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Spin and orbital polarization in layered rare-earth–manganese ternary intermetallic compounds

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Abstract

We report the results of *ab initio* energy-band calculations for the ternary intermetallic compound GdMn_6Ge_6 . The ferrimagnetic arrangement of Gd and Mn magnetic sublattices is reproduced as well as the average moment per Mn atom. The comparatively low strength of the Gd–Mn effective exchange coupling and the occurrence of a weak orbital polarization (3%) at the manganese sites are further results of this analysis. The numerical results are compared with prior magnetization and hyperfine-field analyses.

1. Introduction

Rare-earth–manganese (R–Mn) intermetallic compounds have received considerable attention in recent years, because the existence of a manganese moment and the sign of the exchange coupling depend critically on the Mn distances [1–3]. The layered ternary intermetallic compound GdMn_6Ge_6 (figure 1) crystallizes in the HfFe_6Ge_6 -type structure (space group $P6/mmm$) [4]. The structure is built up of alternate (001) layers containing Gd and transition metal, respectively. The Gd atoms build hexagonal planes and the Mn atoms Kagomé nets, stacked along the c -axis in the sequence $\cdots\text{KHKKHK}\cdots$. The three inequivalent Ge sites possess hexagonal symmetry. The lattice constants, which were also used for the self-consistent energy-band calculations, are $a = 5.2428 \text{ \AA}$ and $c = 8.1813 \text{ \AA}$. GdMn_6Ge_6 orders ferrimagnetically at $T_c = 459 \text{ K}$ but undergoes a complicated sequence of phase transitions at lower temperatures [5–7]. These magnetic phases were unravelled on the basis of temperature- and field-dependent magnetization measurements combined with a detailed NMR analysis [7–10]. In particular, the Mn atoms carry a magnetic moment of about $2 \mu_B$ coupled ferrimagnetically to the Gd moment. For the pseudo-ternary compounds $\text{Gd}_{1-x}\text{Y}_x\text{Mn}_6\text{Ge}_6$ the ordering temperature is essentially independent of the Gd concentration when Y is substituted for Gd, indicating that the ordering is due to the Mn sublattice, and the moment on the Mn sublattice remains constant.

Whereas model calculations in terms of a molecular-field approximation can describe the complex magnetic properties and phase diagrams even for pseudo-ternary compounds such

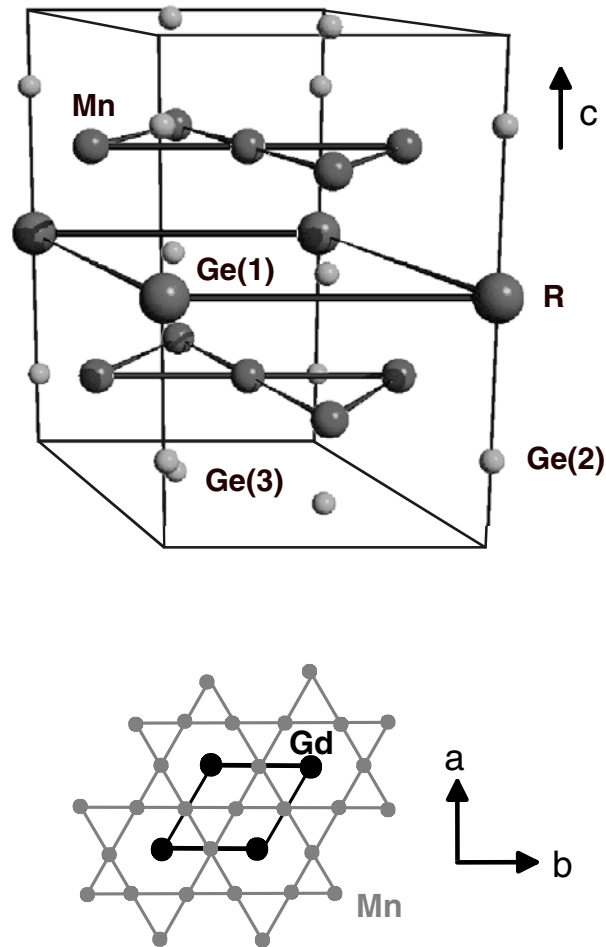


Figure 1. The crystal structure of RMn_6Ge_6 ($HfFe_6Ge_6$ structure) [4]. (a) There are three crystallographically and magnetically inequivalent Ge sites. (b) Gd positions and the Mn Kagomé net (seen along c).

as $Gd_{1-x}Y_xMn_6Ge_6$ reasonably well [8], the physical interpretation of the parameters derived phenomenologically is aided by an *ab initio* calculation. This also enables the manipulation of parameters such as the 4f moment and lattice constant in order to elucidate the physical mechanisms responsible for the observed phenomena. Such an analysis is described here for the ferrimagnetic phase of the parent compound $GdMn_6Ge_6$.

