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R. Nirmala, V. Sankaranarayanan, K. Sethupathi, A. V. Morozkin, Q. Cai, Z. Chu, J. B. Yang, W. B. Yelon, and S. K. Malik

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# Magnetization and neutron diffraction studies on $Dy_5Si_2Ge_2$

R. Nirmala
*Tata Institute of Fundamental Research, Mumbai 400 005, India*

V. Sankaranarayanan and K. Sethupathi
*Department of Physics, Indian Institute of Technology Madras, Chennai 600 036, India*

A. V. Morozkin
*Department of Chemistry, Moscow Lomonosov State University, GSP-3, Moscow, 119899, Russia*

Q. Cai and Z. Chu
*Department of Physics, University of Missouri-Columbia, Columbia, Missouri 65211*

J. B. Yang
*Department of Physics, University of Missouri-Columbia, Columbia, Missouri 65211 and Graduate Center for Materials Research and Departments of Physics and Chemistry, University of Missouri-Rolla, Rolla, Missouri 65409*

W. B. Yelon
*Graduate Center for Materials Research and Departments of Physics and Chemistry, University of Missouri-Rolla, Rolla, Missouri 65409*

S. K. Malik[a)]
*Tata Institute of Fundamental Research, Mumbai 400 005, India*

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The compound $Dy_5Si_2Ge_2$ crystallizes in an orthorhombic structure ($Sm_5Ge_4$ type, space group *Pnma*). Magnetization measurements performed in the temperature range of 2–300 K in applied fields up to 7 T reveal that this compound orders antiferromagnetically at 56 K ($T_N$) but with a positive paramagnetic Curie temperature $\theta_P$. Magnetization-field isotherms, obtained at 5 K and 20 K, display a field-induced antiferromagnetic to ferromagnetic transition. The magnetization approaches saturation in a field of 6 T with a moment value of $\sim 8\mu_B/Dy^{3+}$. Neutron diffraction measurements, carried out at 9.2 K, suggest that Dy moments arrange spirally along the *a* axis giving rise to a canted antiferromagnetic structure. The analysis of neutron diffraction data yields an ordered state magnetic moment of $7.63\mu_B$ per $Dy^{3+}$ ion. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1855646]

## I. INTRODUCTION

The $R_5(Si_xGe_{1-x})_4$-type ($R$=Rare earth) compounds have been the subject of intense research over the last few years because of their interesting magnetic and structural phase diagram.[1] It has been now established that the first-order magnetic phase transition, associated with a concomitant structural change, occurs in some members of this series, giving rise to a giant magnetocaloric effect near the ferromagnetic ordering temperature.[2] It is of considerable importance to identify new members of this series for magnetic refrigeration applications as well as to understand their intricate magnetic properties. In this context, neutron diffraction studies on $R_5(Si_xGe_{1-x})_4$-type compounds are of topical interest. Recently, magnetic structure of several $R_5X_4$ ($X$=Si, Ge) compounds has been reported. In $Pr_5Ge_4$, Pr moments at two different crystallographic sites have been found to order magnetically at two different temperatures[3] and a strong coupling between crystal and magnetic lattice in $Tb_5(Si_xGe_{1-x})_4$ compounds has been observed.[4] High-resolution neutron diffraction measurements on $Nd_5X_4$ ($X$=Si, Ge) compounds reveal a net canted antiferromagnetic structure of Nd moments.[5] In this work, we elucidate the complex magnetic properties of $Dy_5(Si_xGe_{1-x})_4$ ($x$=0.5) compound by means of magnetization and neutron diffraction measurements.

