

Electronic structure and magnetic properties of the Ce_2MnGe_6 compound

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Magnetization, magnetic susceptibility and X-ray photoemission measurements were performed on a Ce_2MnGe_6 polycrystalline sample. This compound crystallizes in an orthorhombic Ce_2CuGe_6 -type structure (space group $Amm2$). The Ce atoms occupy two nonequivalent sites, while the Mn atoms only one site. The magnetic data indicate that the compound is a ferrimagnet with the Curie temperature $T_C = 150$ K. The magnetic moment determined from the magnetization curve measured at 2 K increases from $1.9 \mu_B$ for $H \approx 0$ to $2.5 \mu_B$ for $H = 50$ kOe. Above T_C the reciprocal magnetic susceptibility fulfills the Curie-Weiss law with the effective magnetic moment equal $5.3 \mu_B$. The valence band gives a small peak at 0.3 eV below the Fermi level and a broad one with the maximum at 2.1 eV, corresponding to the Mn 3d states. The structure of the Ce 3d_{5/2} and Ce 3d_{3/2} XPS spectra has been interpreted in terms of the Gunnarsson-Schönhammer theory. Two final-state contributions of f^1 and f^2 , exhibiting a spin-orbit splitting of $\Delta_{SO} = 18.7$ eV, were clearly observed. From the intensity ratio $r = I(f^2)/[I(f^1) + I(f^2)] = 0.20$ a hybridization energy equal 93 eV was determined.

Ternary rare earth germanides / Magnetic ordering / Electronic structure

Introduction

This investigation is part of a broader study, which is expected to systematize the magnetic properties of the $R_mT_nX_p$ intermetallic compounds, where R is a rare-earth atom, T is a d-electron atom and X is a p-electron atom. The compound investigated in this work belongs to the R_2TGe_6 family, where T is Mn, Cu. These compounds crystallize in a orthorhombic crystal structure of the Ce_2CuGe_6 type (space group $Amm2$) [1,2]. The isostructural $R_2\text{CuGe}_6$ (R = Gd, Tb, Dy, Er) compounds order antiferromagnetically at low temperatures with the Néel temperature between 5.6 K (for R = Er) and 33.1 K (for R = Tb) [3].

In this work we report results of magnetic and XPS measurements for Ce_2MnGe_6 . From these data magnetic properties and the electronic structure were determined.

Experimental details

The sample was prepared by arc-melting the elements (cerium, purity 99.85 wt.%; manganese, purity 99.99 wt.%; germanium purity 99.99 wt.%) under a

high-purity Ti-gettered argon atmosphere on a water-cooled copper hearth. The alloy was then annealed at 670 K in an evacuated quartz glass tube for 4 weeks, and subsequently quenched into cold water.

The quality of the sample was checked by X-ray diffraction performed at room temperature on powder samples using a DRON-3.0 diffractometer, CuK_α radiation. All the procedures, including indexing, refinement of the lattice and atomic parameters, were accomplished using the CSD program package [4].

DC magnetic measurements were carried out using a commercial MPMS SQUID magnetometer. Two types of measurement were performed: magnetic susceptibility measurements in a magnetic field of 1 kOe in the temperature range 2-300 K (from these data the effective magnetic moment μ_{eff} and paramagnetic Curie temperature θ_p were obtained) and magnetization measurements in magnetic fields up to 50 kOe at about 2 K (in order to get the value of the pseudo-saturated magnetic moment and the character of the magnetization curve). Since the crystallites had not well defined shapes, no demagnetization effects were taken into account.

XPS spectra were obtained at room temperature using a Leybold LHS10 electron photoemission

spectrometer with MgK_α ($h\nu = 1253.6$ eV) and AlK_α ($h\nu = 1486.6$ eV) radiation in a vacuum of about 10^{-9} mbar. The total energy resolution of the spectrometer with a hemispherical energy analyzer was about 0.75 eV for Ag 3d. Binding energies were referred to the Fermi level ($E_F = 0$). The spectrometer was calibrated using Cu 2p_{3/2} (932.5 eV), Ag 3d_{5/2} (368.1 eV) and Au 4f_{7/2} (84.0 eV) core-level photoemission spectra. The surface of the sample was mechanically cleaned by scraping with a diamond file in a preparation chamber under high vacuum (10^{-9} mbar), and then moved immediately into the analysis chamber. This procedure was repeated until the C 1s and O 1s core-level peaks were negligibly small, or were not changed after further scraping. This cleaning procedure was performed before each XPS measurement. The Shirley method [5] was used to subtract the background and then the experimental spectra were numerically fitted using a 80 % Gaussian and 20 % Lorentzian model.