2. Self-consistent band-structure calculations for rare earths

The *ab initio* self-consistent energy-band calculations were carried out using the linear-muffin-tin-orbital (LMTO) method [12] in the atomic sphere approximation (ASA) with potentials obtained from the local-spin-density approximation [13] (LSDA) to density functional theory [14].

2.1. Constrained DFT theory: localized open-shell states

Since the 4f states in Gd are localized, they were not included in the basis set of the conduction bands. The atomic physics of the 4f states is well understood and is summarized in the standard model for the rare earths [11]. Our objective is to be able to describe the interactions between the localized 4f states and conduction electron states by a reasonable approximation to the LSDA but consistently with the standard model where the lowest energy eigenstates have maximum magnitude of S according to Hund's first rule. The 4f ground state, with a given value of J , has a well defined average component of the spin along the quantization axis and the spin density and charge densities may be obtained by constraining the 4f occupation numbers such that

$$n_{4f} = n_{4f}^+ + n_{4f}^- \quad (1)$$

and

$$m_{4f}^s = 2(g_J - 1)J = n_{4f}^+ - n_{4f}^- \quad (2)$$

where m_{4f}^s is the Russel–Saunders spin component of the moment along the quantization axis. The total radial 4f charge and spin densities are then computed from

$$n_{4f}(r) = n_{4f}^+ |\phi_{4f}^+(r)|^2 + n_{4f}^- |\phi_{4f}^-(r)|^2 \quad (3)$$

and

$$m_{4f}^s(r) = n_{4f}^+ |\phi_{4f}^+(r)|^2 - n_{4f}^- |\phi_{4f}^-(r)|^2 \quad (4)$$

and they are added to the core and conduction electron densities to obtain the total charge and spin densities as part of the self-consistent calculation.

Constrained density functional calculations of this kind deliver ground-state charge and spin densities consistent with a variational calculation of the lowest ground-state energy subject to the above-mentioned condition on the 4f spin and charge [15]. Consequently one would expect to be able to calculate correctly the conduction electron spin magnetic moment and its resolution according to the orbital quantum number and site and to determine the influence of the 4f moment upon the conduction electron moment. Calculations were also made for several values of the 4f spin between zero and seven (with the total number of 4f electrons equal to seven) by changing the occupation of the spin-up and spin-down states, which simulates the substitution of Gd by Y.

2.2. Spin-polarized calculations

GdMn₆Ge₆ is a fairly complex compound with thirteen atoms in the primitive cell; therefore the calculations were first made with the omission of spin–orbit interaction, in which approximation the spin-up and spin-down bands are uncoupled. The calculated electronic structure is summarized by the plot of partial Mn 3d and Gd 5d densities of states against energy shown in figure 2. The low-lying partial 3d and 5d densities of states around -9 eV, which are barely visible, are due to hybridization with Ge states which lie around this energy. The main part of the band structure is composed of hybridized Mn 3d and Gd 5d energy bands extending from -6 eV below, and crossing, the Fermi energy. In an atomic orbital representation in which the d-wave functions are continued outside the Mn spherical potential, these energy bands are essentially Mn 3d bands but, in the LMTO representation, the Mn 3d states must be re-expanded in the Gd spherical potential close to the Gd nuclei from where they appear as Gd 5d states. The small Gd 5d density of states is therefore due to the tails of the Mn 3d wave functions. Gd has about 1 sp and 1.6 5d electrons and there are about 5 Mn 3d electrons. The bonding is due to the Mn 3d and Gd 5d states with the repulsive interactions arising from

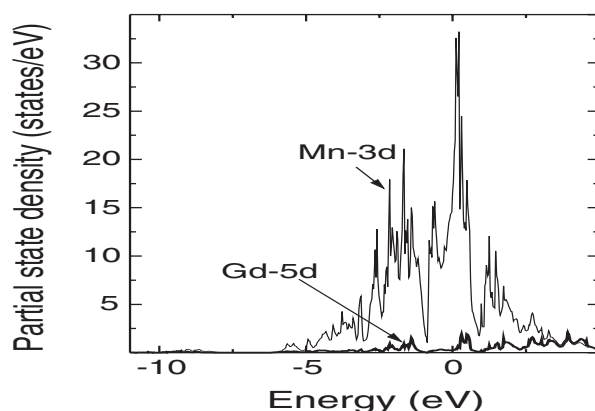


Figure 2. Calculated partial Mn 3d and Gd 5d densities of states for GdMn_6Ge_6 . The zero of energy is the Fermi level.

the cores through the orthogonality of the sp conduction electron states to the core states, leading to positive sp conduction electron pressure. By constraint, the Gd 4f states play no role in the bonding. The calculated lattice constant is almost exactly correct, indicating that the self-consistent calculations are sound.

