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2007 J. Phys.: Condens. Matter 19 326218

(http://iopscience.iop.org/0953-8984/19/32/326218)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 326218 (7pp) doi:10.1088/0953-8984/19/32/326218

Magnetic exchange interactions in the paramagnetic state of hcp Gd

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Received 14 May 2007, in final form 25 June 2007
Published 17 July 2007
Online at stacks.iop.org/JPhysCM/19/326218

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 our *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)

Table 1. Calculated magnetic moments per atom of the valence band and exchange parameters for the first two nearest-neighbour (NN) shells.

	m (valence band) (μ_B)	J_{1NN} (mRyd)	J_{2NN} (mRyd)
FM	0.71	0.239	0.199
DLM	0.47	0.182	0.201

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^{2+} [13].

The valence band was calculated using a basis function expansion up to $l_{max} = 2$. 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 $l^M_{max} = 5$. 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 where 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 Gyorffy *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 μ_B/Gd and 0.44 μ_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

$$H = -\sum_{i,j\in\{Ni\}} J_{ij}\vec{e}_i\vec{e}_j, \tag{1}$$

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 ith lattice site. Since the experimental

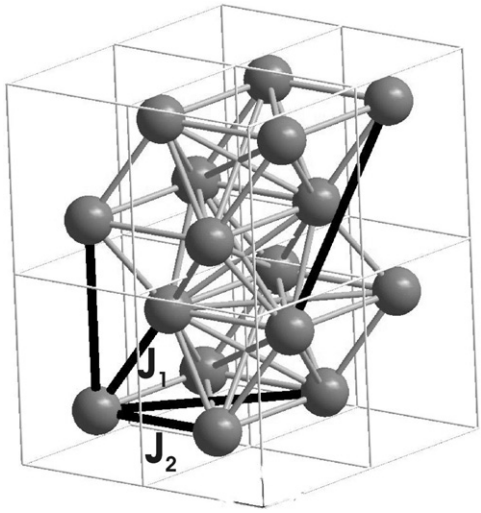

Figure 1. Hexagonal crystal structure of Gd; the first two nearest-neighbour pairs are shown.

c/a ratio (1.597) in Gd is off the ratio of the ideal hcp structure (1.633) the distances from a given atom to the six nearest-neighbour (NN) atoms in the same basal plane and the six NN in adjacent planes are slightly different. 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

$$k_B T_c = 3/2 J_0 \tag{2}$$

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

$$J_0 = \sum_i J_{0i}. \tag{3}$$

The total contribution to J_0 from distant interactions starting from 3 NN is 22.8% in for the FM state and 26.0% for the paramagnetic DLM state. Thus almost a quarter of the mean-field

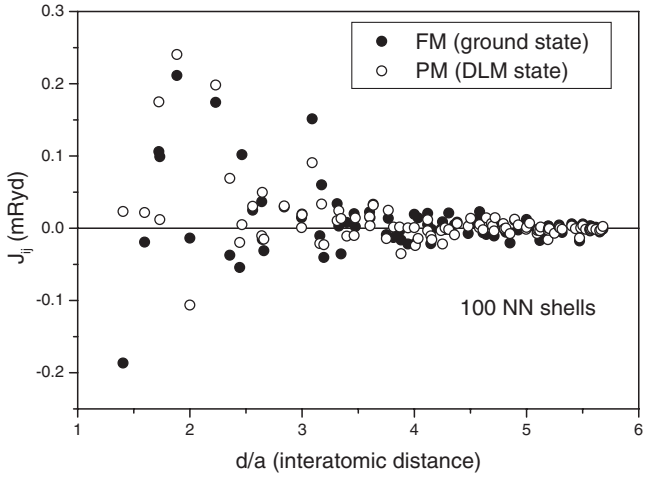

Figure 2. Calculated distant (starting from third nearest neighbour) exchange interactions in the ferromagnetic (FM) and paramagnetic (DLM) state of hcp Gd.

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].

	FM, MFA	DLM, MFA	FM, MC	DLM, MC	Experiment
T_c (K)	351	326	292 ± 1	279 ± 1	293

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 $\sim$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

$$I_3 = \sum_i |J_{0i}|, \tag{4}$$

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 $I_3(\mathrm{DLM}) = 1.73$ mRyd than in the FM state $I_3(\mathrm{DLM}) = 2.11$ mRyd, suggesting a faster decay of the interaction amplitude. The corresponding sum of the absolute values, which contribute to J_0, 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

SK is grateful for partial support from the European COST P16 programme and TK for financial support of Austrian FWF: project W004.

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