Results

The investigated Ce₂MnGe₆ sample has an orthorhombic crystal structure of the Ce₂CuGe₆ type. The lattice parameters refined to $a = 0.4103(5)$ nm, $b = 0.4342(5)$ nm and $c = 2.188(1)$ nm. Fig. 1 shows the temperature dependence of the magnetic moment and of the reciprocal magnetic susceptibility of Ce₂MnGe₆ between 2 and 300 K. In the temperature range 2-150 K a spontaneous magnetic moment exists. Above 150 K the reciprocal magnetic susceptibility obeys the Curie-Weiss law with an effective magnetic moment equal $5.3 \mu_B$ for the formula unit and a paramagnetic Curie temperature equal +150 K. The magnetization curve measured at 2 K in fields up to 50 kOe (inset of Fig. 1) shows the ferromagnetic character. A sharp jump of the magnetization at low field, followed by an increase ($0.012 \mu_B/\text{kOe}$) with increasing magnetic field, is observed. The magnetic moment at 2 K in a magnetic field of 50 kOe is $2.5 \mu_B$.

The XPS valence band spectrum extending from the Fermi energy level located at 0 eV to a binding energy of about 15 eV is presented in Fig. 2. The valence band is dominated by a broad maximum at 2.1 eV corresponding to the Mn 3d states. Near the Fermi level, at 0.3 eV, a small peak corresponding to the Ce 4f state is observed. The peaks at 6.6 and 9.7 eV correspond to the Ge 4s and 4p states. The Ce 4f and Mn 3d states overlap. In order to obtain information on the electronic structure of the Ce atoms, the Ce 4d and Ce 3d states were analyzed (Fig. 3). For both states the spin-orbit splitting dominates in the spectral structure and is equal 2.8 eV for the Ce 4d states and 18.7 eV for the Ce 3d states. This splitting is typical for cerium intermetallic compounds. For both states the spin-orbit splitting dominates in the spectral structure and is equal 2.8 eV for the Ce 4d states and 18.7 eV for the Ce 3d states.

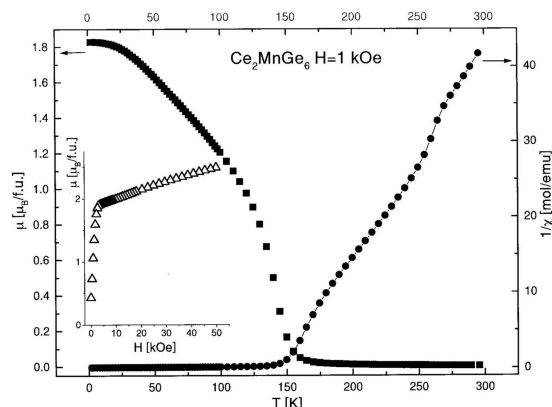


Fig. 1 Temperature dependence of the magnetic moment and the reciprocal magnetic susceptibility of Ce₂MnGe₆ in an external magnetic field equal 1 kOe. The inset shows the magnetization curve at 2 K.

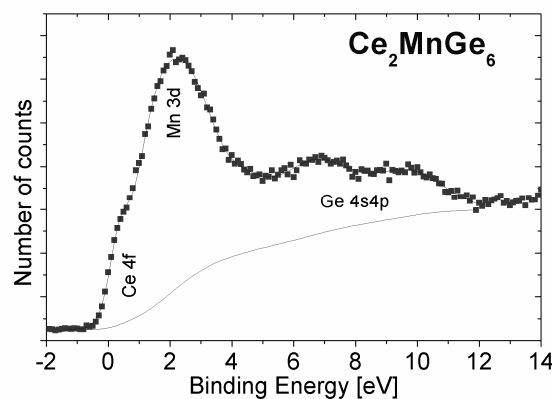


Fig. 2 XPS valence band spectrum of Ce₂MnGe₆.

