

ELECTRONIC AND MAGNETIC STRUCTURE OF GdMnGe

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Abstract: The electronic and magnetic structure of GdMnGe was investigated by the electronic structure calculations and by the X-ray photoemission spectroscopy (XPS) measurements. Spin-polarized calculations were performed for the ferrimagnetic and antiferromagnetic states of GdMnGe. In both cases the calculations have shown that the *d* bands are strongly polarized giving rise to the local magnetic moments of magnitudes of 0.25-0.35 μ_B at Gd sites and over 3 μ_B at Mn sites. For the ferrimagnetic order the calculations resulted in the antiparallel alignment of the local Gd-4*f* and Mn-3*d* moments. The calculations have proved that the antiferromagnetic order is more stable for GdMnGe than the ferrimagnetic one what agree with the most recent magnetic data.

1. INTRODUCTION

The group of RTX compounds, where R is a rare earth element, *T* is a transition 3*d* element and X is Si or Ge has been widely investigated mainly due to a variety of interesting magnetic properties. Recently we have reported on ferromagnetism in GdTiGe and in the compounds obtained by Mn substitution of Ti where T_C varies in the temperature range 374-430 K [1, 2].

Among the known RTX system only Mn compounds have essential magnetic moment in the 3*d* sublattice [3]. The Mn sublattice orders either ferro- or antiferromagnetically. For example TbMnGe orders antiferromagnetically below $T_N = 510$ K and the value of Mn moment at 2 K is 3.53 μ_B [4].

GdMnGe crystallizes in the orthorhombic TiNiSi type of structure (*Pnma*), where the lattice constants, obtained from the x-ray diffraction, are: $a = 7.14$, $b = 4.17$, $c = 8.20$ Å [2]. In this structure Gd, Mn and Ge atoms occupy the 4*c* positions with coordinates given in Table I. The unit cell consists of four formula units. Klosek *et al.* [5] have found that antiferromagnetic Mn₂-Mn₄ (and Mn₁-Mn₃) chains produce a non-zero molecular field on R atoms, yielding an antiferromagnetic R₂-R₄ coupling. The antiferromagnetic order has the layered character (Table I).

GdMnGe exhibits an antiferromagnetic type of ordering with $T_N = 490$ K [5], whereas we have found two additional transitions of the antiferromagnetic like character at 337 and 102 K [2].

The nearest Mn-Mn distance has been found to be a factor determining the magnetic moment and coupling. For $d_{\text{Mn-Mn}} > 2.89$ Å [4, 5] or 2.86 Å [6] an antiferromagnetic coupling has been found, whereas for smaller distances ferromagnetic or mixed interactions have been reported. The shortest Mn-Mn distance within TiNiSi-type of structure equals 3.147 Å and it is in agreement with the antiferromagnetic coupling within the Mn sublattice [2].

Table I. Coordinates and the magnetic alignment in the AFM state of the magnetic atoms in the crystallographic non-equivalent positions (Pos) of GdMnGe ($x_R=0.0236$, $z_R=0.6785$, $x_{Mn}=0.1399$, $z_{Mn}=0.0581$)

	Pos	Coordinates	AFM		Pos	Coordinates	AFM
Gd (4c)	1	$x_R, 1/4, z_R$	↑	Mn (4c)	1	$x_{Mn}, 1/4, z_{Mn}$	↑
	2	$1/2 - x_R, 3/4, 1/2 + z_R$	↓		2	$1/2 - x_{Mn}, 3/4, 1/2 + z_{Mn}$	↓
	3	$x_R, 3/4, -z_R$	↓		3	$x_{Mn}, 3/4, -z_{Mn}$	↓
	4	$1/2 + x_R, 1/4, 1/2 - z_R$	↑		4	$1/2 + x_{Mn}, 1/4, 1/2 - z_{Mn}$	↑

The aim of this paper is to present the comparison between the ferrimagnetic and antiferromagnetic types of the electronic structure calculations for GdMnGe.

