Magnetic exchange interactions in the paramagnetic state of hcp Gd

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Abstract

We use the first-principles magnetic force theorem embodied in the Korringa–Kohn–Rostoker method to calculate pair magnetic exchange interactions in pure hexagonal close packed (hcp) Gd metal in the ferromagnetic as well as in the paramagnetic state with disordered local 4f-moments. It is found that the exchange interactions between the localized 4f-moments, in particular also distant ones, depend on the state of magnetic disorder. Such a dependence is a consequence of the electronic structure changes of the conduction band that mediates the interaction between the local moments. The magnetic ordering temperature has been calculated using a Monte Carlo simulation technique and the results are compared with mean-field based studies.

1. Introduction

Pure metallic Gd with its magnetic half-filled 4f-shell is conventionally regarded as a model metallic Heisenberg ferromagnet, where the magnetic interactions between the well-localized 4f-moments are mediated by the conduction band electrons via the well-known RKKY (Ruderman, Kittel, Kasuya, Yosida) mechanism [1, 2]. Indeed, recent first-principles calculations of the magnetic exchange constants of the ‘classical’ Heisenberg Hamiltonian for pure hexagonal close packed (hcp) Gd [3] have been able to predict the magnetic ordering temperature in fair agreement with experiment, even when considering the shortcomings of the mean-field approximation applied. In this work [3] the exchange interactions were calculated using the magnetic force theorem [4] for the ferromagnetic (FM) ground state and their long-range character has been explicitly shown.

However, intensive photoemission studies (see Maiti et al [5, 6] and references therein) clearly suggest that the electronic structure of the conduction band of bulk Gd changes

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with temperature. In particular, it has been found [6] that local magnetic splitting of the
electronic states in the conduction band becomes reduced by one order of magnitude in the
paramagnetic state above $T_C$ as compared to the low temperature ferromagnetic state, but
remains finite indicating a significant deviation from a straightforward Stoner-like behaviour.
First-principles calculations, performed in the framework of the disordered local moment
(DLM) approximation, have shown [7] that in addition to the decrease of the spin-splitting
further significant changes occur in the electronic structure of the conduction band in the
paramagnetic state of hcp Gd as compared to the ferromagnetic state. The competition of
the band effects and the local atomic exchange splitting of the conducting spd-states leads to
a significant redistribution of the spectral weight between minority and majority spin-channels
of the conduction band in the paramagnetic state [7].

Since the conduction band mediates the magnetic interactions between the localized
$4f$-moments via a RKKY-like mechanism, the above mentioned changes in the electronic
structure entail a question concerning the magnitude of the respective changes in the values
of the magnetic exchange interactions. The aim of the present work is to investigate this
question on a first-principles basis employing the magnetic force theorem [4] as embodied
in the Korringa–Kohn–Rostoker (KKR) method [8] and within the framework of the local
spin density approximation [9]. We performed calculations of the exchange constants in the
paramagnetic state modelled by the DLM state and compared it to similar results obtained
for the ferromagnetic state. We thus extend recent studies by Turek et al [3] where similar
calculations for the ferromagnetic state based on the tight-binding linear muffin tin orbital (TB-
LMTO) scheme were performed. In addition we use the Monte Carlo method for an estimation
of the Curie temperature using out $ab$ initio obtained set of the exchange coupling constants,
eliminating in this way possible errors related to the statistical part of the problem.

