THE ELECTRONIC STRUCTURE OF THE RMn$_2$Ge$_2$
(R = Ca, Y, La, Ba) ANTIMAGNETS

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The electronic structure of the tetragonal RMn$_2$Ge$_2$ (R = Ca, Y, La, Ba) antiferromagnets is presented using the self-consistent Korringa–Kohn–Rostoker method. According to the neutron refiuements, two types of collinear antiferromagnetic structure are taken into account: AFB for YMn$_2$Ge$_2$ and AF2 for the other compounds. The calculated magnetic moments on Mn: $2.17 \mu_B$ (YMn$_2$Ge$_2$), $2.84 \mu_B$ (CaMn$_2$Ge$_2$), $2.95 \mu_B$ (LaMn$_2$Ge$_2$), and $3.47 \mu_B$ (BaMn$_2$Ge$_2$) remain in good agreement with the neutron data (in $\mu_B$) $2.20$, $2.67$, $3.05$, and $3.66$, respectively. As seen on antiferromagnetic density of states, all systems are metallic, however BaMn$_2$Ge$_2$ is found near semimetallic limit. The total energy Korringa–Kohn–Rostoker computations on CaMn$_2$Ge$_2$, performed in both antiferromagnetic phases, result in preferring of the AF$_2$ structure.

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1. Introduction

The magnetic properties of the well-known ternary RMn$_2$Ge$_2$ compounds [1] with the tetragonal ThCr$_2$Si$_2$-type structure have attracted renewed interest in recent years. Detailed neutron diffraction investigations of many RMn$_2$Ge$_2$ have revised previously detected ferromagnetic (F) structures (R = La–Nd) [2, 3] and explored the magnetic behavior of new compounds (CaMn$_2$Ge$_2$ and BaMn$_2$Ge$_2$ [4]). In LaMn$_2$Ge$_2$, antiferromagnetic ordering (AF$_2$) occurs below $T_N \approx 400$ K whereas rather canted magnetic structure than c-axis collinear ferromagnetism appears below $T_C$, with the antiferromagnetic component markedly larger ($\mu_{AF} = 2.7 \mu_B$) than the ferromagnetic one ($\mu_F = 1.5 \mu_B$). These results have been later supported by the Mössbauer effect measurements [5]. The three other entitled compounds show purely AF ordering of the Mn magnetic moments. There is a critical distance between Mn atoms in the $a$–$b$ plane ($d_{in} = a/\sqrt{2} \approx 2.86$ Å), where the magnetic properties change drastically (mostly due to the AF$_1$–AF$_2$ transition).
Thus, in YMn$_2$Ge$_2$ ($d_{\text{in}} = 2.82$ Å) $\mu_{\text{Mn}}$ are arranged parallel in the Mn plane and coupled AF between the planes (AF$_1$-type) [6], while in CaMn$_2$Ge$_2$ ($d_{\text{in}} = 2.94$ Å) and BaMn$_2$Ge$_2$ ($d_{\text{in}} = 3.14$ Å) the neighboring $\mu_{\text{Mn}}$ are aligned antiparallel both in and between the manganese planes (AF$_2$-type) [4]. Ishida et al. [7] have calculated the electronic structure of the "ferromagnetic" LaMn$_2$Ge$_2$ by the Korringa–Kohn–Rostoker (KKR) method. However, the theoretical values of $\mu_{\text{tot}}$ and $\mu_{\text{Mn}}$ have been found rather in disagreement with experimental data available at this time. Furthermore, Kulatov et al. [8] have discussed magnetic ordering of RMn$_2$Si$_2$ and magnetic transition near $d_{\text{in}} \approx 2.86$ Å, using the non-polarized linear muffin-tin orbital (LMTO) results.

The purpose of this paper is to show the electronic structure and magnetism of RMn$_2$Ge$_2$ using experimentally detected magnetic ordering of $\mu_{\text{Mn}}$.

2. Computational details

The spin-polarized calculations on the tetragonal body-centered (bct) RMn$_2$Ge$_2$ compounds are performed by the spin and charge self-consistent KKR method [9, 10] within the local spin density framework (the exchange-correlation potential given by the von Barth–Hedin formula [11]). In the RMn$_2$Ge$_2$ structure (I$4/mmm$) R, Mn, and Ge atoms occupy 2(a) [0,0,0], 4(d) [0,1/2,1/4] and 4(e) [0,0,z] Wyckoff sites, respectively. The crystallographic data measured at $T = 2$ K [2-4] and muffin-tin radii $r_R : r_{\text{Mn}} : r_{\text{Ge}} = 1.5 : 1 : 1$ (giving $\sum V_{\text{MT}}/V_{\text{WS}} \approx 67\%$) are used in the KKR computations. For the final potentials ($\Delta E_{\text{tot}} \approx 1$ mRy) the total densities of states (DOS), site-decomposed DOS and $l$-decomposed DOS (with $l_{\text{max}} = 2$ for R = Ca, Y, Ba and $l_{\text{max}} = 3$ for R = La) are computed. The relativistic effects are incorporated in calculations of core levels in BaMn$_2$Ge$_2$ and LaMn$_2$Ge$_2$. Note that in YMn$_2$Ge$_2$ (AF$_1$), no more bct symmetry is maintained, then the KKR calculations are performed within the simple tetragonal structure. Integration in the $\text{k}$-space is performed using 192 small tetrahedrals and 135 $\text{k}$-points in the irreducible part of the Brillouin zone.