2. RESULTS AND DISCUSSION

The band-structure calculations were carried out with the use of tight-binding linear muffin-tin orbital (TB-LMTO) method of Andersen *et al.* [7]. The calculations were scalar relativistic, without the spin-orbit interaction. The exchange-correlation (XC) potential was taken within local spin-density approximation (LSDA), with the use of the von Barth-Hedin [8] parametrization, explicit form of which was cited in e.g. [9]. The non-local correction to XC potential was taken into account within the Langreth-Mehl-Hu (LMH) gradient approximation [10].

In the TB-LMTO method the crystal potential is treated within the atomic-sphere approximation (ASA) and the crystal volume is divided into overlapping Wigner-Seitz (W-S) spheres of radius r_s^i . To reduce the effect of overlapping spheres the standard combined correction [9] was used in calculations. The ASA demands the volume equation to be obeyed. If by

$$r_s^{av} \left(= \sqrt[3]{\frac{3}{4} \frac{V}{\pi n_{at}}} \right)$$

denote the average *W-S* radius then the volume equation reads

$$\sum_{i=1}^{n_{at}} (w_i)^3 = n_{at}$$

where n_{at} is the number of atoms in the unit cell and $w_i = r_s^i / r_s^{av}$. Because of the loosely packing of the GdMnGe crystal structure the volume equation cannot be satisfied with the reasonable values (< 20%) of the atomic sphere's overlap. To solve this problem the eight artificial atoms with $Z=0$ (so called "empty spheres") were introduced into the calculated unit cell. The crystal space group for the antiferromagnetic order was $P2_1ma$ (No. 26) with the atomic positions specified in Table I.

Figures 1 and 2 show partial and total DOS's for GdMnGe, together with the simulated XPS spectra obtained for two different magnetic structures. The presented in the paper XPS spectra were simulated by convolution of the calculated partial DOS contributions by Lorentzians with a half-width of 0.4 eV and then multiplication by the corresponding cross-sections taken from reference [11].

