structural parameter governing the ferromagnetic ordering temperature of the compounds. The orthorhombic structure of the intermediate phase at low temperature is stabilized by the ferromagnetic exchange interaction.

A milestone in developing an efficient, energy saving and environment friendly magnetic refrigeration technology is the recent discovery of a giant magnetocaloric effect (MCE) in $Gd_5(Si_xGe_{1-x})_4$ compounds ($x \leqslant 0.5$), which exhibit a MCE of 2–10 times larger than that of the best known magnetic refrigeration materials (e.g. Gd) [1]. Of particular interest for potential applications of the materials is that the temperature at which the giant MCE occurs can be tuned conveniently from ∼20 to ∼290 K by adjusting the Si:Ge ratio in $Gd_5(Si_xGe_{1-x})_4$ [2]. The occurrence of the giant magnetocaloric effect in $Gd_5(Si_xGe_{1-x})_4$ is associated with a first-order magnetic transition. For $0.24 \leqslant x \leqslant 0.5$, the magnetic transition is accompanied by a first-order structural transition from a monoclinic to an orthorhombic symmetry [3]. This first-order magnetic (structural) phase transition can be induced by an applied magnetic field, leading to a giant magnetoresistance (GMR) and a large magnetostriction effect [3, 4]. Therefore, the crystal structure couples strongly with the magnetic properties in $Gd_5(Si_xGe_{1-x})_4$. A first-order magnetic transition may originate from a strong dependence of the exchange interaction upon lattice parameter [5, 6]. Kittel showed that if one of the exchange constants goes linearly through zero near a critical value of some lattice coordinate, a first-order order–order magnetic transition may occur [5]. Bean *et al* proposed a linear dependence of the exchange interaction upon lattice volume for a first-order order–disorder magnetic transition [6]. Based on reported structural and magnetic properties of $Gd_5(Si_xGe_{1-x})_4$ compounds, a close correlation between crystal structure and the exchange interaction in $Gd_5(Si_xGe_{1-x})_4$ is worked out in this Letter. It turns out that a specific bond length of M–M (M = Si, Ge or a mixture of Si and Ge) seems to be a crucial structural parameter characterizing the ferromagnetic ordering temperature of the compounds, i.e. T_C varies almost linearly with the bond length. This finding should be of importance for an understanding of the magnetic properties, magnetic phase transition and

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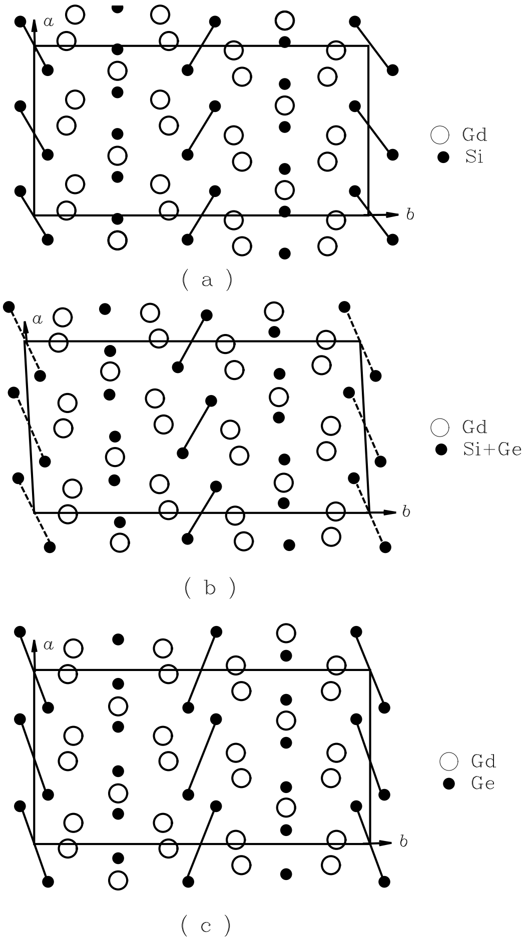

Figure 1. Projection of the crystal structure on *a*–*b* plane of (a) Gd_5Si_4, (b) $Gd_5Si_2Ge_2$, and (c) Gd_5Ge_4. The crystal structure data is taken from reference [9]. The unit cell is depicted by a solid frame. The M–M bond in the M_2 layer is linked by a solid line, and M′–M′ bond in M'_2 layer for $x = 0.5$ is linked by a dashed line.

structure–property relationship of $Gd_5(Si_xGe_{1-x})_4$ and may give a hint for optimizing the physical properties (e.g. MCE, GMR, etc) of the compounds.

