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Magnetic Properties of Ternary $DyMn_2X_2$ Compounds (X = Si and Ge)*

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Synopsis

Magnetic properties of $DyMn_2Si_2$, $DyMn_2Ge_2$ and their mixed compounds $DyMn_2(Si_{1-x}Ge_x)_2$, which display a variety of interesting magnetic behaviors originating in competing magnetic interactions and anisotropy, have been investigated systematically by magnetization mesurements, ^{161}Dy Mössbauer spectroscopy and neutron diffraction experiments. This report presents a review of the results mainly obtained by the magnetization measurements.

I. Introduction

Intermetallic compounds RT_2X_2 (R = a rare earth or Y, T = a transition metal and X = Si or Ge) have attracted a lot of interest because of a variety of magnetic properties and other related effects, e.g., heavy fermion, superconductivity, valence fluctuations and the Kondo effect. As shown in Fig.1, the compounds crystallize in a simple body-centered tetragonal $ThCr_2Si_2$-type structure with space group $I4/mmm(D_{4h}^{17})$, where the R, T and X atoms occupy the $2a$, $4d$ and $4c$ crystallographic sites, respectively. This structure can be described as a stacking of atomic layers along the c-axis with a $-T-X-R-X-T-$ sequence.

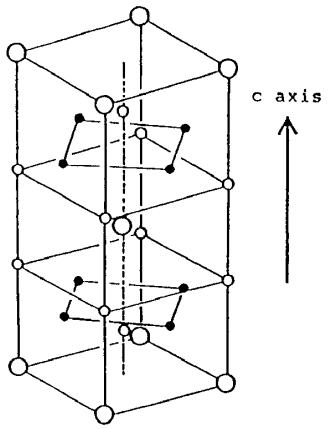

Fig.1 Crystal structure of $DyMn_2X_2$.

Only Mn atoms among the transition metals carry localized magnetic moments in this series of compounds, and exhibit magnetic ordering at relatively high temperatures above room temperature[1-3]. The Mn moments parallel to the c-axis couple ferromagnetically in the c-plane, and antiferromagnetically or ferromagnetically between the successive Mn planes. The R moments start to order at low tempeartures

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in an antiferromagnetic Mn sublattice. Magnetic interactions compete between R–Mn and Mn–Mn along te c-axis in the heavy rare earth–Mn compounds[1,3–5], since both of them are antiferromagnetic. Therefore, one can expect the interesting variety of their magnetic behaviors.

The present report provides a review of the results obtained by magnetometric experiments on $DyMn_2Si_2$, $DyMn_2Ge_2$ and $DyMn_2(Si_{1-x}Ge_x)_2$. These works have been done as a part of systematic investigation including ^{161}Dy Mössbauer spectroscopy and neutron diffraction measurements which have been reported in the references 5–10.

II. Experimental

Starting from Dy and Mn metals of 99.9%, and Si and Ge of 99.999% in purity, the sample compounds were synthesized by a conventional argon arc technique. For insuring homogeneity, each ingot was turned over and remelted several times, followed by annealing at 850–1200°C for 4–7 days. The $ThCr_2Si_2$-type structure of each sample was confirmed by powder X-ray diffraction measurement using Fe Kα radiation. Most of the compounds were used in a form of powdered sample. A single-crystalline sample was obtained only for $DyMn_2Ge_2$.

The magnetization was measured as a function of temperature and magnetic field using a vibrating-sample magnetometer. The temperature dependence of magnetization was measured in the range between 4.2 and 830 K. The magnetic fields were below 20 kOe to observe the magnetic transitions and the paramagnetic susceptibility, and up to 150 kOe to measure magnetization processes. The high magnetic fields were produced using a Bitter-type magnet at the High Field Laboratory for Superconducting Materials (HFLSM) at Tohoku University. In the high-field magnetization measurements, the powdered sample was sealed in a polytetrafluoroethylene (Teflon) capsule with helium gas and BN powders, and then the sample powder particles got a good homogeneous temperature and were free to rotate in the magnetic field.