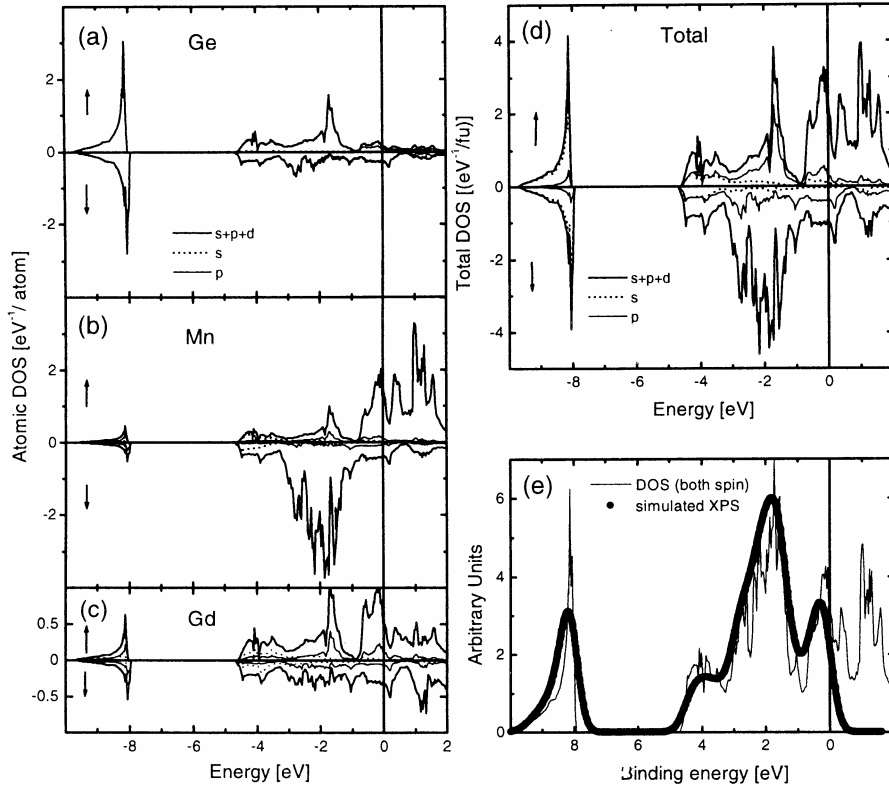


Fig. 1. Spin- and orbital resolved atomic (a, b, c) and total (d) density of states (DOS) from the ferrimagnetic calculations for GdMnGe. Panel (e) shows the total (both spin, $s + p + d$) DOS with the simulated XPS spectrum in front (thick line)

Figure 1 corresponds to the results of ferromagnetic alignment within the Mn and Gd sublattices. For clarity the $4f$ bands of Gd are not included to the figure because they would give a relatively high and unphysical peak at about 4 eV in the calculated spectra. Their positions predicted from calculations are -4 and 1 eV for occupied and unoccupied bands with two times smaller binding energy (BE) than measured (well known deficiency of Local (Spin) Density based methods). The main contribution to the valence bands comes from the Mn d , Gd d and Ge p states. Calculations predict the antiparallel magnetic polarization of Gd and Mn d -bands. It confirms the established model of R-T interaction. The polarization of the Gd d band ($0.35 \mu_B$) is parallel to the $4f$ magnetic moment whereas an average Mn atom carry an anti-parallel moment of $3.17 \mu_B$, so the calculation gives a ferrimagnetic type of magnetic order. It is in general agreement with the magnetic data [5] where a moment on Mn of $3.4(2) \mu_B$ has been obtained. Table II summarizes detailed information on the partial magnetic moments, charge transfer and total densities of states for both types of calculations.

The results of the antiferromagnetic type of calculations, presented in Fig. 2, are based on the following assumptions. Both Mn and Gd sublattices are ordered antiferromagnetically. It leads to a considerable modification of total and partial DOS's. The maximum of the Mn $3d$

DOS is shifted to lower energy in relation to the ferrimagnetic case. The wide pseudo-gap obtained within the ferromagnetic solution for majority spin DOS at binding energy of about 1 eV disappears. The total energy is also lower indicating to preferential antiferromagnetic order. The calculated gain of total energy for the antiferromagnetic structure with respect to the ferrimagnetic case is of the order of 400 K per atom. It corresponds well with the reported experimental Neel temperature (490 K). The experimental XPS spectrum of GdMnGe is reproduced better by the antiferromagnetic density of states.