The crystal structure and magnetic properties of the pseudobinary system Gd_5Si_4–Gd_5Ge_4 were studied 30 years ago [7, 8]. The phase relationship, crystallography and magnetic properties of this pseudobinary system were re-investigated recently by Pecharsky and Gschneidner [2, 9]. Both the end compounds, Gd_5Si_4 and Gd_5Ge_4, crystallize in the Sm_5Ge_4-type orthorhombic structure (Pnma) in which atomic layers can be regarded as stacking along the *b*-axis in a sequence . . . Ge, Sm, Ge–Sm, Sm, Ge, . . . (figure 1). The lattice parameters *b* and *c* of Gd_5Ge_4 are a little larger than those of Gd_5Si_4 because of the larger size of Ge than Si, whereas the lattice parameter *a* of Gd_5Ge_4 is significantly larger than that of Gd_5Si_4 [7, 9]. Such a lattice mismatch results in limited solubilities of Si in Gd_5Ge_4 ($x \leqslant 0.2$) and Ge in Gd_5Si_4 ($x > 0.5$) on the one hand, and a monoclinic distortion of the orthorhombic Sm_5Ge_4-type structure in the intermediate composition range ($0.24 \leqslant x \leqslant 0.5$) on the other hand.

The magnetic properties of $Gd_5(Si_xGe_{1-x})_4$ exhibit a strong dependence on the crystal structure [2, 9]. Gd_5Si_4 shows a second-order paramagnetic–ferromagnetic transition at $T_C \cong 335$ K, and T_C is gradually lowered by partial substitution of Ge for Si to $\sim$ 300 K at $x \approx 0.5$. However, Gd_5Ge_4 orders antiferromagnetically (or ferrimagnetically) at $T_N \cong 125$ K and undergoes a first-order antiferromagnetic (or ferrimagnetic)–ferromagnetic transition at $T_C \cong 20$ K. T_N of the Gd_5Ge_4-based solid solution increases slightly with the substitution of Si for Ge, while T_C increases rapidly. In the intermediate composition range of $0.24 \leqslant x \leqslant 0.5$, the monoclinic phase first undergoes a second-order paramagnetic–ferromagnetic (or ferrimagnetic) transition to a state with a low net magnetic moment and then a first-order ferromagnetic (ferrimagnetic)–ferromagnetic transition to a high net magnetic moment state upon further cooling, accompanied by a first-order structural transition from the monoclinic to the orthorhombic symmetry. At present, the existence of the high temperature magnetic transition seems still in debate and further investigation is necessary [3]. Nevertheless, $Gd_5(Si_xGe_{1-x})_4$ orders ferromagnetically at low temperature (below T_C) in the whole composition range ($0 \leqslant x \leqslant 1$).

It is well established that the saturation magnetization of $Gd_5(Si_xGe_{1-x})_4$ at low temperature is very close to the theoretical value contributed exclusively by the free trivalent Gd ions, which implies that the moments of Gd couple ferromagnetically in the compounds [7]. Refinement of crystal structure at room temperature reveals that the most prominent difference between Gd_5Si_4 and Gd_5Ge_4 is the large shifts of all atoms along just one of the crystallographic axes, *a*, leading to a large difference in lattice parameter *a* [9]. The largest change in the interatomic distances occurs between M–M (M = Si, Ge or a mixture of Si and Ge) in the M_2 layer separating the Gd–(Gd, M)–Gd blocks. The Si–Si (M = Si) distance in the Si_2 layer in Gd_5Si_4 is 2.47 Å and the Si–Si bond (linked by a solid line in figure 1(a)) can be considered as a covalent one (the typical covalent Si–Si bond length is ~2.34 Å [10]), while the corresponding Ge–Ge (M = Ge) distance in Gd_5Ge_4 is 3.59 Å and the covalency of the Ge–Ge bond (linked by a solid line in figure 1(c)) in the Ge_2 layer is therefore lost (the typical covalent Ge–Ge bond length is ~2.44 Å) [9]. Taking into account the saturation magnetization data of $Gd_5(Si_xGe_{1-x})_4$, one can conveniently view the magnetic structure of the compounds as an alternative stacking along the *b*-axis of ferromagnetic (FM) Gd–(Gd, M)–Gd blocks, in which all Gd ions couple ferromagnetically, and the M_2 layers. The FM blocks couple with each other ferromagnetically via the M_2 layer. In this case, the M–M bond length in the M_2 layer should play a crucial role in determining the strength of the magnetic coupling. The observed T_C for Gd_5Si_4 and Gd_5Ge_4 seems to coincide with this picture.