III. Results

Based on the results of low-field magnetization measurements on $DyMn_2(Si_{1-x}Ge_x)_2$, a magnetic phase diagram in respect to the temperature and the concentration is drawn up as shown in Fig.1[8], where eight phases are distinguished as indicated by I–VIII. As is clear in the figure, remarkable features have been found in the concentration dependence of magnetic phase. Four low-temperature phases III, VI, VII and VIII in $DyMn_2Si_2$ have never appeared in the compounds of $x \geq 0.1$. The phase II which has appeared only in the mixed compounds differs in the magnetic structure from both of the phasee I and III

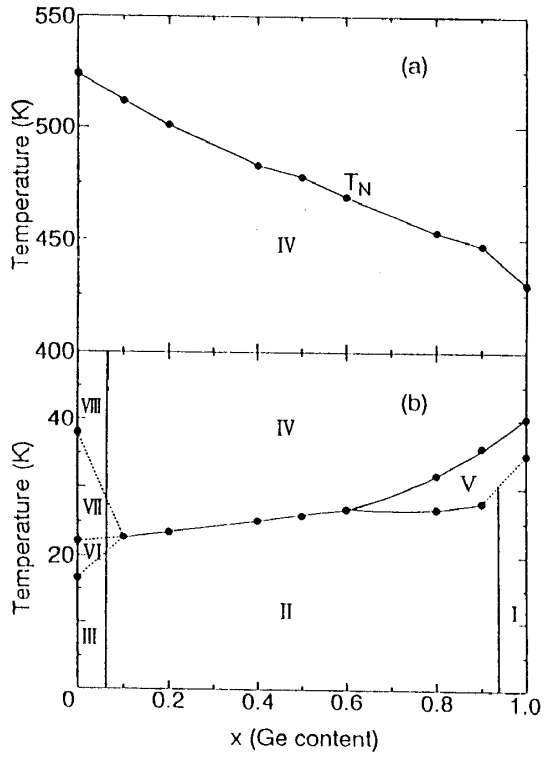

Fig.2 Magnetic $x - T$ phase diagram of $DyMn_2(Si_{1-x}Ge_x)_2$ at (a) high temperatures and (b) low tempeartures[8].

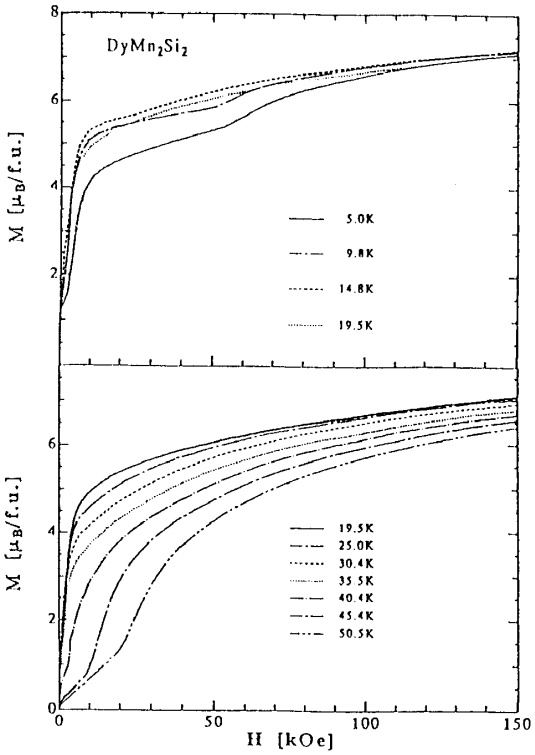

Fig.4 Magnetization curves of $DyMn_2Si_2$ whose powder particles are free to rotate under high magnetic fields up to 150 kOe[8].