A summary of the numerical results is shown in table 1, and the main contributions to the calculated conduction electron moment as a function of 4f spin are plotted in figure 3. Clearly the compound is ferrimagnetic and the magnetic moment arises almost entirely from the Mn 3d and Gd 4f electrons. The total moment remains almost constant as the 4f moment is changed. The ferrimagnetically coupled Mn 3d and Gd 5d contributions both increase with the Gd 5d moment, changing more rapidly than the Mn 3d moment per atom. But there are six Mn atoms for each Gd atom and the total Mn 3d moment per cell just cancels the increase in Gd 5d moment with the net result that the total spin remains unchanged but the conduction electron spin density is transferred from the Mn sites to the Gd site.

Table 1. Resolved spin moments of gadolinium, manganese, and germanium in GdMn_6Ge_6 .

Atoms	$nl(l)$	μ_l^s/μ_B	$\sum_{n,l} \mu_l^s/\mu_B$
Gd	5d(2)	-0.35	-7.45
	4f(3)	-7.00	
6Mn	3d(2)	+12.49	+12.54
Ge(1)	4p(1)	-0.24	-0.24
Ge(2)	4p(1)	-0.26	-0.26
Ge(3)	4p(1)	-0.24	-0.21

The Gd 5d spin density plays a crucial role in coupling the Gd 4f and Mn 3d moments. In the LSDA, exchange interactions are strictly local and there is no exchange interaction between Gd 4f and Mn 3d states since they do not overlap in the LMTO representation. The

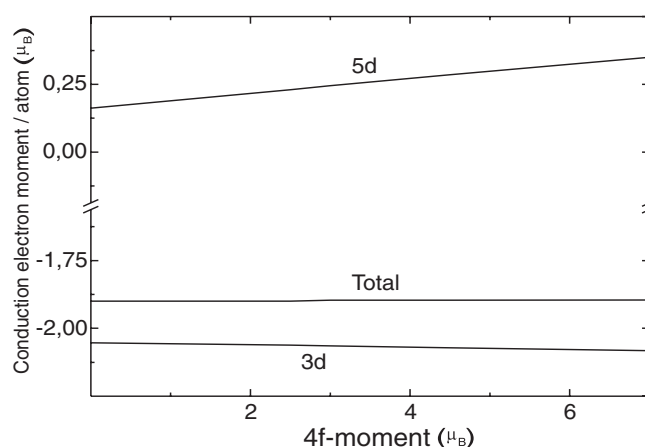


Figure 3. The calculated influence of the 4f moment on the spin polarization of the d shell at the manganese and rare-earth sites in hypothetical $(\text{Gd/Y})\text{Mn}_6\text{Ge}_6$. The sign of the moments is relative to the Gd 4f moment and the Mn 3d moment is per atom.

exchange interaction between Gd 4f and Gd 5d states is positive and they polarize parallel, whereas hybridization between Gd 5d and Mn 3d states leads to a negative interaction and they are coupled antiparallel [2]. However, since the Gd 5d states are continuations of the Mn 3d states, in an extended orbital representation the exchange interaction between 4f and 3d states would be direct. As the larger total moment of the six Mn atoms will be parallel to the external field, the Gd moment is antiparallel to the field.

The ferrimagnetic hybridization between the Gd 5d and Mn 3d moments thus gives rise to the overall ferrimagnetic arrangement of the Gd 4f and Mn 3d moments [2]. The calculated total moment per formula unit of GdMn_6Ge_6 is $4.4 \mu_B$. For a Gd moment of $-7 \mu_B$ this yields an ‘average Mn moment’ of about $1.9 \mu_B$, in very good agreement with the result of the macroscopic magnetization measurements [8] and the NMR analysis [10].

