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Magnetic structure of the rare earth intermetallic compound Ce_4Ge_3

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ABSTRACT

Neutron powder diffraction experiments and magnetization measurements have been carried out on the intermetallic compound Ce_4Ge_3 (Cubic, Th_3P_4-type). The neutron diffraction data obtained in zero field at 2 K, reveal commensurate antiferromagnetic ordering with magnetic moments of Ce directed along (0 0 1) axis ($M_{Ce} = 1.55(4)\ \mu_B$) whereas the magnetization data depict two magnetic transitions at ~12 K and at ~6 K, respectively. Isothermal magnetization data obtained at 2 K present complex metamagnetic transition with two plateaus corresponding to magnetic moment values of ~$0.35\mu_B/Ce^{3+}$ in 2 T and ~$0.94\ \mu_B/Ce^{3+}$ in 9 T field.

1. Introduction

Ce-based rare earth intermetallic compounds often exhibit interesting physical properties such as valence fluctuation, heavy fermion superconductivity, mixed valence and Kondo behaviour. Recently the magnetic properties of the Th_3P_4-type Tb_4Sb_3 and Ce_4Sb_3 compounds were understood by means of magnetic property and neutron diffraction studies [1,2]. In an attempt to understand the magnetic structure of isostructural compounds, we investigate the magnetic properties of Th_3P_4-type Ce_4Ge_3 compound using neutron powder diffraction and magnetization data.

2. Experimental

The Ce_4Ge_3 compound was made in an electric arc furnace under argon atmosphere using a non-consumable tungsten electrode and a water-cooled copper tray. Germanium (purity 99.999 wt.%) and cerium (purity 99.9 wt.%) were used as the starting components. Zirconium was used as a getter during the melting process. The alloy was annealed in a quartz ampoule that was back-filled with argon at 970 K for a 100 h with following quenching in ice-cold water.

The quality of the polycrystalline alloy was investigated using X-ray powder diffraction and analysis by electron microscopy (SEM) equipped with EDX microprobe analysis (a "Camebax" microanalyser was employed to perform microprobe X-ray spectral analyses of the specimen).

X-ray powder pattern was obtained on a diffractometer DRON-3 ($Cu_{K\alpha}$-radiation, $2\theta = 20.90^\circ$, step 0.05°, 1402 points). The obtained diffractogram was identified and intensity calculations were made in the isotropic approximation using the Rietan-programs [4].

The neutron diffraction investigation was carried out from 150 K down to 2 K with temperature step 10 K in the absence of applied magnetic field at the Institute Laue-Langevin, Grenoble, France, using the high resolution powder diffractometer *D1B* [5], operating at a wavelength $\lambda = 0.252$ nm selected by a pyrolitic graphite monochromator. In the configuration used, the resolution of D1B was about 0.3° (FWHM) the multicounter is composed of 400 cells covering a total angular domain of 80° ($2\theta = 4$–84°). The diffraction patterns were indexed, and the calculations were performed, by using the FULLPROF 98-program [6].

DC magnetization studies were carried out using commercial magnetometer (PPMS-VSM, Quantum Design) in the temperature range of 1.8–300 K, in applied magnetic fields up to 9 T.

3. Results and discussion

Polycrystalline Ce_4Ge_3 compound is known to crystallize in cubic, Th_3P_4-type crystal structure [3]. Our room temperature X-ray and neutron powder diffraction data confirm the same. Magnetization (M) of Ce_4Ge_3 compound in 10 mT field has been plotted as a function of temperature in Fig. 1a. This data reveal magnetic transitions at ~12 K and at ~6 K, respectively. The zero-field-cooled and field-cooled magnetization data bifurcate at 12 K and hence suggest the presence of competing magnetic interactions in this compound. The cusp in magnetization at 6 K hints possible dominant antiferromagnetic interactions at this temperature. The magnetization has also been measured in a field of 0.5 T (inset in Fig. 1a). The paramagnetic susceptibility is fitted to Curie-Weiss law and the effective paramagnetic moment value is found to be about $2.87\mu_B/Ce^{3+}$ (against the free ion value of $2.54\mu_B$) and the paramagnetic Curie

