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Competing magnetic interactions in the intermetallic compounds Pr_5Ge_3 and Nd_5Ge_3

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Magnetic properties of polycrystalline Pr_5Ge_3 and Nd_5Ge_3 (hexagonal, Mn_5Si_3-type) compounds have been studied. Magnetization measurements in 0.5 T field indicate that the Pr_5Ge_3 orders antiferromagnetically at 18 K (T_N). However, in an applied field of 10 mT, the zero-field-cooled and field-cooled magnetization bifurcates below ~65 K. This and the positive paramagnetic Curie temperature, obtained from the Curie–Weiss fit to the paramagnetic susceptibility, suggest the presence of competing ferromagnetic and antiferromagnetic interactions. The magnetization versus field isotherm at 5 K shows an S-shaped curve and a weak tendency to saturation in fields of 9 T with negligible hysteresis. The magnetic moment attains a value of 1.6 μ_B/Pr^{3+} at 5 K in 9 T. The magnetic entropy change near the magnetic transition has been calculated by measuring magnetization versus field isotherms close to T_N. The entropy change is found to be considerably large. Neutron diffraction study indicates that below ~43 K the Nd_5Ge_3 has flat spiral ordering with wave vector $K = [0, 0, \pm 1/5]$ (the flat spiral axis coincides with cell parameter, *a*). Neutron diffraction study of Pr_5Ge_3 suggests that the magnetic structure of Pr_5Ge_3 could be similar to that in Nd_5Ge_3. © *2011 American Institute of Physics*. [doi:10.1063/1.3556920]

I. INTRODUCTION

Rare-earth rich, intermetallic compounds of type R_5Ge_3 (R = rare earth) crystallize in hexagonal, Mn_5Si_3-type structure (Space group *P6₃/mcm*, No. 193) and in this structure type the rare earth occupies two inequivalent lattice sites.[1,2] As the nearest neighbors of these rare-earth ions are different, the magnetic interactions are intrinsically anisotropic.[3] These lead to interesting magnetic properties and complex magnetic structures.[2,4–7] In the present work, the Pr_5Ge_3 compound has been studied by means of magnetization and neutron powder diffraction experiments. The magnetic entropy change in the neighborhood of the magnetic transition is computed using the magnetization-field (M-H) isotherm data.

II. EXPERIMENTAL DETAILS

Polycrystalline Pr_5Ge_3 and Nd_5Ge_3 were synthesized by arc melting under argon atmosphere starting from stoichiometric amounts of pure elements (Pr and Nd 99.9% pure, Ge 99.999% pure). The samples were characterized by room temperature x-ray diffraction and energy dispersive analysis by x ray (EDAX). The obtained diffractograms were identified and intensity calculations were made in the isotropic approximation using the RIETAN-program.[8] DC magnetization was measured using a commercial superconducting quantum interference device (SQUID) (MPMS XL, Quantum Design) and Physical Property Measurement System (PPMS) magnetometers in the temperature range of 1.8–300 K. The neutron diffraction investigation was carried out from room temperature down to 2 K in zero magnetic field at the Institute Laue-Langevin, Grenoble, France, using the *D1B* powder diffractometer,[9] operating at a wavelength $\lambda = 0.2522$ nm ($2\theta = 2.0–84°$). The diffraction patterns were indexed and the calculations performed by using the FULLPROF 98-program.[10]

III. RESULTS AND DISCUSSION

Powder x-ray diffraction pattern of Pr_5Ge_3, obtained at room temperature, confirms the single phase nature and hexagonal crystal structure of this compound. The nominal composition and stoichiometry was verified by the EDAX analysis. The magnetization of the Pr_5Ge_3 has been measured in the temperature range from 5 to 300 K, in 0.5 T applied field (Fig. 1). The compound orders antiferromagnetically at

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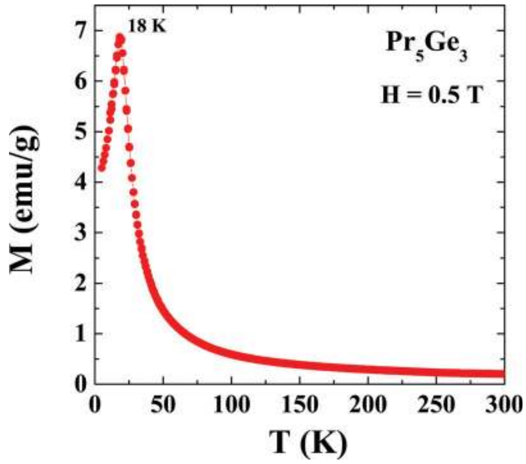

FIG. 1. (Color online) Magnetization vs temperature of Pr_5Ge_3 in the applied field of 0.5 T.