This splitting is typical for cerium intermetallic compounds. On the low-binding-energy side of the 3d_{5/2} and 3d_{3/2} main lines shake-down satellites are observed. The separation of these peaks is explained by the Doniach-Šunjić theory [6], which yields the intensity ratio $r = I(f^2)/[I(f^1) + I(f^2)]$. On the basis of the Gunnarsson-Schönhammer model [7] it was possible to determine the hybridization energy Δ between the 4f states and the conduction electrons. The parameter Δ is defined as $\pi V^2 \rho_{\text{max}}$, where V is the hybridization matrix element and ρ_{max} is the maximum of the density of states of the conduction band. The r value is equal 0.2 and the corresponding hybridization energy is 93 meV. The absence of a peak corresponding to the Ce 4f⁰ state indicates that cerium is present as trivalent ions.

The Mn 2p states form band peaks with a spin-orbit splitting equal 11.4 eV and a complex structure, which is caused by different atomic surroundings and oxidation (Fig. 4).

The analysis of the Ge 3p and Ge 2p states indicates that the values of the binding energy and the spin-orbit splittings 4.0 eV for the Ge 3p states and 31.0 eV for Ge 2p states are near the values of the pure element given in [8].

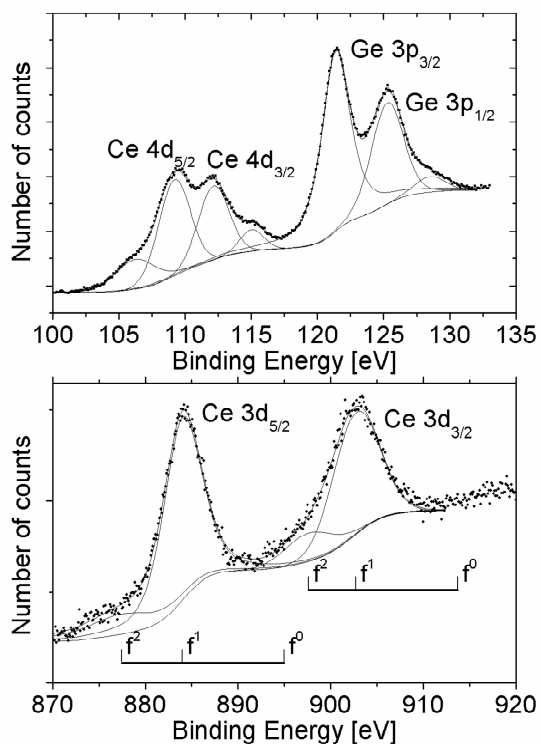


Fig. 3 (a) Ce $4d_{5/2}$, Ce $4d_{3/2}$, Ge $3p_{3/2}$ and Ge $3p_{1/2}$, and (b) Ce $3d_{5/2}$ and Ce $3d_{3/2}$ XPS spectra of Ce_2MnGe_6 .

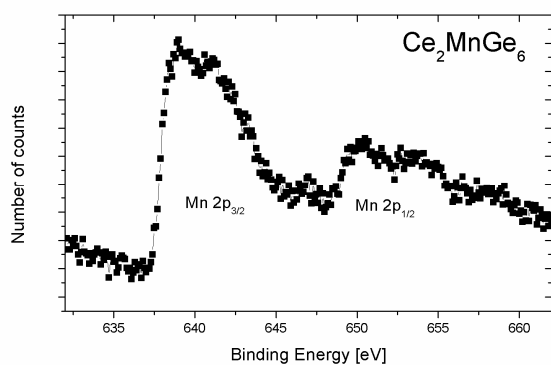


Fig. 4 Mn $2p_{3/2}$ and Mn $2p_{1/2}$ spectrum of Ce_2MnGe_6 .

Conclusions

The results presented in this work indicate that Ce_2MnGe_6 is a ferrimagnet with a Curie temperature of 150 K. A comparison of the value of the critical temperature of the magnetic order of Ce_2CuGe_6 with those observed for other R_2CuGe_6 compounds [3], and the high value of the Curie temperature of Ce_2MnGe_6 , indicate that the Mn magnetic moments order in the latter. The field dependence of the magnetization suggests a complex ferrimagnetic ordering.