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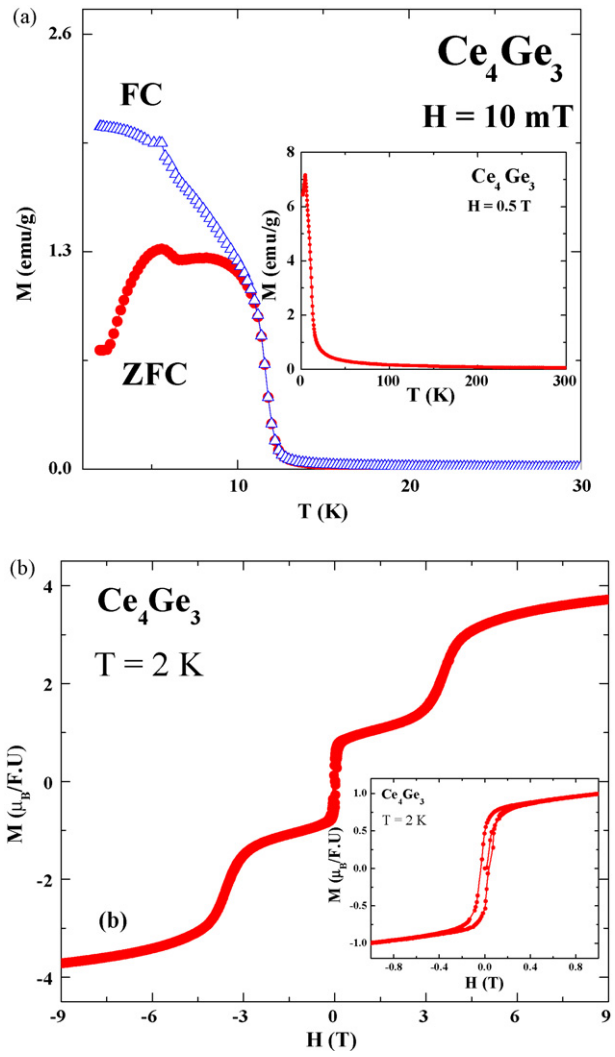

Fig. 1. Magnetization vs. temperature of Ce_4Ge_3 compound in applied field of 10 mT in the temperature range of 2–30 K and the inset shows magnetization vs. temperature in 0.5 T applied field in the temperature range of 2–300 K (a). Magnetization vs. field of Ce_4Ge_3 at 2 K in fields up to 9 T (b). Inset in Fig. 1b shows enlarged view of magnetization vs. field in low fields.

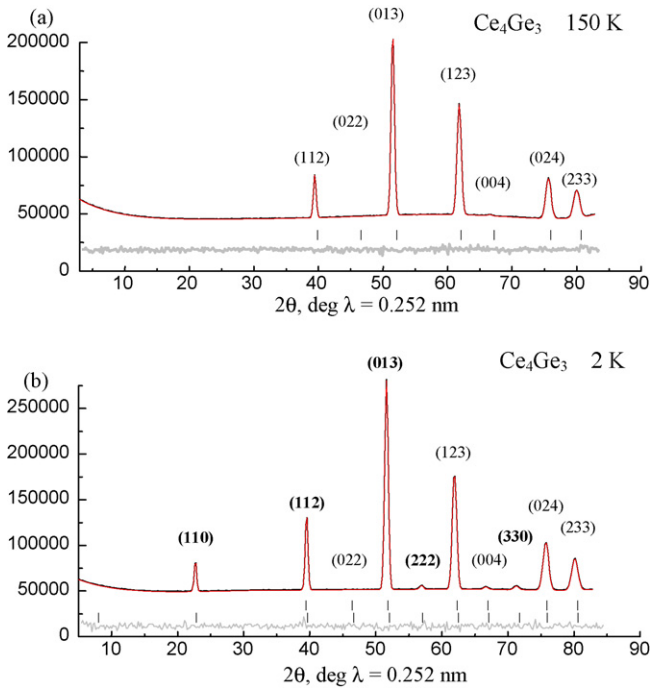

Fig. 2. Neutron diffraction patterns of Ce_4Ge_3 at 150 K (paramagnetic state) (a) and at 2 K (magnetically ordered state) (b).

temperature is found to be ~ −16 K. These fit parameters indicate that Ce is possibly in tripositive state in the title compound and antiferromagnetic interactions are dominant interactions. The effective magnetic moment value is slightly larger than the free ion value suggesting possible conduction electron polarization.