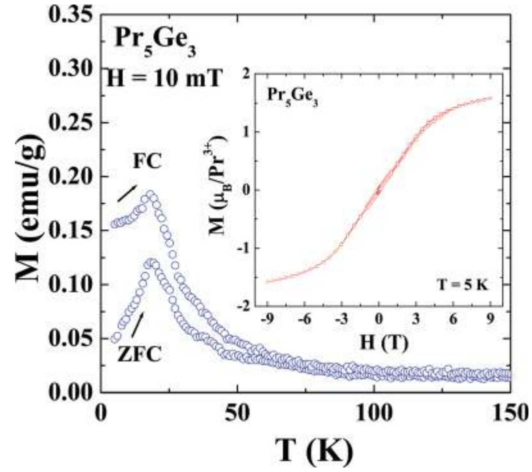

FIG. 2. (Color online) Magnetization vs temperature of Pr_5Ge_3 in the applied field of 10 mT in zero-field-cooled and field-cooled states (Inset: Magnetization vs field at 5 K in the fields up to 9 T).

18 K (T_N). However, in the applied field of 10 mT, a bifurcation between zero-field-cooled and field-cooled magnetization is observed below ~65 K (Fig. 2). This could originate from the in-plane ferromagnetic interactions. From the Curie–Weiss fit to the paramagnetic susceptibility above ~40 K, paramagnetic Curie temperature (θ_P) of about +5 K and the effective magnetic moment value of ~3.8 μ_B are obtained. The positive value of θ_P indicates the presence of competing ferromagnetic interactions.

The magnetization versus field isotherm of Pr_5Ge_3 was measured at 5 K in fields up to 9 T. This data indicates a weak tendency to saturation in fields of 9 T with negligible hysteresis (Inset in Fig. 2). The magnetic moment attains value of 1.6 μ_B/Pr^{3+} at 5 K in 9 T which is just 50% of the theoretical ordered state value ($gJ = 3.2\ \mu_B$) expected for free Pr^{3+} ion. This could be caused by competing antiferromagnetic components and/or by strong crystal field effects.

Magnetization versus field isotherms in the temperature range of 50–5 K in fields up to 7 T have been used to calculate the magnetic entropy change in the vicinity of the magnetic transition in Pr_5Ge_3 [Fig. 3(a)]. The magnetic entropy change is substantial near and above T_N, reaching values of ~5.8 J/kg/K for 7 T field change at 22.5 K [Fig. 3(b)]. The M-H data at 15 and 10 K indicate that magnetization is indeed larger in low fields at 15 K, clearly indicating the role of competing ferromagnetic and antiferromagnetic interactions. The competition does not lead to frustration (as evidenced by the absence of frequency dependent ac magnetic susceptibility), but gives rise to a magnetic state with a fine equilibrium that can be influenced by an application of external field.

To understand the microscopic magnetic structure, powder neutron diffraction experiments were carried out on Pr_5Ge_3 first down to about 12 K (MURR, USA) and then down to 2 K (ILL, France) and no magnetic reflection was observed down to 2 K in zero magnetic field.

This observation has motivated us to study isostructural Nd_5Ge_3 compound in order to possibly compare and contrast with that of Pr-compound. Powder neutron diffraction measurements were carried out at various temperatures from 300 to 2 K for Nd_5Ge_3. Below ~43 K the neutron diffraction pattern of Nd_5Ge_3 indicates the development of the low-angle magnetic reflection that corresponds to the $\mathbf{K} = [0, 0, \pm 1/5]$ wave vector and slow magnetic reflections that may correspond to the [±1/5, 0, 0] or [0, 0, ±7/10] wave vectors (Fig. 4). The previously reported magnetic structure of Nd_5Ge_3 with wave vector [1/4, 0, 0][2] was not confirmed in the present work. The model of flat spiral ordering (spiral axis along *a*-direction) is in best agreement with the experimental data for magnetic component with $\mathbf{K} = [0, 0, \pm 1/5]$ wave vector. In terms of this model, the Nd magnetic moment value at 2 K is about 0.5(1) and 0.9(1) μ_B at *6g* and *4d* sites,