## II. EXPERIMENTAL DETAILS

A polycrystalline sample of $Dy_5Si_2Ge_2$ was prepared by arc melting of constituent elements (Dy–99.9% pure, Si, Ge–99.999% pure) in argon atmosphere. X-ray diffraction data were obtained at room temperature (DRON-3.0 diffractometer, Cu K$\alpha$ radiation, $2\theta$=20°–70°). Magnetization measurements were carried out in the temperature range of 2–300 K using a superconducting quantum interference device (SQUID) magnetometer (MPMS XL, Quantum design) in applied fields up to 7 T. Neutron diffraction measurements, at 300 K and at 9.2 K, were carried out using the high resolution diffractometer at the University of Missouri Research Reactor (Columbia, MO, USA) on a ~1 g of finely ground sample placed in a thin-walled vanadium container.[6] The incident neutron wavelength was 0.14875 nm. The neutron diffraction patterns were analyzed using the Rietveld program, FULLPROF.

[a)]Author to whom correspondence should be addressed; Electronic mail: skm@tifr.res.in

 

TABLE I. Cell parameters $(a,b,c)$ and atomic position parameters $(x,y,z)$ of $Sm_5Ge_4$-type $Dy_5Si_2Ge_2$ compound (space group Pnma, No. 62).

| Atom | Type position | $x$ | $y$ | $z$ |
|---|---|---|---|---|
| (a) At 300 K [$a$=0.7527(2) nm, $b$=1.4574(3) nm, $c$=0.7628(2) nm, $R_F$=9.0%] | | | | |
| Dy1 | 4($c$) | 0.291(2) | 1/4 | 0.000(2) |
| Dy2 | 8($d$) | 0.1240(9) | 0.1206(5) | 0.334(1) |
| Dy3 | 8($d$) | 0.9762(9) | 0.1004(4) | 0.824(1) |
| (Si,Ge)1 | 4($c$) | 0.928(4) | 1/4 | 0.126(3) |
| (Si,Ge)2 | 4($c$) | 0.165(3) | 1/4 | 0.634(4) |
| (Si,Ge)3 | 8($d$) | 0.208(3) | 0.953(1) | 0.539(2) |
| (b) At 9.2 K [$a$=0.7504(1) nm, $b$=1.4559(1) nm, $c$=0.7610(2) nm, $R_F$=5.7%] | | | | |
| Dy1 | 4($c$) | 0.301(2) | 1/4 | 0.001(2) |
| Dy2 | 8($d$) | 0.124(1) | 0.1193(4) | 0.3405(9) |
| Dy3 | 8($d$) | 0.975(1) | 0.1031(4) | 0.8211(9) |
| (Si,Ge)1 | 4($c$) | 0.9229(4) | 1/4 | 0.114(3) |
| (Si,Ge)2 | 4($c$) | 0.175(3) | 1/4 | 0.652(4) |
| (Si,Ge)3 | 8($d$) | 0.217(3) | 0.953(1) | 0.528(3) |

## III. RESULTS AND DISCUSSION

The room temperature x-ray diffraction and neutron diffraction patterns confirm the structure of the $Dy_5Si_2Ge_2$ compound to be orthorhombic, $Sm_5Ge_4$ type (space group *Pnma*, No. 62). The Dy atoms occupy three distinct sites (Dy1 in 4$c$ site, Dy2 and Dy3 in two different 8$d$ sites) and Si and Ge atoms statistically occupy three sites (two 4$c$ sites and one 8$d$ site) (Table I).

Magnetization data on $Dy_5Si_2Ge_2$, obtained in an applied field of 0.5 T, in the temperature range of 2–300 K indicate an antiferromagneticlike peak at 56 K (Fig. 1). The paramagnetic susceptibility follows Curie–Weiss law. The effective paramagnetic moment is found to be $10.54\mu_B/Dy^{3+}$ which is close to the $Dy^{3+}$ free ion value of $10.63\mu_B$. However, the paramagnetic Curie temperature $\theta_P$ is found to be positive ($\theta_P$=38 K) which is not expected for an antiferromagnet. Such large positive $\theta_P$ was earlier reported for $Gd_5Ge_4$ compound which had a Néel temperature of 130 K.[7] Since $\theta_P$ reflects the sum of all exchange interactions present in the compound, a positive paramagnetic Curie temperature in these systems indicates that ferromagnetic interactions are also present in addition to the dominant antiferromagnetic exchange interactions.

