Journal of Alloys and Compounds 408–412 (2006) 930–933

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Ab initio calculations of Curie temperatures in GdX compounds

Ján Rusz*, Ilja Turek, Martin Diviš

Department of Electronic Structures, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5,
CZ-121 16 Prague 2, Czech Republic

Received 29 July 2004; received in revised form 30 November 2004; accepted 1 December 2004
Available online 29 June 2005

Abstract

We present calculations of Curie temperatures of selected GdX (X = Zn, Rh, Mg, Cd) compounds with a cubic CsCl structure. Exchange interactions are obtained from ab initio electronic structure calculations in the framework of density functional theory. Critical temperatures are evaluated using two approaches, namely the mean-field approximation (MFA) and a more involved, random phase approximation (RPA). Calculated critical temperatures serve as theoretical upper estimate (MFA) and lower estimate (RPA) of an exact critical temperature given by the Heisenberg model. Obtained results are in fair agreement with experimental values.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Critical temperature; Density functional theory; Heisenberg model; Random phase approximation; Mean-field approximation; GdZn; GdRh; GdMg; GdCd

1. Introduction

Calculation of properties of solids at non-zero temperatures from first principles is a difficult and not fully solved problem in solid-state physics. Most ground state calculations are based on density functional theory (DFT) [1] and local spin density approximation (LSDA) [2]. A straightforward extension of DFT to non-zero temperatures by Mermin [3] however fails within LSDA on the quantitative level. For example, for elemental ferromagnetic metals Fe, Co and Ni, it largely overestimates the critical temperatures. The main reason is, that it lacks a proper description of collective excitations—spin waves in these cases.

Another way is based on a Heisenberg model Hamiltonian. Zero-temperature DFT calculations allow to obtain parameters of exchange interactions and finite-temperature properties can be studied in the framework of the Heisenberg model [4] using methods of statistical physics.

There are various approaches to extracting physical properties from Heisenberg Hamiltonian. The simplest approach is the mean-field approximation (MFA). However, published results based on the MFA usually overestimate critical temperatures in comparison to experimental values [5]. These can be considered as an upper bound of exact solution of Heisenberg Hamiltonian. More involved treatment is based on random phase approximation (RPA) [6], which has been shown to be a lower bound of exact solution of Heisenberg Hamiltonian under the conditions, that all exchange interactions are of equal sign [7].

In this paper we present calculations of critical temperatures of selected Gd-based binary compounds with CsCl structure (GdX, X = Zn, Rh, Mg, Cd). First principles calculations are used to obtain parameters of Heisenberg Hamiltonian. These parameters – exchange constants – are evaluated up to rather distant neighbors. Recently, similar method was successfully applied to calculation of the Curie temperature of bulk Gd within MFA [8]. In this work, we extend these results. Heisenberg Hamiltonian is treated in both MFA and RPA, taking into account interactions between all atoms in the basis. To our best knowledge, this extension for more-

---

* Corresponding author. Tel.: +420 22191 1352; fax: +420 22191 1617.
E-mail address: rusz@mag.mff.cuni.cz (J. Rusz).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.12.099

atomic basis in the framework of RPA is presented for the first time.

2. Details of calculations

We use classical Heisenberg Hamiltonian in the following form:

$$H = -\sum_{\mathbf{RR'}} J_{\mathbf{RR'}} \mathbf{e}_{\mathbf{R}} \cdot \mathbf{e}_{\mathbf{R'}}, \qquad (1)$$

where $\mathbf{R}$ labels sites of atoms in the lattice and $\mathbf{e}_{\mathbf{R}}$ is a unit vector parallel to magnetic moment of atom at the site $\mathbf{R}$.

Exchange parameters are obtained using magnetic force theorem applied to evaluation of energy changes due to infinitesimal rotations of local moments with respect to the ferromagnetic state [4]. This procedure in the framework of tight-binding linear muffin-tin orbitals (TB-LMTO) within the atomic spheres approximation (ASA) results in formula [5]:

$$J_{\mathbf{RR'}} = \frac{1}{8\pi i}\int_{C} \mathrm{Tr}_L[\Delta_{\mathbf{R}}(z) g^{\uparrow}_{\mathbf{RR'}}(z) \Delta_{\mathbf{R'}}(z) g^{\downarrow}_{\mathbf{R'R}}(z)]\,\mathrm{d}z. \qquad (2)$$

Integration is performed along a contour in complex plane, which encircles occupied part of valence band. The trace sums over the angular momentum indices $L = (l, m)$. Quantities $g^{\sigma}_{\mathbf{RR'}}(z)$ ($\sigma = \uparrow, \downarrow$–spin index) and $\Delta_{\mathbf{R}}(z)$ are connected with so-called auxiliary Green functions and potential functions, respectively, of the TB-LMTO-ASA method [9].

All electronic structure calculations are performed using the TB-LMTO-ASA method [9]. Structure parameters were taken from experiment [10]. To improve the description of 4f states beyond standard LSDA, the 4f electrons of Gd were treated using the open-core method due to their localized character. This method usually performs better for rare-earth compounds than including 4f states into valence band, as has been shown for example, in Ref. [11].