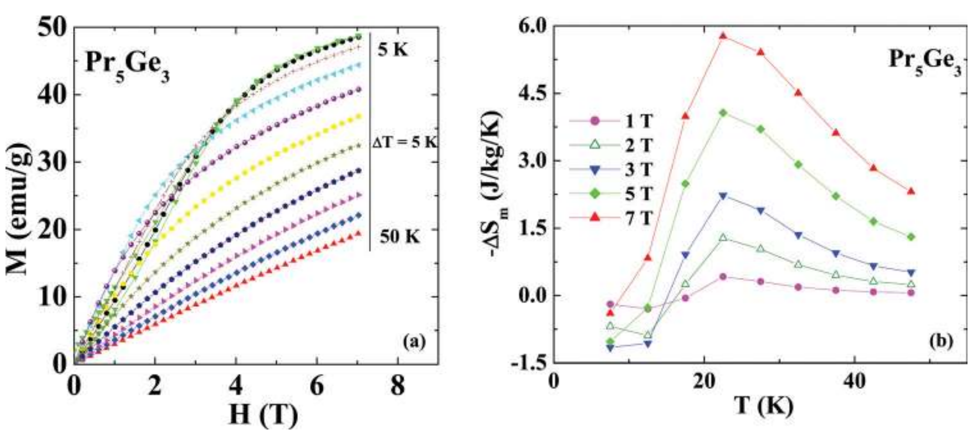

FIG. 3. (Color online) (a) Magnetization vs field isotherms of Pr_5Ge_3 in the applied fields of 7 in the temperature range of 5–50 K T and (b) magnetic entropy change near the magnetic transition.

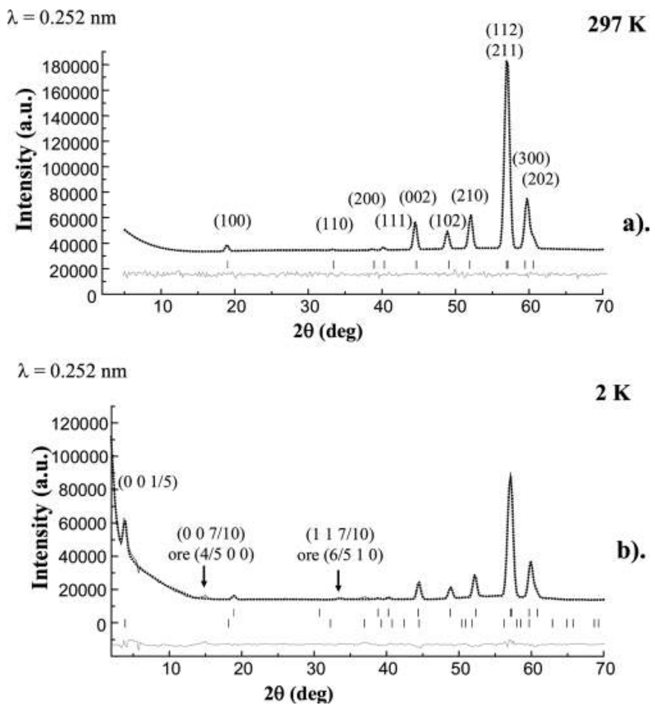

FIG. 4. Neutron diffraction patterns of Nd_5Ge_3 at (a) 297 K and (b) 2 K. The upper vertical bars indicate crystal-lattice Bragg angles; the lower vertical bars indicate magnetic reflection angles with **K** = [0, 0, ±1/5] wave vector; the lower profile gives the difference between observed and calculated data in terms of flat spiral with **K** = [0, 0, ±1/5] (see Table I).

respectively (Table I). As these compounds seem to follow the de Gennes rule (Fig. 5), the magnetic structure of Pr_5Ge_3 is expected to be similar to that of Nd_5Ge_3. For Pr_5Ge_3, the (0, 0, 1/5) magnetic reflection seems to coincide with background of incident beam. Perhaps, for this reason we have not observed the development of any magnetic reflection in the neutron diffraction patterns of Pr_5Ge_3 down to 2 K. Thus, extension of powder neutron diffraction experiments in low-angle range and in the presence of magnetic field is highly desired for Pr_5Ge_3 and Nd_5Ge_3 compounds.

TABLE I. Crystallographic and magnetic parameters of Nd_5Ge_3 compound: Cell parameters, *a* and *c*, atomic position parameters, X_{Nd1} and X_{Ge} at temperature T, and magnetic moment of the Nd atom in the *6g* site M_{Nd1} and *4d* site M_{Nd2}. Reliability factors R_F (crystal structure) and $R_F{}^m$ (magnetic structure) are given in percentage (%). The flat spiral axis coincides with cell parameter, *a*. Wave vector is **K** = [0, 0, ±1/5].