3. Results and discussion

The main KKR results for RMn$_2$Ge$_2$, calculated both in F and AF states, are summarised in Table. The theoretical values of $\mu_{\text{Mn}}$ remain in close agreement with the neutron diffraction data, recently measured at $T = 2$ K [2-4]. The magnetisation (4.22 $\mu_B$) as well as the Mn magnetic moments (2.29 $\mu_B$) found in the ferromagnetic LaMn$_2$Ge$_2$ are also close to the earlier theoretical values (3.9 $\mu_B$ and 2.1 $\mu_B$) [7]. From comparison of the F and AF results one notes that $\mu_{\text{Mn}}$ in the AF$_2$-type compounds are rather larger than these computed in the F state (particularly in LaMn$_2$Ge$_2$), while they are almost the same in YMn$_2$Ge$_2$ (AF$_1$-type ordering).

If plotting the theoretical $\mu_{\text{Mn}}$ versus $d_{\text{in}}$ in the RMn$_2$Ge$_2$ antiferromagnets (Fig. 1) we observe that the Mn magnetic moment increases more or less proportionally to $d_{\text{in}}$, which well corresponds to the phenomenological relations established among $d_{\text{in}}$, $\mu_{\text{Mn}}$ and magnetic ordering type [12]. Nevertheless, one should take care using this simple model (Fig. 1), since in real samples when lattice constants increase, $z_{\text{Ge}}$ also changes. A number of the KKR computations on
the RMn$_2$X$_2$ systems, carried out with the use of different $a$, $c$ and $z_X$ parameters, lead to conclusion that the $z_X$ value (like $d_{in}$) has a strong influence on a magnitude of $\mu_{Mn}$ in RMn$_2$X$_2$. Moreover, both $z_X$ and $d_{in}$ seem crucial in appearing of magnetic properties in RT$_2$X$_2$ (with $T \neq Mn$) [13].

![Graph](image)

Fig. 1. The Mn magnetic moment (in $\mu_B$) versus the Mn–Mn distance ($d_{in}$) in RMn$_2$Ge$_2$.

**TABLE**

The KKR results in RMn$_2$Ge$_2$ (magnetic moments in $\mu_B$, DOS in states/Ry/spin).

<table>
<thead>
<tr>
<th></th>
<th>R = Y</th>
<th>R = Ca</th>
<th>R = La</th>
<th>R = Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$ state</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_{\text{tot}}$</td>
<td>4.02</td>
<td>4.99</td>
<td>4.22</td>
<td>6.78</td>
</tr>
<tr>
<td>$\mu_{\text{Mn}}$</td>
<td>2.15</td>
<td>2.59</td>
<td>2.29</td>
<td>3.33</td>
</tr>
<tr>
<td>$n_1(E_F)$</td>
<td>18.79</td>
<td>18.69</td>
<td>20.16</td>
<td>27.55</td>
</tr>
<tr>
<td>$n_4(E_F)$</td>
<td>32.80</td>
<td>51.42</td>
<td>65.52</td>
<td>41.14</td>
</tr>
<tr>
<td>$AF$ state</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KKR</td>
<td>2.17</td>
<td>2.84</td>
<td>2.95</td>
<td>3.48</td>
</tr>
<tr>
<td>exp.</td>
<td>2.20</td>
<td>2.67</td>
<td>3.05</td>
<td>3.66</td>
</tr>
<tr>
<td>$n_{11}(E_F)$</td>
<td>47.51*</td>
<td>10.96</td>
<td>48.99</td>
<td>3.06</td>
</tr>
</tbody>
</table>

*per two formula units

The DOS of YMn$_2$Ge$_2$ (AF$_1$) (Fig. 2) consists of two broad peaks coming mostly from the Mn sites. Unlike, the DOS of CaMn$_2$Ge$_2$, LaMn$_2$Ge$_2$, and BaMn$_2$Ge$_2$ (AF$_2$) presents complex structure with few narrow $d$-like peaks arising also on Mn atoms (note that the highest $d$-like peaks are localized well below $E_F$ in contrast to $d$-DOS in YMn$_2$Ge$_2$). The conduction band in RMn$_2$Ge$_2$ is formed mostly by $d$-states on Mn and R with some admixture of $p$-states on Ge.
The s-states (not plotted in Fig. 2) form two separate bands and are located 0.13–0.15 Ry below the conduction band bottom. When passing from \( R = Y \) to \( R = Ba \) (increasing \( d_{in} \)), less overlapping of d-like wave functions occurs, giving rise to narrow bands. Consequently, Mn atoms keep successively larger magnetic moment reaching the 3.48 \( \mu_B \) value (3.66 \( \mu_B \) from experiment) in \( BaMn_2Ge_2 \). Interestingly, from the KKR calculations, this compound is found near the semimetallic limit (Fig. 2). The \( E(k) \) computations (not shown) result in two strongly dispersive bands crossing the Fermi level, while an energy gap occurs along most of \( k \)-vector directions. As \( CaMn_2Ge_2 \) and \( BaMn_2Ge_2 \) have the same number of valence electrons, the low DOS at \( E_F \) is also detected in \( CaMn_2Ge_2 \). In \( LaMn_2Ge_2 \) \( E_F \) is shifted into the DOS peak due to one more electron. To investigate a reason for the changing of the AF-type structure, near \( d_{in} \approx 2.86 \text{ Å} \) the total energy KKR computations are done on \( CaMn_2Ge_2 \) applying \( AF_1 \) and \( AF_2 \). Indeed, \( E_{tot} \) has a slightly lower value when using the \( AF_2 \) structure. But the similar comparison in \( YMn_2Ge_2 \) does not give reliable preference for \( AF_1 \). Then, more detailed analysis \( E_{tot} = f(a, c, z_G) \) should be undertaken to clarify this point.

Acknowledgments

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References

The Electronic Structure ...

[13] YCr2Si2 has been predicted to be magnetic from the KKR method, which is now confirmed by the neutron diffraction measurements (I. Ijjaali, G. Venturini, B. Malaman, J. Alloys Comp. 279, 102 (1998)).