One advantage of the constrained self-consistent calculations is that it is possible to eliminate the influence of the exchange polarization by the Gd 4f moments in GdMn_6Ge_6 without changing the lattice structure or electronic configuration—in contrast to the case for the pseudo-ternary series $\text{Gd}_{1-x}\text{Y}_x\text{Mn}_6\text{Ge}_6$ that was used in experiment [8]. There is only a small reduction of the manganese moment when μ_{4f} is reduced to zero (figure 3). This tendency was also observed in experiment for reduced Gd concentration in the pseudo-ternary series [8]. We also note that the 5d spin polarization at the rare-earth site is reduced by a little more than a factor of two, leaving substantial rare-earth 5d spin density even for zero 4f moment. This is in agreement with the experimental finding that substantial hyperfine field is transferred from Mn moments to the Gd nucleus also above the ordering temperature of the Gd sublattice in GdMn_6Ge_6 (see e.g. figure 13 of [9]).

2.3. Spin–orbit interaction and orbital magnetism

Relativistic self-consistent calculations were also made to determine the orbital magnetic moments at the different sites and their resolution according to quantum number. As expected, the orbital magnetism in the conduction bands was found to be quite weak with orbital moments of about $0.07 \mu_B$ at the Mn sites. The isotropic part of the hyperfine field at the $^{155,157}\text{Gd}$, ^{55}Mn , and ^{73}Ge nuclei was estimated with the known coupling constants [17]. Correct order

of magnitude and sign (as far as experimentally known) were obtained, with disagreement in the hyperfine-field ratios for the three Ge sites, however [10]. This discrepancy could be due to the limited accuracy of the hyperfine coupling parameters and the counteraction of *s* and *p* polarizations at the Ge nucleus.

It has been reported already that the hyperfine interaction at the ^{55}Mn site is anisotropic by at least 10% [9, 10]. This points to the influence of an orbital moment at the Mn site. Assuming that *only* orbital polarization causes the anisotropy, the respective moments

$$\mu_{l,\parallel} = -\langle l_{\parallel} \rangle \mu_{\text{B}} \quad (5)$$

can be estimated from

$$H_{\text{hf,orb}} = -2\mu_{\text{B}} \langle r_{3\text{d}}^{-3} \rangle \langle l_{\parallel} \rangle \quad (6)$$

with $\langle r_{3\text{d}}^{-3} \rangle = 2.868 \times 10^{25} \text{ cm}^{-3}$ [18]. The range of $\mu_l = -3.1 \times 10^{-2} \mu_{\text{B}}$ to $+4.8 \times 10^{-2} \mu_{\text{B}}$ estimated with equations (5) and (6) from the anisotropic Mn hyperfine contribution [10] compares favourably with the average value of the calculated Mn 3d orbital moments

$$\mu_l = -\sum p_{lm} m_l \mu_{\text{B}} \quad (7)$$

of $5.6 \times 10^{-2} \mu_{\text{B}}$ for the crystallographic *c*-direction. Thus we may reasonably conclude that an orbital moment of about 3% of the spin moment is induced by spin-orbit interaction at the low-symmetry (*2mm*) manganese sites of GdMn_6Ge_6 in the ferrimagnetically ordered phase.

3. Model electronic structure

The model electronic structure proposed for LuFe_2 [16] applies quite well to GdMn_6Ge_6 and YMn_6Ge_6 . The 60 unhybridized Mn 3d bands lie below the Fermi energy and contain about 34 electrons. The 10 unhybridized Gd 5d bands lie above the Fermi energy and are empty. The amount of charge transferred to the Gd 5d bands, which we calculate to be $n_{5\text{d}} = 1.64$ electrons, may be estimated in second-order perturbation theory in terms of the hybridization structure constants, the bandwidths, the fractional occupation of the Mn 3d bands (34/60), and the difference in energy between the centres of the Mn 3d and Gd 5d bands ($\Delta C = 260 \text{ mRyd}$). The model may also be used to estimate the Gd 5d moment through the formula [16]

$$\mu_{5\text{d}} = N_{3\text{d}-5\text{d}} \frac{g_{3\text{d}} + f_{3\text{d}} [J_{3\text{d}} \mu_{3\text{d}} - J_{5\text{d}} \mu_{5\text{d}} - J_{4\text{f}-5\text{d}} \mu_{4\text{f}}^s] / \Delta C}{1 + n_{5\text{d}} J_{5\text{d}} / \Delta C} \quad (8)$$