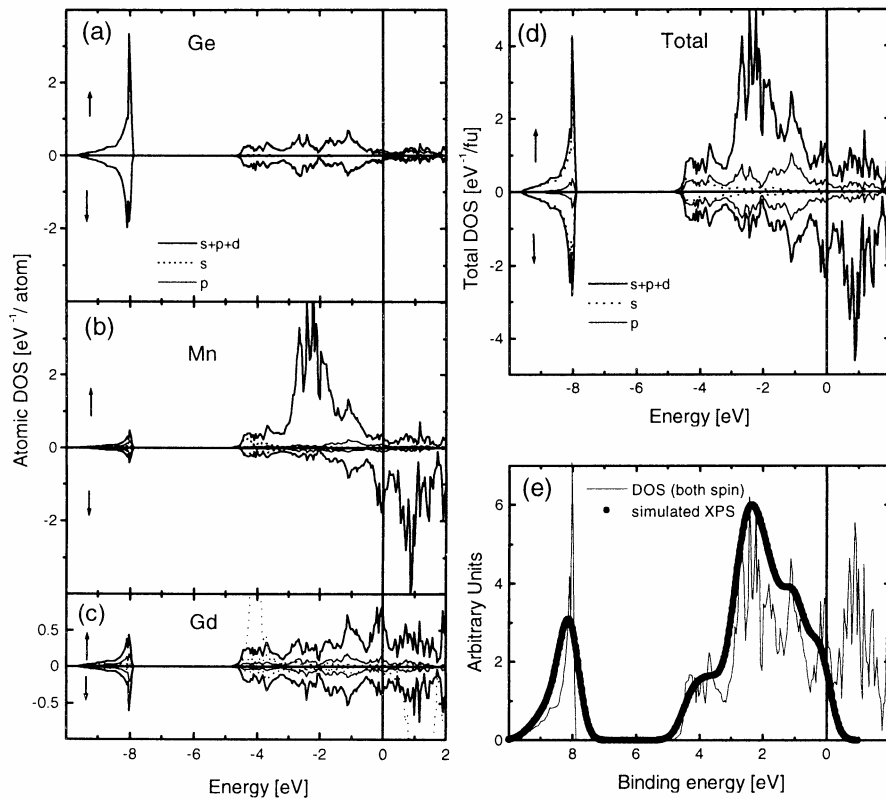


Fig. 2. DOS and simulated XPS for the antiferromagnetic calculations. Description as for Fig. 1

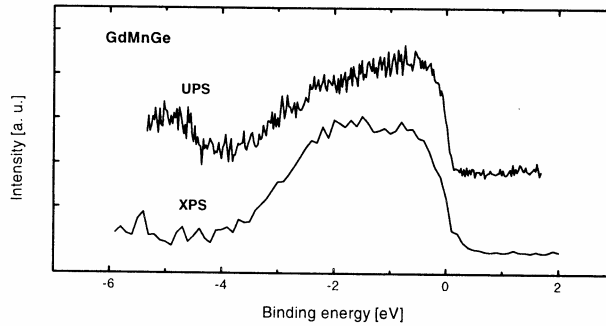
The modeled spectrum is characterized by a very pronounced peak at about 2 eV. It may be related to some overestimation of the photoionization cross section for Mn 3d states. We have used the values obtained for atomic orbitals [11].

The DOS at the Fermi level is dominated by the d bands of Gd and Mn, the density of states is larger in the antiferromagnetic case (Table II). Hybridization effects can be noticed in the atomic DOS's especially in the region of BE about 2 eV and for Gd and Mn *d*-states just below the Fermi level. Despite the measured XPS (and UPS) spectrum (Fig. 3) is much less featured than the simulated one, some common elements can be found. Both have the highest amplitude peak at 2~eV of BE and a small bump at BE of 4 eV.

Table II. Partial atomic magnetic moments with separated orbital components resulted from the ferromagnetic (FM) and antiferromagnetic (AFM) calculations for GdMnGe. For the AFM case only the up-spin-sublattice magnetic moments are reported. The $D(\epsilon_F)$ denotes the total DOS at the Fermi energy

Magnetic case	Atom	ΔQ	μ (μ_B /atom)			Total
			$s+p$	d	f	
AFM	Gd	0.034	0.05	0.24	6.86	7.15
	Mn	-0.190	0.13	3.18	0.00	3.31
	Ge	-0.110	0.01	-0.01	0.00	0.00
$D(\epsilon_F) = 4.0 \text{ eV}^{-1}/\text{fu}$ $M_{\text{tot}}^{\uparrow} = 10.46 \mu_B/\text{fu}$						
FM	Gd	0.044	0.1	0.35	6.87	7.32
	Mn	-0.170	-0.07	-3.10	0.00	-3.17
	Ge	-0.144	0.11	0.00	-0.01	0.10
$D(\epsilon_F) = 3.13 \text{ eV}^{-1}/\text{fu}$ $M_{\text{tot}} = 4.25 \mu_B$						

Fig 3. XPS and UPS He II spectra of the valence band of GdMnGe after background subtraction



The band structure calculations have shown that the magnetic ground state of GdMnGe is of the antiferromagnetic type, in agreement with the preliminary magnetic measurements. The further investigations of the local magnetic properties will be performed using the XMCD method.

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