In the RPA approximation, we obtain for ferromagnetic structures a set of self-consistent equations for mean values of the reduced local moments in the vicinity of critical temperature in the following form:

$$\langle S^z_A \rangle = \frac{2\beta_C}{3}\left(\frac{1}{\Omega}\int \mathrm{d}\mathbf{q}(N(\mathbf{q})^{-1})_{AA}\right)^{-1}, \qquad (3)$$

where $\langle S^z_A \rangle$ is a statistical mean value of reduced local magnetic moment (angular momentum vector of size one—unit vector $\mathbf{e}_{\mathbf{R}}$) on sites with basis index A, $\beta_C = 1/(k_B T_C)$ where T_C is a critical temperature. Integration is performed (taking an advantage of crystal symmetry) over irreducible wedge of the first Brillouin zone (IBZ). Elements of matrix $N(\mathbf{q})$ are defined using exchange constants and mean values of reduced local moments as follows:

$$N(\mathbf{q})_{AB} = \delta_{AB}\sum_{C} J_{AC}(0)\langle S^z_C \rangle - \sqrt{\langle S^z_A \rangle} J_{AB}(\mathbf{q}) \sqrt{\langle S^z_B \rangle}, \qquad (4)$$

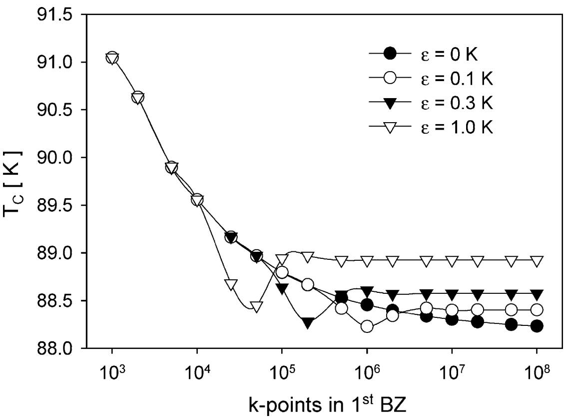

Fig. 1. Dependence of calculated RPA critical temperature of GdCd on the number of k-points in first Brillouin zone for different deconvolution parameters ε.

where δ_{AB} is Kronecker delta ($\delta_{AB} = 1$ if $A = B$, zero otherwise), $J_{AB}(\mathbf{q})$ are lattice Fourier transformed exchange constants, $\mathbf{q}$ is a vector of IBZ. Details of derivation of Eqs. (3) and (4) were published elsewhere [12].

The form of Eq. (3) is suitable for iterative methods. As the starting values of mean values of moments we use MFA results. RPA moments are usually similar to MFA moments; RPA critical temperature is always lower than MFA T_C.

Calculation of integral in Eq. (3) is problematic due to the divergence at $\mathbf{q} = 0$. To overcome this difficulty we use an analytic deconvolution method [5], where we replace matrix $N(\mathbf{q})$ by $N(\mathbf{q}) + z1$ with z a small (in general complex) number and 1 stands for unity matrix. One can easily verify that,

$$f(0) \approx 4f(i\varepsilon) - f(2i\varepsilon) - f(\varepsilon + i\varepsilon) - f(-\varepsilon + i\varepsilon) \qquad (5)$$

up to the fourth order (ε is a small real number). The error approaches zero as ε approaches zero. Fig. 1 shows convergence of GdCd T_C with respect to number of k-points in IBZ for various values of deconvolution parameter ε.

3. Results and discussion

Experimental and calculated critical temperatures of GdX (X = Zn, Rh, Mg, Cd) are summarized in Table 1 together with mean values of reduced magnetic moments on both sites. Please note, that in our semi-classical treatment we replaced magnetic moment operators in Eq. (1) by vectors of size one. Moreover, Eq. (3) is derived in the approximation $T \to T_C$ and as a consequence, the equality will not change, if we multiply all magnetic moments by a same constant. This allows us to restrict the vector of reduced magnetic moments to be of size unit. Therefore, the mean values shown do not denote absolute mean values of moments near the onset of ferromagnetism. Their ratio is related to relative polarization at individual sites.

GdX systems are intermetallic compounds with long-range RKKY-like exchange interactions. In our calculations,

Table 1
Calculated MFA and RPA critical temperatures and relative polarizations at individual sites of GdX (X = Rh, Mg, Cd, Zn) compounds

	Experiment		RPA			MFA		
	a (nm)	T_C (K)	T_C (K)	$\langle S^z_{Gd} \rangle$	$\langle S^z_X \rangle$	T_C (K)	$\langle S^z_{Gd} \rangle$	$\langle S^z_X \rangle$
GdRh	0.3435	24–29.5	21 ± 1	0.725	0.689	33.4 ± 0.5	0.780	0.626
GdMg	0.3808	119–120	85 ± 1	0.868	0.497	91 ± 1	0.876	0.482
GdCd	0.3731	254–265	92 ± 2	0.952	0.307	100 ± 1	0.959	0.283
GdZn	0.3602	268–270	107 ± 2	0.944	0.331	117 ± 1	0.952	0.306

we included exchange interactions between approximately 250 non-equivalent neighbors of each atomic site. This corresponds to a cut-off distance of approximately $10a$, where a is a lattice parameter. Fig. 2 displays the dependence of calculated Curie temperature on the cut-off distance for GdCd. This figure shows an importance to include into account interactions between rather distant neighbors to obtain well-converged results for T_C in such metallic systems.