State	T (K)	Unit cell data	R_F (%)	M_{Nd} (μ_B)	$R_F{}^m$ (%)
Paramagnet	300[a]	a = 0.8745(1) nm	5.8		
		c = 0.66225(6) nm			
		X_{Nd1} = 0.2404(5)			
		X_{Ge} = 0.602(1)			
	297	a = 0.8749(5) nm	5.2		
		c = 0.6628(5) nm			
		X_{Nd1} = 0.2424(9)			
		X_{Ge} = 0.605(1)			
AF	2	a = 0.8703(1) nm	6.5	M_{Nd1} = 0.5(1)	13.7
(flat spiral)		c = 0.6615(1) nm		M_{Nd1} = 0.9(1)	
		X_{Nd1} = 0.238(3)			
		X_{Ge} = 0.606(3)			

[a]X-ray data.

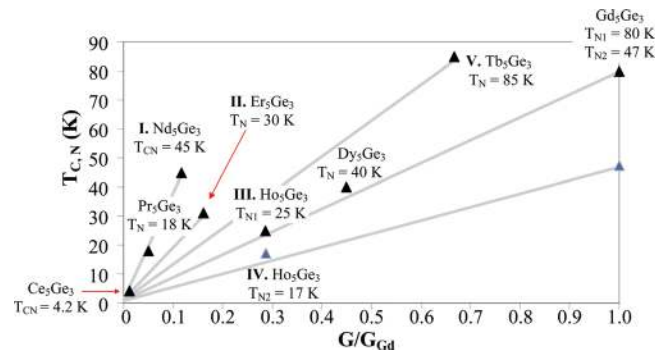

FIG. 5. (Color online) Magnetic ordering temperature vs de Gennes factor (G) ratio for Mn_5Si_3-type R_5Ge_3 compounds. The phases with the known magnetic structure are listed in the figure. I. Nd_5Ge_3: Flat spiral (**K** = [0, 0, ±1/5]) [this work]; II. Er_5Ge_3: Sine modulated AF (**K** = [0, 0, ±3/10]);[6] III. Ho_5Ge_3-HT: Sine modulated AF (**K** = [0, 0, ±3/10]) and square modulated AF (**K** = [0, 1/2, 0] components; IV. Ho_5Ge_3-LT: Sine modulated components with **K** = [0, 0, ±3/10]), **K** = [0, 0, ±2/5] and **K** = [±1/5, ±1/5, 0] and square modulated component with **K** = [0, 1/2, 0];[7] and V. Tb_5Ge_3: Flat spiral (**K** = [0, 0, ±0.475,1/2].[4,5]

A strong ferromagnetic component was also observed in the applied magnetic fields for Nd_5Ge_3 sample[2] and recently detailed field dependent magnetization measurements on Nd_5Ge_3 single crystal have been reported.[11] Indeed large anisotropy between *c*-axis and c-plane magnetism is observed in applied magnetic fields for this compound.

IV. CONCLUSIONS

In summary, the compound Pr_5Ge_3 exhibits antiferromagnetic ordering at ~18 K with competing short range ferromagnetic interactions just above and below T_N. The magnetic entropy change is substantial near and above T_N reaching values of ~5.8 J/kg/K for 7 T field change at 22.5 K. The competing nature of interactions in Pr_5Ge_3 that is intrinsic to the structure itself could possibly lead to the observed interesting magnetic and magnetocaloric properties.

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[1]K. H. J. Buschow and J. F. Fast, Phys. Status Solidi **21**, 593 (1967).
[2]P. Schobinger-Papamantellos and K. H. J. Buschow, J. Magn. Magn. Mater. **49**, 349 (1985).
[3]D. A. Joshi, A. Tamizhavel, and S. K. Dhar, Phys. Rev. B **79**, 014425 (2009).
[4]P. Schobinger-Papamantellos, J. Magn. Magn. Mater. **28**, 97 (1982).
[5]O. Halpern and M. H. Johnson, Phys. Rev. **55**, 898 (1939).
[6]A. V. Morozkin, O. Isnard, P. Henry, and P. Manfrinetti, J. Magn. Magn. Mater. **307**, 124 (2006).
[7]A. V. Morozkin, O. Isnard, P. Henry, and P. Manfrinetti, J. Alloys Compd. **464**, 219 (2008).
[8]F. Izumi, in The Rietveld Method, edited by R.A. Young (Oxford University Press, Oxford, 1993), Chap. 13.
[9]See http://www.ill.eu/instruments-support/instruments-groups/yellowbook/ for The ILL Yellow Book (The Guide to the ILL Instruments suite and its characteristics).
[10]J. Rodriguez-Carvajal, Physica B **192**, 55 (1993).
[11]T. Tsutaoka, A. Tanaka, Y. Narumi, M. Iwaki, and K. Kindo, Physica B **405**, 180 (2010).