The magnetization vs. field (M–H) data of Ce_4Ge_3 compound obtained at 2 K indicate a complex metamagnetic transition. The magnetic moment value of $\sim 0.35\mu_B/Ce^{3+}$ is achieved in 2 T and $\sim 0.94\mu_B$/Ce is obtained in 9 T field (Fig. 1b). Magnetization vs. field data obtained at 8 K (figure not shown) shows a steady linear increase in magnetization in fields up to 9 T, indicating the dominant antiferromagnetic behaviour of this compound at this temperature. In the case of isostructural Ce_4Sb_3 compound, a saturation magnetic moment value of $\sim 0.93\mu_B$/Ce has been obtained by magnetization measurements at 1.8 K [2].

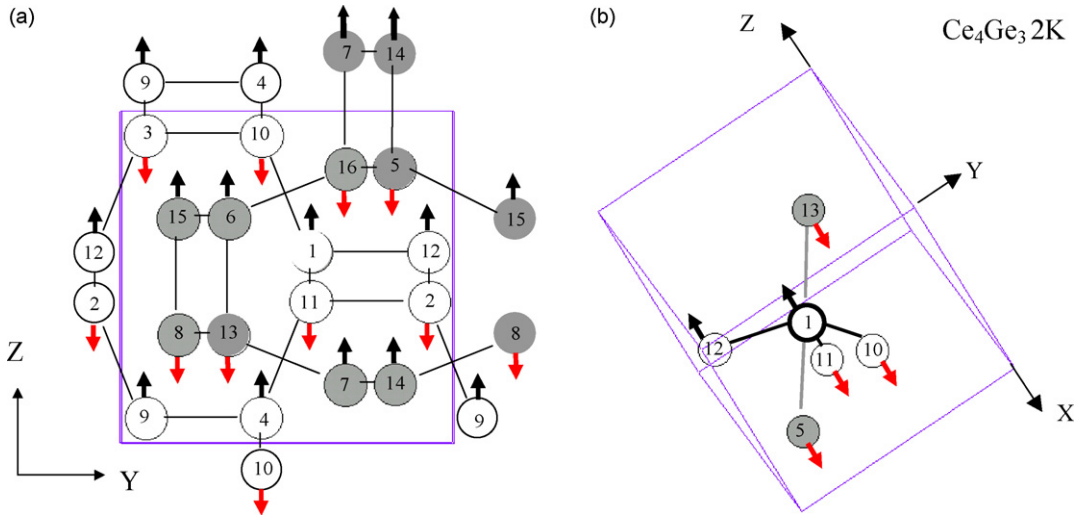

Fig. 3. Magnetic structure of Ce_4Ge_3 at 2 K in zero point field (projection of Th_3P_4-type unit cell on *YZ* plane without Ge atoms) (a). The shortest Ce–Ce distances and Ce 1, 2, 3, 4, 9, 10, 11, 12 and Ce 5, 6, 7, 8, 13, 14, 15, 16 sublattices are marked in the figure and the arrangement of Ce magnetic moments in the Ce cluster (b).

Table 1
Crystallographic and magnetic parameters of Ce_4Ge_3 compound: cell parameter a, atomic position parameters X_{Ce}, magnetic moment of the Ce atom M_{Ce} at temperature T.

T_N (K)	State	T (K)	a (nm)	X_{Ce}	R_F (%)	M_{Ce} (μ_B)	Atomic position	θ (°)	R_F^m(%)
	Para	300[a]	0.9198 (1)	0.5693 (7)	9.0				
		150	0.9240 (2)	0.5663 (7)	2.2				
		50	0.9235 (2)	0.5674 (7)	2.0				
		35	0.9223 (2)	0.5675 (7)	1.9				
<14	AF	2	0.9127 (3)	0.570 (5)	4.6	1.55 (4)	Ce 1, 4, 6, 7, 9, 12, 14, 15	0	10.3
							Ce2, 3, 5, 8, 10, 11, 13, 16	180	

The θ is angle of Ce magnetic moment with Z-axis of the unit cell. The temperature T_N refers to a magnetic transition from neutron diffraction experiment. Reliability factors R_F (crystal structure) and R_F^m (magnetic structure) are given in percent (%).
[a] X-ray data.