$Gd_5Si_2Ge_2$ is a prototype of the intermediate phase that crystallizes in a monoclinically distorted Sm_5Ge_4-type structure ($P2_1/a$). Crystal structure refinement reveals no signs of atomic ordering of Si and Ge in the monoclinic structure [9]. Since the lattice distortion essentially results from the large lattice mismatch along the *a*-axis of the parent compounds Gd_5Si_4 and Gd_5Ge_4, the structure of the monoclinic phase is in many ways intermediate (or transitional) between the two orthorhombic parents. In fact, the refinement of crystal structure shows that the atomic parameters in the monoclinic phase are intermediate between the corresponding parameters in the two orthorhombic parents. In particular, the M_2 layers in the orthorhombic structure are divided into two kinds of inequivalent layers: M_2- and M'_2-layers (M, M′ = mixture of Si and Ge), in the monoclinic structure. The M–M bond length is close to that in Gd_5Si_4 ($d_{M-M} = 2.68$ Å for $x = 0.5$), while the M′–M′ bond length is close to that in Gd_5Ge_4 ($d_{M'-M'} = 3.40$ Å for $x = 0.5$). The M_2- and M'_2-layers separate the FM blocks alternatively along the *b*-axis (figure 1(b)). Therefore, the monoclinic phase retains the structural characters of both the orthorhombic parents, and it is reasonable to anticipate a complex magnetic ordering process in the monoclinic phase. Taking into account the magnetic ordering behaviours in the parent compounds, an occurrence of two successive magnetic phase transitions in the monoclinic phase is plausible: the second-order transition at high temperature can be associated with a transition to a weak ferromagnetic or ferrimagnetic state due to the coexistence of the short M–M bonds and the long M′–M′ bonds, while the first-order transition at lower temperature can be associated with a transition from the weak ferromagnetic or ferrimagnetic state to the fully saturated ferromagnetic state. Once the long-range ferromagnetic coupling sets in the energy of the system is lowered by the exchange interaction. If the exchange energy can compensate for the elastic energy due to the lattice mismatch in the intermediate compounds $Gd_5(Si_xGe_{1-x})_4$ ($0.24 \leqslant x \leqslant 0.5$), the M′–M′ bonds have to shrink to the value of the M–M bonds and an orthorhombic structure can be stabilized, leading to substantial contractions of the *a*-axis and the unit-cell volume as well as a first-order structural transition [3].

Both the lattice parameters and magnetic transition temperature of $Gd_5(Si_xGe_{1-x})_4$ exhibit abnormalities at the phase boundaries, i.e. at $x \approx 0.2$ and $x = 0.5$ if the very narrow two-phase range between 0.2 and 0.24 is neglected (figure 2(a)) [9]. The abnormalities at $x = 0.5$ are most prominent. The fact that the fully saturated ferromagnetic state of the compounds occurs exclusively in the orthorhombic structure makes it possible to establish a close correlation between structural parameters and the ferromagnetic transition temperature. Figures 2(b) and (c) show the dependence of T_c of the fully saturated ferromagnetic state upon *a*, which subjects the largest variation from $x = 0$ to $x = 1.0$, and the unit-cell volume. However, prominent