One needs to note that in addition to the changes in the electronic structure of the
conduction band there is also another mechanism, described earlier on a semi-empirical
level [10–12], that eventually alters the values of the inter-atomic exchange interactions in
the paramagnetic state. It is related to a thermal paramagnetic disorder in the orientations
of the local $4f$-moments that leads to a random scattering of the conduction electrons and
consequently to an additional damping of the distant exchange interactions. Although the
inter-atomic exchange in the paramagnetic states is more relevant for the estimation of the
Curie temperature than those in the ferromagnetic state, the latter clearly should be used for
the description of the low temperature properties of the system. For example the exchange
calculated on a first-principles basis for a simple collinear FM state, mapped to a Heisenberg
like model, is found to provide an excellent description of the ground state non-collinear
magnetic configurations in bcc Eu [13], fcc Fe [14] and MnAu$_2$ [15]. However, FM exchange
constants determined from the magnetic force theorem are also quite frequently used in the
literature [16] for the calculation of the ordering temperature. These facts motivated us to
perform the present study for one of the best model metallic ferromagnets, hcp Gd, which is
close to the limit of a full magnetic moment localization. We find that even in this case the
changes in the values of the inter-atomic exchange constants, although are not dramatically
large, lead almost to a 10% change in the value of the Curie temperature, thus establishing
respective limits for the accuracy of the application of a canonical Heisenberg model with
temperature independent parameters.

2. Details of calculation

Electronic structure calculations of hcp Gd have been performed by applying the Korringa–
Kohn–Rostoker Green’s function method in the atomic sphere approximation (KKR-ASA)
as described in [17, 18] within the framework of the local spin density approximation [9]. Similarly to previous studies [3, 7] the Gd 4f-states were treated in the open core approximation so that the occupation of spin-split 4f-core levels was chosen such that the magnetic moment of the atomic core states is equal to $7\mu_B$ as in the ground state of the free Gd$^{3+}$ ion. This simple open-core approach is particularly justified by the zero orbital moment of the half-filled 4f-shell of Gd and consequently the negligible crystal field splitting effects on the localized 4f-states. For a deeper discussion of the open-core constraint and why it should be chosen instead of a treatment of the 4f-states as the valence state in Gd we refer to the original papers [19, 20] and also to [3, 7]. Let us note that also in bcc Eu the open core treatment led recently to success in the prediction of the magnetic ground state due to the half-filling of the 4f-shell in Eu$^{3+}$ [13].

The valence band was calculated using a basis function expansion up to $l_{\text{max}} = 2$. Multipole moment contributions to the non-spherical part of the electrostatic contribution to the one-electron potential inside the ASA spheres were also determined by carrying out the summation up to $l_{\text{max}}^M = 5$. The band structure calculations were converged with 2088 $k$-points in the irreducible wedge of the Brillouin zone (IBZ) of the hexagonal unit cell. For the convergence of the exchange constants in the magnetic force theorem calculations 45,563 $k$-points in the IBZ were used. The magnetic force theorem was applied as described in [8] and the scheme of the calculations is essentially similar to the TB-LMTO based investigations by Turek et al [3] for the ferromagnetic state of Gd. Since we extend this investigation to calculate the exchange in the paramagnetic (PM) state the PM state was modelled using the DLM approximation according to the formulation of Györffy et al [21]. A more detailed description of the application of the DLM approximation to the calculation of the PM electronic structure of hcp Gd can be found in [7].

3. Results and discussion

In our study we use the experimental [22] geometry of the hcp Gd crystal (see figure 1) with a $c/a$ ratio equal to 1.597 and lattice constants $a = 3.629$ Å and $c = 5.796$ Å. The calculated induced magnetic moments of the conduction band electrons (see table 1) are in good agreement with the previous TB-LMTO studies—0.67 $\mu_B$/Gd and 0.44 $\mu_B$/Gd [3, 7] in FM and DLM states, respectively. It is important to note that the spd-band keeps a local atomic spin-splitting even in the paramagnetic DLM state, in full agreement with results from photoemission experiments [6]. It has been discussed previously [7] that this finite spin-splitting is due to the strong on-site interaction of the valence state with the spin-polarization of the localized 4f-states. This interaction is essentially local in its character rather than being defined by total magnetization of 4f-moments.