In order to examine the magnetic structure of Ce_4Ge_3 compound, a powder neutron diffraction study was undertaken. The powder neutron diffraction patterns obtained at 150 K and 2 K in zero magnetic magnetic field show the development of commensurate reflections (Fig. 2) that correspond to pure antiferromagnetic structure with details as given in Fig. 3 and Table 1. The Ce atoms positions in the unit cell are stated in Table 2. The Fig. 2a shows that Ce sublattice consists of two similar Ce sublattices corresponding to the following labelled Ce positions: Ce 1, 2, 3, 4, 9, 10, 11, 12 and Ce 5, 6, 7, 8, 13, 14, 15, 16. The shortest Ce 1, 2, 3, 4 – Ce 9, 10, 11, 12 (Ce 5, 6, 7, 8 – Ce 13, 14, 15, 16) interatomic distance is 0.3560 nm, a value close to the sum of two Ce atomic radii (R_{Ce} = 0.1825 nm) [7]. Concerning other distances encountered in the structure: Ce 1, 2, 3, 4, 9, 10, 11, 12 – Ce 5, 6, 7, 8, 13, 14, 15, 16 a much larger value is obtained as 0.3983 nm at room temperature. The appearance of ferromagnetic interaction upon applying a magnetic field on the antiferromagnetic Ce_4Ge_3 structure suggest weakening of the antiferromagnetic interactions in applied field or to the presence of competing ferromagnetic and antiferromagnetic interactions in this compound. Such behaviour is not surprising since RKKY type interactions are expected in Ce_4Ge_3. Magnetic interactions that are known to be very sensitive to the interatomic distances and to even change sign depending on the distances between magnetic atoms. As described above, the two different Ce–Ce interatomic bonds that are expected to play a key role in deciding the magnetic interactions in Ce_4Ge_3 have lengths of 0.3983 nm and 0.3560 nm.

All the Ce sites are found to carry an ordered magnetic moment at 2 K. According to neutron diffraction data, the magnetic moment at Ce site is found to be 1.55(4) μ_B/Ce^{3+}, somewhat larger than that observed by magnetization data. This may result from the negative polarization of the conduction electrons which is not easily estimated from unpolarized powder diffraction data, a technique more sensitive to the localised 4f states. The Ce-moments are directed along (0 0 1) axis of the unit cell. Such magnitude of Ce magnetic moment is much less than that expected from the theoretical Ce^{3+} free ion value of 2.14μ_B (gJ) [8]. This could possibly originate from the presence of competing antiferromagnetic interactions at the low temperature. In addition, we would like to note that cerium valence deviating from the purely trivalent state is not unusual for cerium based Kondo lattice systems, nevertheless the Ce 4f magnetic moment is known to vanish rapidly when the Ce valence slightly differs from the purely trivalent state. One can expect that the magnetic properties the 4f electron state in these Ce_4Ge_3 and Ce_4Sb_3 compounds are most probably closer to the Kondo like regime than to the valence fluctuation regime. We interpret the fact that the ordered magnetic moment value is smaller than the Ce free ion value as resulting from crystal field effects and/or Kondo screening. A possible explanation is that this observed value of the ordered magnetic moment of Ce results from the competition between the demagnetising Kondo and the magnetic RKKY interactions. Similar reduced magnetic moments are indeed often observed for Ce containing intermetallics [9,10]. However, the negative paramagnetic Curie temperature, the presence of antiferromagnetic like cusp at low temperature and the presence of two plateaus in the magnetization curve of Ce_4Ge_3 indicates that an intermediate configuration can be obtained between the zero-field antiferromagnetic structure and the high field ferromagnetic order. For field larger than 2.5 T a second metamagnetic transition occurs. The origin of such intermediate magnetic configuration is not yet known. A deviation from the zero-field magnetic structure involving a partial canting of the Ce magnetic moment can be expected or even a flipping of magnetic moments at some Ce sites can occur in applied magnetic fields.

Table 2
Atomic positions of Ce ions in the Th_3P_4-type Ce_4Ge_3 unit cell.