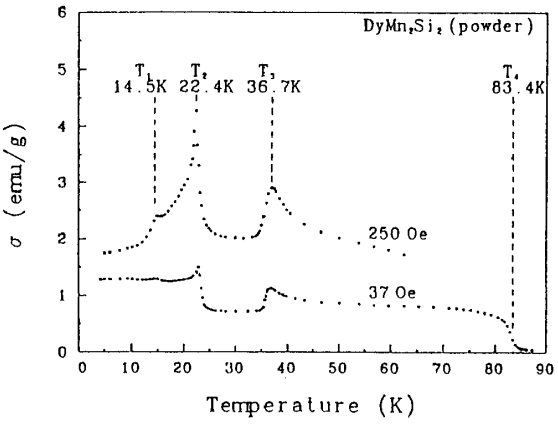

Fig.3 Temperature dependences of the magnetization for the powdered $DyMn_2Si_2$ sample under weak magnetic fields[7].

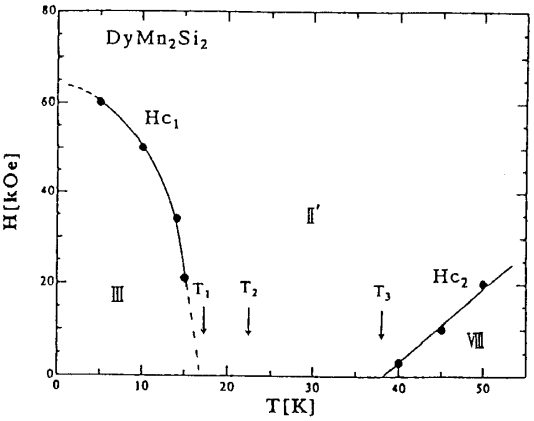

Fig.5 Magnetic $H-T$ phase diagram of $DyMn_2Si_2$[8]. The critical fields were determined from the magnetization curves in Fig.3.

appeared in $DyMn_2Si_2$ and $DyMn_2Ge_2$, respectively. The high-temperature phase IV has the well-known antiferromagnetic structure on the Mn sublattice, where the Mn moments along the c-axis couple ferromagnetically in the c-plane and the adjacent Mn layers couple antiferromagnetically with each other.

Fig.3 shows the temperature dependences of magnetization for $DyMn_2Si_2$ measured under weak magnetic fields of 37 and 250 kOe. it is clearly observed that there are three distinct peaks at 14.5, 22.4 and 36.7 K and a rapid decrease something like a ferromagnetic-paramagnetic transition at 83.4 K. These anomalies are very sensitive to the magnitude of applied field, and then the M-T curves obtained in fields of near 10 kOe appear to be very similar to that reported by Szyutuła and Szott[3] which has been interpreted as a ferrimagnet below 55 K. Fig.4 shows the high-field magnetization curves of $DyMn_2Si_2$ at various temperatures. Two kinds of field-induced transitions are observed below 14.8 K and above 40.4 K. The magnetic H-T phase diagram is obtained by plotting these critical fields as shown in Fig.5.

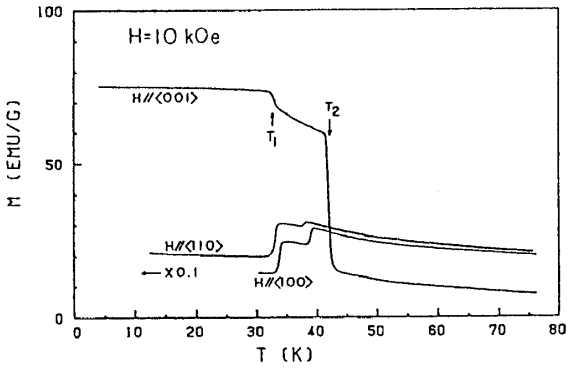

Fig.6 Temperature dependences of the magnetization for the single-crystalline $DyMn_2Ge_2$[6].