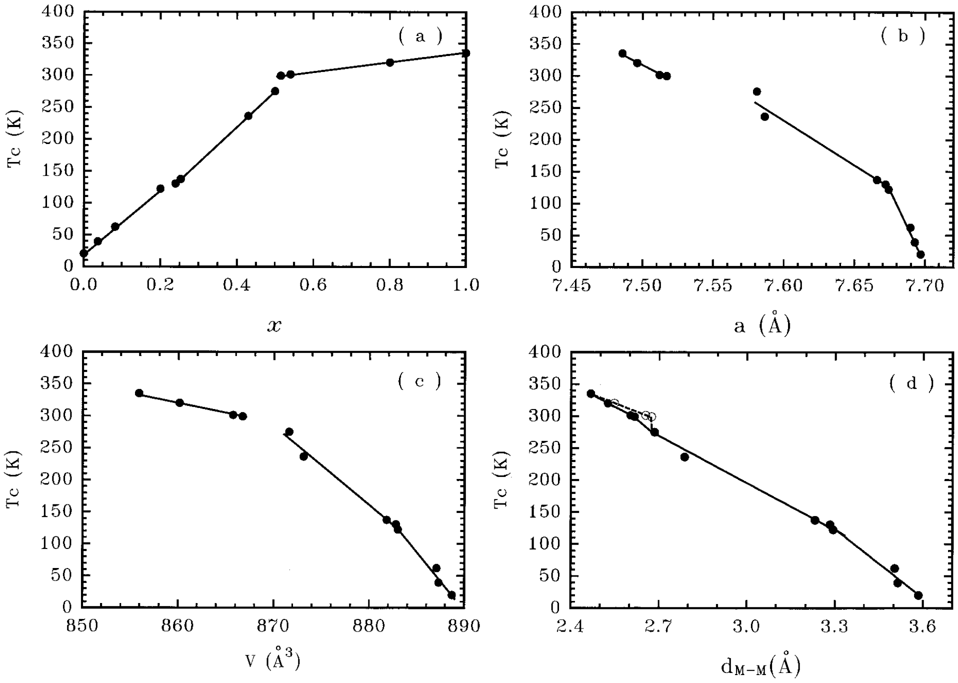

Figure 2. Dependence of ferromagnetic ordering temperature of $Gd_5(Si_xGe_{1-x})_4$ on (a) Si content x, (b) lattice parameter a, (c) unit-cell volume V and (d) the M–M bond length d_{M-M}, in which d_{M-M} is derived by approach I (solid line) and approach II (dashed line, see text), respectively. Symbols are experimental data from reference [9]. In (a)–(c) the lines are guides to the eye, and in (d) the open circle represents a relation between T_C and d_{M-M} estimated by approach II.

abnormalities remain at the phase boundaries. Within the framework of the molecular field theory of ferromagnetism, the magnetic ordering temperature is proportional to the molecular field coefficient λ, which is again proportional to the exchange integral A. As discussed above, the ferromagnetic structure of $Gd_5(Si_xGe_{1-x})_4$ can be viewed as consisting of the FM Gd–(Gd, M)–Gd blocks coupling ferromagnetically via the M_2 layer in the orthorhombic phase. It is reasonable to assume that the coupling constant (or exchange integral) A is closely related to the M–M bond length in the M_2 layer. Temperature dependent x-ray diffraction reveals that the lattice constants of the orthorhombic phase do not decrease much as temperature decreases [3]. So it seems that the occurrence of the FM state at low temperature in Gd_5Ge_4 solid solution is not due to a significant shortening of the M–M bond length. Considering the simultaneous occurrence of the magnetic and structural phase transitions as well as the shrinking of the M′–M′ bond length at the transitions in $Gd_5(Si_xGe_{1-x})_4$ for $0.24 \leqslant x \leqslant 0.5$, one can associate the ferromagnetic ordering temperature with the M–M bond length in the M_2 layer at room temperature, assuming that the M–M bond length does not undergo a significant change at the transition and attributing the bulk of the discontinuous change of the lattice parameters to the shrinking of the longer M′–M′ bond length to accommodate itself to the ferromagnetic orthorhombic structure. In the orthorhombic structure M and M′ become equivalent.

As reported in [9] T_C and the unit-cell volume V exhibit very similar variations to the composition in $Gd_5(Si_xGe_{1-x})_4$, while other lattice parameters a, b and c do not. Provided that there exists a correlation between T_C and the M–M bond length d_{M-M}, it is reasonable to expect a simple correlation between d_{M-M} and the unit-cell volume V within a first approximation. From the reported refinement results of crystal structure at room temperature [9], one can easily calculate the M–M bond length in the M_2 layer: $d_{M-M} = 3.59$, 2.68 and 2.47 Å for $x = 0$, 0.5 and 1.0, respectively. To estimate d_{M-M} for the whole composition range, two approaches can be proposed. The first one (approach I) assumes a linear relation between d_{M-M} and V and interpolates d_{M-M} in $0 \leqslant x \leqslant 0.5$ and $0.5 \leqslant x \leqslant 1.0$ regions separately, taking the experimental value (871.6 Å^3) as the unit-cell volume of $Gd_5Si_2Ge_2$. The volume dependence of d_{M-M} is shown in figure 3 as a solid line. Another approach (II) differs from the approach I in that an extrapolated unit-cell volume (866.8 Å^3) of the Gd_5Si_4-based solid solution is taken as the unit-cell volume of $Gd_5Si_2Ge_2$ for interpolating the d_{M-M} between $x = 0.5$ and 1.0, while the experimental unit-cell volume of $Gd_5Si_2Ge_2$ is used for the interpolation between $x = 0$ and 0.5. The result is shown in figure 3 as a dashed line. However, both approaches adopt the experimental d_{M-M} (= 2.68 Å) at $x = 0.5$, which is the shortest M–M bond length of the monoclinic $Gd_5Si_2Ge_2$ at room temperature. In addition, a possible abnormality at the phase boundary at $x \approx 0.2$ is ignored in the estimation, because of the lack of the crystal structure data for the compounds nearby the phase boundary. Since both T_C and V exhibit a very small abnormality at the phase boundary at $x \approx 0.2$ (figure 2 and [9]), such an approximation is reasonable.