We calculate the exchange constants $J_{ij}$ of the following classical Heisenberg-like Hamiltonian

$$H = -\sum_{i,j\in[N]} J_{ij}\vec{e}_i\cdot\vec{e}_j,$$

for two reference states, namely the FM and DLM as described above. The $\vec{e}_i$ are the unit directional vectors of the magnetic moment on the $i$th lattice site. Since the experimental

<table>
<thead>
<tr>
<th>FM</th>
<th>DLM</th>
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<tbody>
<tr>
<td>$m$ (valence band) ($\mu_B$)</td>
<td>0.71</td>
</tr>
<tr>
<td>$J_{1SS}$ (mRyd)</td>
<td>0.239</td>
</tr>
<tr>
<td>$J_{2SS}$ (mRyd)</td>
<td>0.199</td>
</tr>
</tbody>
</table>
The interplane NN distance is closer by about 1.5% then the in-plane one. We then define as $J_1$ and $J_2$ as exchange constants from equation (1) corresponding to the respective pairs (see figure 1). Their calculated values in the FM and paramagnetic DLM states are given in table 1. These interactions have a positive sign (ferromagnetic) and they are about one order of magnitude larger than any next NN pair interactions. These more distant interactions are plotted in figure 2 in their dependence on the inter-atomic distance in units of lattice constant $a$. In figure 2 we show the values calculated for the first 100 NN shells starting from the third one. In full agreement with the qualitative predictions of the phenomenological RKKY theory the values are oscillating. However, due to the non-spherical Fermi surface in hcp Gd, the period and amplitude of these oscillations depend on direction in the crystal. Thus, the behaviour of $J_{ij}$ in figure 2, at least for the FM state, is a superposition of different RKKY oscillations of conventional form. A discussion on the directional dependences of the exchange in the FM state can be found in [3]. Our results show that these sign oscillations also occur in the PM state.

Although the more distant interactions are much smaller than first two NN ones and, in addition, they partially compensate each other, they provide a quite essential contribution. This can be seen from the following mean-field type analysis, which we discuss prior to the Monte Carlo calculations also for providing a subject for comparison with the previous study by Turek et al [3]. The absolute value of the magnetic ordering temperature, $T_c$, derived from a mean field approximation is

$$k_B T_c = \frac{3}{2} J_0$$

where the total effective exchange $J_0$ is a sum of $J_{ij}$ connecting a given lattice site to all remaining ones

$$J_0 = \sum_i J_{i\theta}.$$
The calculated distant (starting from third nearest neighbour) exchange interactions in the ferromagnetic (FM) and paramagnetic (DLM) state of hcp Gd.

Table 2. Magnetic ordering temperatures calculated with parameters obtained for the FM and DLM states by two methods: mean-field approximation (MFA) and Monte Carlo (MC). The experimental \( T_c \) is taken from [2].

<table>
<thead>
<tr>
<th>( T_c ) (K)</th>
<th>FM, MFA</th>
<th>DLM, MFA</th>
<th>FM, MC</th>
<th>DLM, MC</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>351</td>
<td>326</td>
<td>292 ± 1</td>
<td>279 ± 1</td>
<td>293</td>
<td></td>
</tr>
</tbody>
</table>

value of \( T_c \) is determined by the long range part of the interactions. We note that our mean-field value, determined from the \( J_{ij} \) calculated in the FM state (351 K) is similar but slightly higher than that given in [3] (334 K) using the TB-LMTO formalism.

Our main result is that the exchange interactions are quite different in the paramagnetic state and in the ferromagnetic one (see figure 2 and table 1)—some of them even change their sign. It is quite interesting to note, however, that on the average some sort of compensation occurs. The mean-field \( T_c \) calculated with DLM exchange constants is only moderately lower than the respective FM based value. The difference in \( T_c \) calculated using a Monte Carlo (MC) technique is even smaller (see table 2). The MC results are obtained from a simulation on a lattice containing 8192 lattice sites with the Hamiltonian given in (1), which includes the first 23 NN interactions (these shells make a contribution of more than 99% to \( J_0 \)). A standard Metropolis algorithm with periodical boundary conditions has been used. As expected, the \( T_c \) provided by DLM exchange constants is smaller than for the FM ones. We should not be misled by the almost exact coincidence of \( T_c \) derived with the FM exchange constants and the experimental value. The DLM value, which is lower, is more physically relevant, since the ordering occurs from the paramagnetic state by lowering the temperature towards \( T_c \). However, this DLM value also provides quite a good estimate for the experimental \( T_c \), being lower by only ~5%.