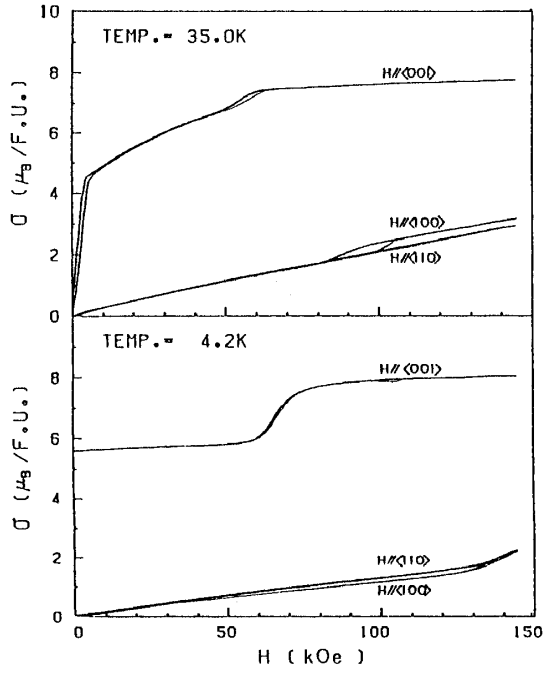

Fig.7 Magnetization curves along the three direction of the single-crystalline $DyMn_2Ge_2$[6].

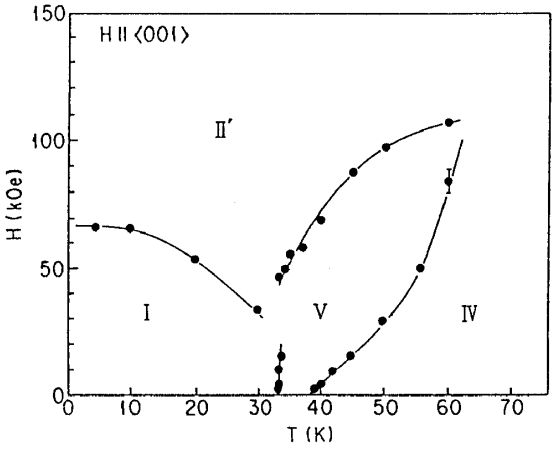

Fig.8 Magnetic $H-T$ phase diagram of $DyMn_2Ge_2$[6]. The critical fields were determined by the magnetization curves along the c-axis.

In $DyMn_2Ge_2$, two magnetic transitions at 33.0 and 37.5 K are observed accompanied with the magnetic ordering of Dy moments as shown in Fig.6. These transitions seem to be of first order. Fig.7 shows the high-field magnetization curves at 4.2 and 35.0 K which are in the region of the phases I and V, respectively. The field-induced magnetic transitions are observed at temperatures below 65 K, and the magnetic H-T phase diagram are determined from the critical fields as shown in Fig.8.

Fig.9 shows the high-field magnetization curves of all the compounds at 5 K. These were obtained using the powdered samples whose particles were free to rotate in the applied field. The field-induced magnetic transitions occur in $DyMn_2Si_2$ and $DyMn_2Ge_2$ as mentioned above, while the compounds with $0.1 \leq x \leq 0.9$ exhibit a similar behavior without any magnetic transition.