The dependence of T_C on the estimated d_{M-M} is shown in figure 2(d). In contrast to the dependence of T_C on x, a or V (figure 2(a)–(c)), the abnormalities at the phase boundaries are substantially reduced on the T_C versus d_{M-M} plot and T_C decreases with d_{M-M} almost linearly if d_{M-M} is estimated by approach I. Taking into account the approximations used in interpolating d_{M-M} and possible experimental errors in determining the structural parameters and transition temperature, a linear correlation between T_C and d_{M-M} can be reasonably assumed. When d_{M-M} is estimated by approach II, however, T_C exhibits a prominent abnormality at $d_{M-M} = 2.68$ Å corresponding to $x = 0.5$. Approach I implies that d_{M-M} undergoes a discontinuous increase at the phase boundary at $x = 0.5$ when the orthorhombic phase transfers to the monoclinic phase, while the expansion of the unit-cell volume is mainly due to the formation of the longer M′–M′ bond in the monoclinic structure. In contrast,

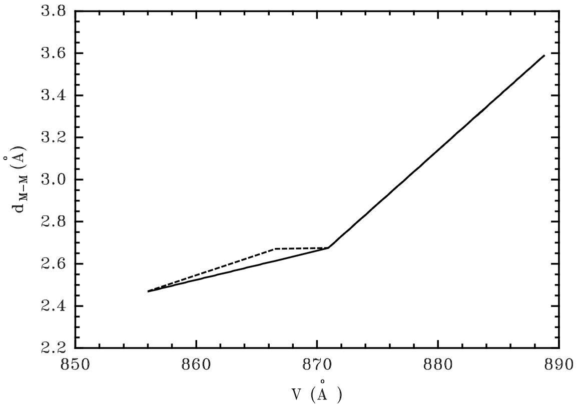

Figure 3. Dependence of the M–M bond length in the M_2 layer in $Gd_5(Si_xGe_{1-x})_4$ ($x = 0$–1.0) at room temperature on the unit-cell volume. Solid line is derived by approach I and dashed line by approach II (see text).

approach II means that d_{M-M} does not change at the phase boundary and the expansion of the unit-cell volume results exclusively from the formation of the M′–M′ bond in the monoclinic phase (figure 3). Since the discontinuous change in d_{M-M} at the phase boundaries coincides with the character of a first-order phase transition, approach I seems more acceptable than approach II and the accordingly derived correlation between T_C and d_{M-M} is likely to exist. Figure 3 shows that d_{M-M} increases rapidly with the unit-cell volume in the monoclinic phase and the Gd_5Ge_4-based solid solution. Since the M′–M′ bond length ($d_{M'-M'} = 3.40$ Å for $x = 0.5$) is close to that of Gd_5Ge_4 ($d_{Ge-Ge} = 3.59$ Å), it is expected that the difference between d_{M-M} and $d_{M'-M'}$ in the monoclinic phase decreases as the Ge content (or the unit-cell volume) increases, which gives rise to a smaller change in the lattice parameters at the phase boundary at $x \approx 0.2$ than that at $x = 0.5$, as reported in [9].

In summary, a close correlation between the crystal structure and magnetic properties of $Gd_5(Si_xGe_{1-x})_4$ compounds is discussed. Within a first approximation, an almost linear dependence of the ferromagnetic ordering temperature T_C on the M–M bond length in the M_2 layer, d_{M-M}, is established. Based upon this result, the ferromagnetic structure can be viewed as a layered structure along the *b*-axis in which the FM Gd–(Gd, M)–Gd blocks couple with each other via the M_2 layers in the orthorhombic phase. However, it is argued that the covalency of the M–M bond in the M_2 layer is not a prerequisite for the occurrence of the fully saturated ferromagnetic state, instead the strength of the coupling, equivalently the ferromagnetic ordering temperature, depends on the length of the M–M bond in the M_2 layer, d_{M-M}, regardless of the crystal structure of the compounds at room temperature. Therefore, the M–M bond length in the M_2 layer is a crucial structural parameter governing the magnetic interaction in $Gd_5(Si_xGe_{1-x})_4$ compounds. In the intermediate composition range ($0.24 \leqslant x \leqslant 0.5$), the orthorhombic structure is stabilized at low temperature when the exchange energy compensates for the elastic energy due to the lattice mismatch of the parent compounds, leading to a simultaneous occurrence of the first-order magnetic and structural phase transitions.

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