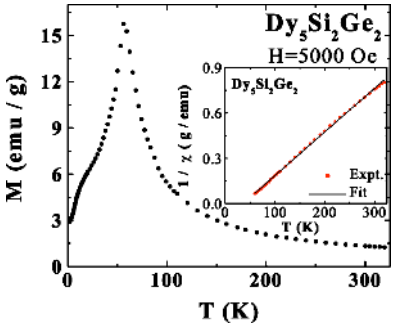


FIG. 1. Magnetization $M$ vs temperature $T$ for $Dy_5Si_2Ge_2$ (inset: Curie–Weiss fit to paramagnetic susceptibility).

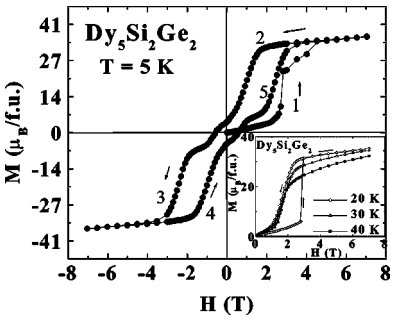


FIG. 2. Magnetization $M$ vs field $H$ isotherms obtained at 5 K for $Dy_5Si_2Ge_2$. (The different quadrants of isotherm are numbered in accordance with the sequence of measurement. Curve 1 was obtained in a zero-field cooled state.) (Inset: $M$ vs $H$ isotherms at 20 K, 30 K, and 40 K.)

Below 40 K, a magnetic field induced, irreversible, antiferromagnetic to ferromagnetic transition is observed in $Dy_5Si_2Ge_2$ (Fig. 2). Magnetization vs field isotherms at 5 K and 20 K display a sharp, steplike, metamagnetic transition at a critical field of ~2.8 T. At 30 K and 40 K, the sharpness of the transition is lost and an "S" shaped $M$-$H$ curve is observed. The magnetization approaches saturation in 6 T field with a value of $\sim 8\mu_B/Dy^{3+}$ion.

Neutron diffraction measurements were performed at 300 K (in paramagnetic state) and at 9.2 K (in the magnetically ordered state). Neutron diffraction data were analyzed assuming various Dy sites in $Dy_5Si_2Ge_2$ compound in a triclinic unit cell. Additional Bragg peaks, namely, (0 0 1), (0 3 0), (0 3 2), and (1 4 1) of magnetic origin, appear at 9.2 K compared to the neutron diffraction pattern obtained at 300 K. Analysis of the magnetically ordered state neutron diffraction data suggests that Dy moments arrange spirally along the $a$ axis giving rise to a canted antiferromagnetic structure. This canted antiferromagnetic structure is similar to that of elemental Dy where the antiparallel helicons are directed along the $c$ axis. The magnetic unit cell at 300 K and 9.2 K are shown in Fig. 3. The lattice parameters, atomic position parameters, and magnetic moment values obtained from the

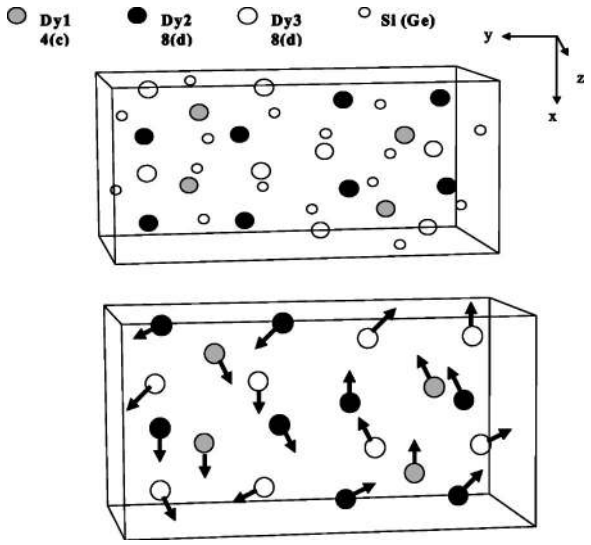


FIG. 3. (a) Unit cell of $Dy_5Si_2Ge_2$. (b) Magnetic structure of $Dy_5Si_2Ge_2$ at 9.2 K.