The XPS data indicate that cerium is trivalent and that the hybridization of the Ce 4f states with electrons of the conduction band is weak. Assuming a trivalent cerium ion, the effective manganese moment is $3.9 \mu_B$. The value of the magnetic moment in the ordered state equals $2.5 \mu_B$, indicating a ferri- or complex magnetic structure.

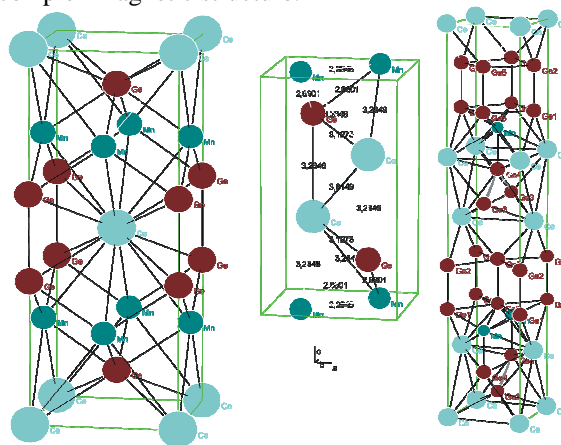


Fig. 5 Crystal structures of (a) CeMn_2Ge_2 , (b) CeMnGe and (c) Ce_2MnGe_6 .

Two other compounds in the Ce-Mn-Ge ternary system have different magnetic structures. The CeMnGe and CeMn_2Ge_2 compounds have tetragonal crystal structures of the CeFeSi type (space group $P4/nmm$) and CeAl_2Ga_2 type (space group $I4/mmm$), respectively. The crystal structures of these compounds and of Ce_2MnGe_6 are shown in Fig. 5. In CeMnGe below $T_t = 130$ K both the Ce and the Mn

Table 1 Values of $\Delta_{ij} = d_{ij} - (R_i + R_j)$ for CeMnGe , CeMn_2Ge_2 and Ce_2MnGe_6 ; d_{ij} is the interatomic distance between the atoms i and j , R_i and R_j are their atomic radii.

CeMn_2Ge_2			CeMnGe			Ce_2MnGe_6		
Ce	- Ge	$\Delta = 0$	Ce	- Ce	$\Delta = -0.04$	Ce	- Ce	$\Delta = +0.61$
Ce	- Mn	$\Delta = +0.35$	Ce	- Mn	$\Delta = +0.20$	Ce	- Mn	$\Delta = +0.24$
Mn	- Mn	$\Delta = +0.41$	Ce	- Ge	$\Delta = +0.07$	Ce	- Ge1	$\Delta = +0.1$
Mn	- Ge	$\Delta = -0.08$	Ge	- Ge	$\Delta = -0.06$	Ge2	- Ge2	$\Delta = +0.01$
			Mn	- Mn	$\Delta = +0.47$	Ge3	- Ge3	$\Delta = +0.2$
			Mn	- Ge	$\Delta = -0.03$	Ge4	- Ge4	$\Delta = -0.07$
						Ge5	- Ge5	$\Delta = -0.15$
						Ge6	- Ge6	$\Delta = +0.06$

moments form collinear antiferromagnetic structures. At 2 K the moments of Ce and Mn are equal 2.24(6) μ_B and 3.15(4) μ_B , respectively. Above 130 K up to the Néel temperature equal 532 K only the Mn moments order [9].

In the temperature range 2-300 K, CeMn₂Ge₂ ($T_C = 320$ K) exhibits an easy axis conical magnetic structure with a total Mn moment of about 2.7 μ_B at 2 K. The Ce magnetic moments do not order above 1.6 K [10].

These results indicate that the magnetic ordering changes with the crystal structure and the concentration of Ce and Mn atoms. A comparison of the interatomic distances in the three compounds discussed above with the sum of atomic radii is given in Table 1.

Neutron diffraction experiments are necessary to explain the magnetic properties of Ce₂MnGe₆ at low temperatures.

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