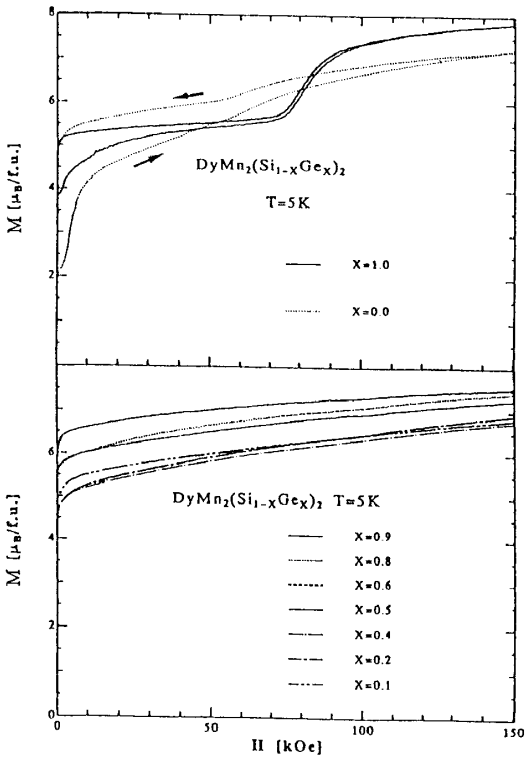

Fig.9 Magnetization curves of $DyMn_2(Si_{1-x}Ge_x)_2$ at 5 K[8]. The sample powder particles were free to rotate under the magnetic fields.

IV. Discussion

In the RMn_2Ge_2 compounds, it is known that the magnetic transition temperature $T_N(T_C)$ of the Mn sublattice decreases as the nearest Mn-Mn intralayer distance $R^a_{Mn-Mn}(= a/\sqrt{2})$ increases[11]. This dependency holds in $DyMn_2(Si_{1-x}Ge_x)_2$, that is, the lattice parameters increase monotonously from $a = 3.902$ Å and $c = 10.41$ Å at $x = 0$ to $a = 3.974$ Å and $c = 10.79$ Å at $x = 1$, and then the Néel temperature T_N decreases monotonously from 523 K to 430 K as x increases.

$DyMn_2Si_2$ exhibits the intricated magnetic transitions accompanied with the magnetic ordering of Dy moments. If one applies the de Gennes rule for RMn_2Si_2, the ordring temperature T_M of Dy is estimated to be 26 or 29 K from $T_M = 60$ K or 65 K of $GdMn_2Si_2$[2,12], and 44 K from $T_M = 65$ K of $TbMn_2Si_2$[13]. In the other RT_2Si_2 compounds, the T_M values of Dy are 0.44–0.56 of that for

Tb. The factors are 0.40–0.73 in the Ge compounds. Applying these factors for RMn$_2$Si$_2$, the T_M value is estimated to be 26–47 K in DyMn$_2$Si$_2$. Consequently, it is natural to suppose that a long-range magnetic order of Dy moments occurs at 36.7 K. This discussion makes us to presume that the phase VIII may have a short-range magnetic order of Dy moments. The ^{161}Dy Mössbauer spectra of DyMn$_2$Si$_2$ consist of a static subspectrum and a relaxational one below 22.4 K[7]. This result has indicated that the magnetic phases III and VI are canted-ferrimagnetic structures of long periods, where a considerable amount of Dy ions surrounded by canted Mn moments with a mismatched arrangements show a small magnetic hyperfine field due to the Dy-Mn magnetic interactions frustrating easy magnetizatin directions of Dy moments. The fact that the analyses of the Mössbauer spectra in the phase VII require three subspectra with small hyperfine fields compared with that of a free Dy^{3+} ion has suggested that there is no Dy ions accepting the strong molecular field from the neighboring Mn moments, that is, the Mn moments have an essentially antiferromagnetic arrangement. It is supposed that the long-periodic arrangement of Dy moments has a ferromagnetic component of magnetization, since Fig.5 indicates that the magnetic structure of the phase VII transforms under a very low field into the canted-ferrimagnetic phase II' (vide infra).