TABLE II. Various Dy sites in $Dy_5Si_2Ge_2$ compound in the magnetic unit cell and their magnetic moments at 9.2 K [lattice parameters $a=0.7504(1)$ nm, $b=1.4559(1)$ nm, $c=0.7610(2)$ nm, $\alpha=\beta=\gamma=90$ deg]. $M_x$, $M_y$, and $M_z$ magnetic moments along $x$, $y$, and $z$ directions in $\mu_B$. [$R_F^m=13.5\%$]

| Atom | Type position | $x/a$ | $y/b$ | $z/c$ | $M_x$ | $M_y$ | $M_z$ | $M$ |
|---|---|---|---|---|---|---|---|---|
| Dy1*a* | 4(*c*) | 0.301(2) | 1/4 | 0.001(2) | −6.82(7) | 2.40(8) | −2.40(8) | 7.62(9) |
| Dy1*b* | 4(*c*) | 1/2−*x* | 1/2+*y* | 1/2+*z* | 6.82(7) | −2.40(8) | 2.40(8) | 7.62(9) |
| Dy1*c* | 4(*c*) | 1−*x* | 1/2+*y* | −*z* | 6.82(7) | −2.40(8) | −2.40(8) | 7.62(9) |
| Dy1*d* | 4(*c*) | 1/2+*x* | *y* | −1/2−*z* | −6.82(7) | 2.40(8) | 2.40(8) | 7.62(9) |
| Dy2*a* | 8(*d*) | 0.124(1) | 0.1193(4) | 0.3405(9) | −6.82(7) | 2.40(8) | 2.40(8) | 7.62(9) |
| Dy2*b* | 8(*d*) | 1/2−*x* | 1−*y* | 1/2+*z* | 6.82(7) | 2.40(8) | −2.40(8) | 7.62(9) |
| Dy2*c* | 8(*d*) | 1−*x* | 1/2+*y* | 1−*z* | 6.82(7) | 2.40(8) | 2.40(8) | 7.62(9) |
| Dy2*d* | 8(*d*) | 1/2+*x* | 1/2−*y* | 1/2−*z* | −6.82(7) | 2.40(8) | −2.40(8) | 7.62(9) |
| Dy2*e* | 8(*d*) | 1−*x* | 1−*y* | 1−*z* | 6.82(7) | −2.40(8) | 2.40(8) | 7.62(9) |
| Dy2*f* | 8(*d*) | 1/2+*x* | *y* | 1/2−*z* | −6.82(7) | −2.40(8) | −2.40(8) | 7.62(9) |
| Dy2*g* | 8(*d*) | *x* | 1/2−*y* | *z* | −6.82(7) | −2.40(8) | 2.40(8) | 7.62(9) |
| Dy2*h* | 8(*d*) | 1/2−*x* | 1/2+*y* | 1/2+*z* | 6.82(7) | −2.40(8) | −2.40(8) | 7.62(9) |
| Dy3*a* | 8(*d*) | 0.975(1) | 0.1031(4) | 0.8211(9) | −6.82(7) | −2.40(8) | 2.40(8) | 7.62(9) |
| Dy3*b* | 8(*d*) | 1/2−*x* | 1−*y* | 1/2+*z* | 6.82(7) | −2.40(8) | −2.40(8) | 7.62(9) |
| Dy3*c* | 8(*d*) | 1−*x* | 1/2+*y* | 1−*z* | 6.82(7) | 2.40(8) | −2.40(8) | 7.62(9) |
| Dy3*d* | 8(*d*) | 1/2+*x* | 1/2−*y* | 1/2−*z* | −6.82(7) | 2.40(8) | 2.40(8) | 7.62(9) |
| Dy3*e* | 8(*d*) | 1−*x* | 1−*y* | 1−*z* | 6.82(7) | 2.40(8) | 2.40(8) | 7.62(9) |
| Dy3*f* | 8(*d*) | 1/2+*x* | *y* | 1/2−*z* | −6.82(7) | 2.40(8) | −2.40(8) | 7.62(9) |
| Dy3*g* | 8(*d*) | *x* | 1/2−*y* | *z* | −6.82(7) | −2.40(8) | −2.40(8) | 7.62(9) |
| Dy3*h* | 8(*d*) | 1/2−*x* | 1/2+*y* | 1/2+*z* | 6.82(7) | −2.40(8) | 2.40(8) | 7.62(9) |