where $N_{3\text{d}-5\text{d}} = 3.03$ is the charge transferred from completely filled Mn 3d bands to Gd 5d bands, $g_{3\text{d}} = 12/60$ is the fractional spin of the Mn 3d bands; $J_{3\text{d}} = 54 \text{ mRyd}$, $J_{5\text{d}} = 48 \text{ mRyd}$, and $J_{4\text{f}-5\text{d}} = 6.9 \text{ mRyd}$ are the Mn 3d3d, Gd 5d5d, and Gd 4f5d exchange integrals, respectively. $\mu_{3\text{d}} (=2 \mu_{\text{B}})$ and $\mu_{4\text{f}}^s$ are the Mn 3d and Gd 4f moments. This formula yields

$$\mu_{5\text{d}} = \frac{3.03[0.20 - 0.226]}{0.7} = -0.11$$

for $\mu_{4\text{f}}^s = 0$ compared with a value of -0.16 calculated self-consistently, and reveals that the two contributions—one due to spin transfer from Mn 3d to Gd 5d bands proportional to $\mu_{3\text{d}}$ (which is positive) and the other due to greater hybridization of the spin-down bands (which is negative)—almost cancel for YMn_6Ge_6 . Consequently the coupling between the Mn 3d and Gd 5d moments is weak. The reasons for the cancellation are the relatively large values of $\mu_{3\text{d}}$ and $g_{3\text{d}}$ due to the Mn 3d bands being close to half-filled. A Gd 4f moment increases the second contribution in equation (8) and strengthens the coupling between the Mn 3d and Gd 5d moments.

4. Relationship to molecular-field models

The magnetic energy of the conduction electrons, relative to the energy of the state with no 4f moment, may be written approximately in terms of the spin moment density:

$$E[m_c, m_f] = \frac{1}{2} \int A(\mathbf{r})(m_c^s(\mathbf{r}) - m_0^s(\mathbf{r}))^2 d\mathbf{r} - \frac{1}{2} \int J_{4f-5d}(\mathbf{r})m_{4f}^s(\mathbf{r})m_{5d}^s(\mathbf{r}) d\mathbf{r} \quad (9)$$

where m_0^s and m_c^s are the conduction electron moments corresponding to m_{4f}^s equal to zero or otherwise, respectively, m_{4f}^s is the 4f spin moment, J_{4f-5d} is the 4f–5d exchange interaction, and $A(\mathbf{r})$ is the inverse of the local susceptibility function. In equation (9) it is assumed that the rare-earth s and p spin densities are negligible, as is found in the self-consistent calculations. Due to the variational principle, changes in the energy due to fluctuations of spin density cancel to first order in $\delta m(\mathbf{r})$ and it may be shown that the change in energy, when the 4f moment is changed, may be written—after integrating over the atoms and using the fact that the total conduction electron moment remains constant as spin density is transferred from the Mn to Gd site—as

$$\delta E[m_c, m_f] = -\frac{1}{2} J_{4f-5d} \delta m_{4f}^s \left[m_{5d}^s + \frac{1}{2} \delta m_{5d}^s \right]. \quad (10)$$

The conduction electron moment which gives the energy change correct to $O(\delta m^2)$ is intermediate between the conduction electron moments in the initial and final 4f spin states. This energy may be compared with the energy in a molecular-field model derived from the Hamiltonian [8]

$$H = - \sum_{R \neq T} A_5 S_R S_T \quad (11)$$

in which case

$$A_5 = \frac{1}{6} (g_R - 1) J_{4f-5d} \frac{m_{5d}^s}{m_{3d}^s} \quad (12)$$

with $J_{4f-5d} = 94 \text{ meV} = 1018 \text{ K}$; $A_5 = 14 \text{ K}$ is calculated, compared with a value derived from the molecular-field model of 1 K. Despite the overestimate, both values are extremely small and there is consistency regarding the weak coupling between the sublattices.

5. Discussion

The results of *ab initio* energy-band-structure calculations for the ternary intermetallic compound GdMn_6Ge_6 yield the measured ferrimagnetic arrangement with all Mn moments mutually parallel but antiparallel to the Gd 4f moment. The average moment per manganese atom, derived from magnetization and nuclear magnetic resonance analysis, was reproduced. The weak coupling between rare-earth and manganese moments deduced from the phenomenological mean-field description [8] is supported by this *ab initio* analysis although the size of the coupling is overestimated by an order of magnitude. A weak orbital moment at the manganese sites is induced by spin–orbit coupling and explains the remarkable anisotropy of the manganese hyperfine interaction encountered in GdMn_6Ge_6 and related pseudo-ternary rare-earth–manganese compounds [10].

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