In DyMn$_2$Ge$_2$, the spontaneous magnetization is 5.6 μ_B/f.u. at 4.2 K as shown in Fig.7. This value is easily obtained by postulating a collinear ferrimagnetic structure where Dy moment of 10 μ_B and Mn moment of 2.2 μ_B couple antiferromagnetically along the c-axis. This structure and the magnitudes of moments have been confirmed by the neutron diffraction[6] and Mössbauer spectroscopy[5]. The high-field magnetic phase II' having 7.6 μ_B/f.u. is a canted-ferrimagnetic structure in which the Mn moments tilt about 57° from the c-axis. In the phase V, the Mössbauer studies[5,9,10] have revealed that there exist two kind of Dy ions with different magnetic states, i.e., the one is the same with the Dy magnetic state in the collinear-ferrimagnetic structure appeared in the phase I and the otheris the same with the paramagnetic state of Dy ions surrounded by the antiferromagnetically ordered Mn moments in the phase IV. Therefore, each local structure around Dy moment can be easily supposed, that is, the neighbor Mn moments are collinear-ferromagnetic in the former and collinear-antiferromagnetic in the latter. The ratio of two magnetic states is about 1:2. Consequently, the simplest and most probable long-periodic magnetic structure in the phase V is proposed to be the one shown in the Fig.10, where the Mn-moment layers stack with a $++-++-$ sequence along the c-axis. The Dy ion sandwiched in between two + layers aligns in antiparallel with the Mn moments and has a full moment (10 μ_B), and the Dy ion sandwiched in between + and − layers behaves as a paramagnetic state

The results as shown in Fig.9 imply that the phase II of $0.1 \leq x \leq 0.9$ differs from both the phase I of $x = 1$ and the phase III of $x = 0$. Therefore, it is

concluded that the phase boundaries exist around the x contents shown by the dotted lines in Fig.2. The magnetization of the compounds with large x is nearly equal to that of the high-field phase of $x = 1$; the saturation value decreases gradually and closes to the value of high-field phase of $x = 0$ as x decreases. It is considered that the magnetic structures of the phase II and the high-field phase II' in $DyMn_2Si_2$ are the canted-ferrimagnetic structure. Assuming that $\mu_{Dy} = 10$ μ_B and $\mu_{Mn} = 2$ μ_B in the compound with $x = 0.9$, the canting angle of Mn moments is estimated to be 53° from the c-axis using a spontaneous magnetization of 6.8 μ_B, which is obtained by extrapolation from the high-field magnetization curve. By the estimation of magnitude of transferred hyperfine field from the neighboring Mn moments, the Mössbauer study[9,10] has indicated that the canting angle is about 60°.

V. Summary

The present report has revealed that there are eight magnetically ordered phases, of which seven phases appear in $DyMn_2Si_2$ and/or $DyMn_2Ge_2$. It has been found that the phases appeared in $DyMn_2Si_2$ and $DyMn_2Ge_2$ except the phases IV and V do not exist in the mixed compounds. This fact implies that the magnetic ordering in these compounds develops on delicate balances of competing magnetic interactions and anisotropies. Fig.10 shows the schematic magnetic structures which have been confirmed by the studies done hitherto. The magnetic structures III, VI and VII in $DyMn_2Si_2$ have not yet determined in detail. By the powder neutron dffraction on $DyMn_2Si_2$, some magnetic reflections indicating long-periodic magnetic structures which have been predicted by the ^{161}Dy Mössbauer study have been found in each magnetic phase, although they are not indexed perfectly in the present stage.

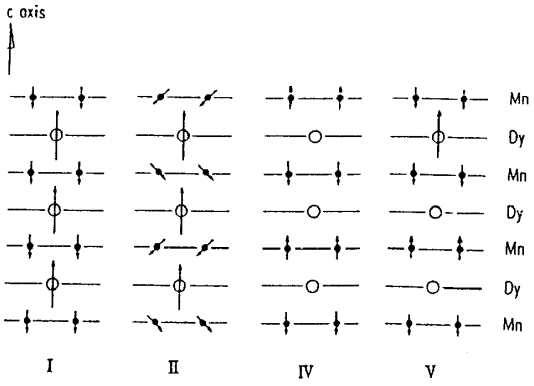

Fig.10 Scheme of magnetic structures $DyMn_2(Si_{1-x}Ge_x)_2$[10]. The magnetic structures in $DyMn_2Si_2$ are unknown in detail.

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