Rietveld fit are listed in Tables I and II. It is this canted nature of the spins and the presence of short-range two-dimensional (2D) ferromagnetic interactions among the Dy spins along the layer and long-range 3D antiferromagnetic interactions across the layers that give rise to the possible reorientation of spins in applied magnetic field. When the applied magnetic field is beyond the critical value, the spin flip occurs resulting in a collinear or nearly collinear spin arrangement minimizing the free energy via a martensitic-like, metamagnetic transition.

From the analysis of neutron diffraction data, the ordered state magnetic moment at the Dy site is found to be $7.63\mu_B$ which is close to the moment value obtained from magnetization measurements. The ordered state moment is considerably lower than the $Dy^{3+}$ free ion value ($10\mu_B$) suggesting the presence of crystal-field effects in this compound. No structural transition was detected by neutron diffraction between 9.2 K and 300 K though several other members of $R_5(Si_xGe_{1-x})_4$ series are known to undergo such a structural transition concomitant with the magnetic transition. But a magnetic field-induced structural transformation in this compound cannot be ruled out and further x-ray and neutron diffraction data in the presence of magnetic field are necessary. In $Gd_5Ge_4$, the interlayer Gd–Gd distances are found to increase by ~27% as detected by high resolution x-ray diffraction experiments in applied magnetic field of 3.5 T (Ref. 8) which leads to a steplike, antiferromagnetic to ferromagnetic transition at temperatures below 8 K.[7]

## IV. CONCLUSION

The compound $Dy_5Si_2Ge_2$ is found to be a canted antiferromagnet below its Néel temperature of 56 K by neutron diffraction experiments. The complex magnetic behavior of $Dy_5Si_2Ge_2$, with a field-induced transition at temperatures below 20 K, is attributed to the possible magnetic reorientations as a result of competing short-range 2D ferromagnetic interactions and long-range 3D antiferromagnetic interactions present in such compounds of layered $Sm_5Ge_4$ structure.

[1] V. K. Pecharsky, G. D. Samolyuk, V. P. Antropov, A. O. Pecharsky, and K. A. Gschneidner, Jr., J. Solid State Chem. **171**, 57 (2003).
[2] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[3] G. H. Rao, Q. Huang, H. F. Yang, D. L. Ho, J. W. Lynn, and J. K. Liang, Phys. Rev. B **69**, 094430 (2004).
[4] C. Ritter, L. Morellon, P. A. Algarabel, C. Magen, and M. R. Ibarra, Phys. Rev. B **65**, 094405 (2002).
[5] J. M. Cadogan, D. H. Ryan, Z. Altounian, H. B. Wang, and I. P. Swainson, J. Phys.: Condens. Matter **14**, 7191 (2002).
[6] E. M. Levin, K. A. Gschneidner, Jr., T. A. Lograsso, D. L. Schlagel, and V. K. Pecharsky, Phys. Rev. B **69**, 144428 (2004).
[7] H. Tang, V. K. Pecharsky, K. A. Gschneidner, Jr., and A. O. Pecharsky, Phys. Rev. B **69**, 064410 (2004).
[8] V. K. Pecharsky, A. P. Holm, K. A. Gschneidner, Jr., and R. Rink, Phys. Rev. Lett. **91**, 197204 (2003).