An interesting result is related to the contribution from more distant interactions to the total one, which appear to be larger in the PM than in the FM state. It is in some sense even more surprising since the more distant interactions in the disordered PM state are expected to decay faster than in the fully ordered FM state, which should be due to additional random scattering. However, the calculated DLM exchange constants indeed decay faster. To clarify this point
we introduce an auxiliary quantity (as an analogue of $J_0$ from equation (3) but which has no immediate physical meaning), namely the sum of modules of the distant interactions

$$I_3 = \sum |J_{0i}|,$$

where the summation runs over all sites belonging to the first 100 NN shells except for the two NN shells. This sum is smaller for interactions in the DLM state $I_3(DLM) = 1.73$ mRyd than in the FM state $I_3(FM) = 2.11$ mRyd, suggesting a faster decay of the interaction amplitude. The corresponding sum of the absolute values, which contribute to $J_{0i}$, has the opposite trend, being larger in the DLM (0.81 mRyd) than in the FM state (0.72 mRyd). This situation is due to alternating signs, which revert the most important distant negative exchange constant in the FM state to being positive in the DLM state. The latter feature of course is material specific, being dependent on the structure of the Fermi surface and its dependence on the magnetic disorder. The conclusion we can draw is that despite the disorder-induced damping of the distant interactions, a feature being valid in general, the influence of these changes on $T_c$ is material specific and can be quite small. One can imagine also that in some systems one may even find a $T_c$ enhancement due to magnetic disorder.

Despite the rather satisfactory agreement of our calculated $T_c$ with experiment, there is an intrinsic limitation on the accuracy of our proposed approach, which is related to the use of the classical Heisenberg Hamiltonian instead of a fully quantum mechanical description based on spin operators. The use of the classical magnetic Hamiltonian for the calculation of $T_c$ can in principle be justified in the high temperature limit [23], and should work rather well for transition metal ferromagnets like bcc Fe (see e.g. a study by Halilov et al [24]), where, however, additional care should be taken with longitudinal components of spin-fluctuations [25]. Due to the high degree of the 4f-moment localization in Gd, quantum effects are still important at elevated temperatures. One can estimate the order of magnitude of the error related to the use of the classical spin model (equation (1)) by noting that the classical limit is achieved by allowing the $S_z$ component of the spin to take on an infinite number of values. Thus the overestimation of $T_c$ is of the order of the ratio $S(S+1)/S^2$, which in the case of Gd ($S = 7$) is about 14%. This number should be regarded as a principal inaccuracy of $T_c$ determination within our applied model. The classical model thus underestimates $T_c$ as compared to the quantum formulation. This gives an additional hint that the use of DLM exchange constants, which lead to an underestimation of $T_c$, is more physically relevant.

4. Conclusions

We show, from first-principles calculations, that the exchange constants in Gd depend on the state of the magnetic disorder of the localized 4f-moments. The use of exchange constants calculated in the paramagnetic state is physically more relevant than of those calculated in the ordered ground state. However, the degree of the influence of these changes on the value of $T_c$ is strongly material specific, although the faster decay of distant interactions in the paramagnetic state is a general property. The simulated value of $T_c$ is in reasonable agreement with experiment. The improvement in this value, provided by a Monte Carlo technique instead of the mean field approximation, is quite significant and comparable to the principal inaccuracy of the classical model Hamiltonian.

Acknowledgments

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References

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