Atomic position	X/a	Y/b	Z/c
Ce1	X_{Ce}	X_{Ce}	X_{Ce}
Ce2	$X_{Ce} - 1/2$	$3/2 - X_{Ce}$	$1 - X_{Ce}$
Ce3	$1 - X_{Ce}$	$X_{Ce} - 1/2$	$3/2 - X_{Ce}$
Ce4	$3/2 - X_{Ce}$	$1 - X_{Ce}$	$X_{Ce} - 1/2$
Ce5	$X_{Ce} + 1/4$	$X_{Ce} + 1/4$	$X_{Ce} + 1/4$
Ce6	$3/4 - X_{Ce}$	$X_{Ce} - 1/4$	$5/4 - X_{Ce}$
Ce7	$X_{Ce} - 1/4$	$5/4 - X_{Ce}$	$3/4 - X_{Ce}$
Ce8	$5/4 - X_{Ce}$	$3/4 - X_{Ce}$	$X_{Ce} - 1/4$
Ce9	$X_{Ce} - 1/2$	$X_{Ce} - 1/2$	$X_{Ce} - 1/2$
Ce10	X_{Ce}	$1 - X_{Ce}$	$3/2 - X_{Ce}$
Ce11	$3/2 - X_{Ce}$	X_{Ce}	$1 - X_{Ce}$
Ce12	$1 - X_{Ce}$	$3/2 - X_{Ce}$	X_{Ce}
Ce13	$X_{Ce} - 1/4$	$X_{Ce} - 1/4$	$X_{Ce} - 1/4$
Ce14	$5/4 - X_{Ce}$	$1/4 + X_{Ce}$	$3/4 - X_{Ce}$
Ce15	$1/4 + X_{Ce}$	$3/4 - X_{Ce}$	$5/4 - X_{Ce}$
Ce16	$3/4 - X_{Ce}$	$5/4 - X_{Ce}$	$1/4 + X_{Ce}$

4. Conclusions

Magnetic properties of Ce_4Ge_3 compound have been explored by neutron powder diffraction experiments and magnetization measurements. Analysis of neutron diffraction data on this compound suggests an antiferromagnetic order of the Ce magnetic moments involving two Ce sublattices at 2 K. However, the temperature dependent magnetization data reveal two magnetic transitions one at ~12 K and the other at ~5 K, respectively. The magnetic moment value of ~0.94 μ_B/Ce has been obtained for Ce_4Ge_3 at 2 K in 9 T field. The reduced Ce magnetic moment value comparison to the expected theoretical Ce^{3+} free ion value may originate from the Kondo screening and/or the antiferromagnetic interactions. The finer details of the magnetic structure can be understood by extending neutron diffraction study as a function of temperature and applied magnetic fields.

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References

[1] R. Nirmala, A.V. Morozkin, O. Isnard, A.K. Nigam, J. Magn. Magn. Mater. 321 (2009) 188–191.
[2] A.V. Morozkin, R. Nirmala, A.K. Nigam, J. Alloys Compd. 450 (2008) 131–135.
[3] Pearson's Handbook of Crystallographic Data for Intermetallic Phases, American Society for Metals, Metals Park, Oh 44073, 2, 3, 1985.
[4] F. Izumi, in: R.A. Young (Ed.), The Rietveld Method, Oxford University Press, Oxford, 1993, Chapter 13.
[5] www.ill.fr, Yellow Book.
[6] J. Rodriguez-Carvajal, Physica B 192 (1993) 55–69.
[7] J. Emsley, The Elements, second ed., Clarendon press, Oxford, 1991.
[8] S. Legvold, Rare Earth Metals and Alloys, Ferromagnetic Materials, in: E.P.Wohlfarth (Ed.), Amsterdam, North-Holland Publish. Comp., 1 (1980) 183–295.
[9] V.A. Yartys, B. Ouladdiaf, O. Isnard, O.Yu. Khyzun, K.H.J. Buschow, J. Alloys Compd. 359 (2003) 62–65.
[10] L. Durivault, F. Bourée, B. Chevalier, O. Isnard, G. André, F. Weill, J. Etourneau Acta Polonica B 34 (2003) 1393–1397.