We see, that our results for GdMg and GdRh are in good agreement with experiment. For GdCd and GdZn both RPA and MFA underestimate the critical temperature by factor of approximately 2.5 (within RPA). For the latter two compounds, there was a difficulty in the treatment of d-states of non-magnetic atoms within TB-LMTO-ASA method, because both occupied 3d (4d) and unoccupied 4d (5d) bands of Zn (Cd) are hybridized with other valence states near the Fermi level. The TB-LMTO-ASA method offers however only one set of basis functions of d-character per atomic sphere. Detailed investigation of this issue is however beyond the scope of this paper.

Most of recent calculations of critical temperatures usually neglect exchange interactions with non-magnetic atoms in the basis. In our compounds, converged magnetic moments on X elements are usually two orders lower than the magnetic moment on Gd. This is reflected in two orders lower exchange parameters between Gd and X in our treatment with reduced magnetic moments. However, their influence on Curie temperature is non-negligible. To demonstrate this statement we calculated the critical temperatures again, while in this set of calculations we completely neglected all exchange interactions of Gd–X of X–X type. Our results are summarized in Table 2. They show, that omission of non-magnetic elements in calculations makes results worse and the difference is up to 40% for GdMg. From these results we can conclude, that including exchange interactions between all types of atoms (even those with small induced magnetic moments) is important. We note, that for GdRh we did not obtain a converged solution of critical temperature, while neglecting Rh sites. The reason is, that in such case maximum of $J(\mathbf{q})$ occurs for non-zero $\mathbf{q}$. This would indicate an appearance of a more complicated magnetic structure than the ferromagnetic one [11].

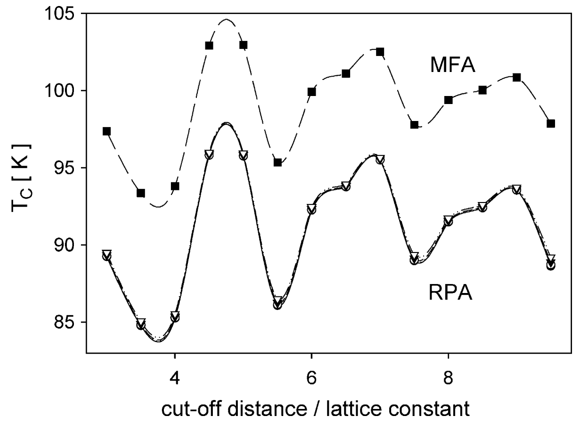

Fig. 2. Dependence of calculated MFA and RPA critical temperatures of GdCd as a function of cut-off distance for included exchange parameters. RPA values are presented for several different deconvolution parameters ε (see the legend of Fig. 1).

Table 2
Calculated MFA and RPA critical temperatures of GdX (X = Rh, Mg, Cd, Zn) compounds, where all exchange interactions with X atoms were neglected

	T_C^{exp} (K)	$\tilde{T}_C^{RPA}$ (K)	$\tilde{T}_C^{MFA}$ (K)
GdRh	24–29.5	–	16 ± 1
GdMg	119–120	60 ± 1	66 ± 1
GdCd	254–265	80 ± 2	89 ± 1
GdZn	268–270	93 ± 2	104 ± 2

Although the results for GdRh and GdMg are in nice agreement with experiment, for GdCd and GdZn we obviously reached the limitations of the TB-LMTO-ASA method. These compounds require more careful treatment of their electronic structure. Another direction for improvement of our treatment (for all studied compounds) would be to go beyond the open-core method within LSDA. One such possibility would be to employ LDA + U method. These tasks are left for future studies.

4. Conclusions

We calculated critical temperatures of selected GdX compounds within mean-field approximation and random phase approximation. Our results underestimate critical temperatures, when compared to experimental results. On the other hand, our results reproduce the trends observed by experiment and are in better agreement with experiment, than calculations neglecting non-magnetic atoms in the structure. We have observed the importance of including exchange interactions between rather distant atoms into the treatment of metallic systems with exchange interactions of RKKY type.

Acknowledgements

This work is a part of the research program MSM 0021620834 financed by the Ministry of Education of the Czech Republic.

References

[1] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864;
W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133.

[2] U. von Barth, L. Hedin, J. Phys. C: Solid State Phys. 5 (1972) 1629.

[3] N.D. Mermin, Phys. Rev. 137 (1965) A1441.

[4] V.P. Antropov, B.N. Harmon, A.N. Smirnov, J. Magn. Magn. Mater. 200 (1999) 148.

[5] M. Pajda, J. Kudrnovský, I. Turek, V. Drchal, P. Bruno, Phys. Rev. B 64 (2001) 174402.

[6] S.V. Tyablikov, Methods of Quantum Theory of Magnetism, Plenum Press, New York, 1967.

[7] Ya. G. Sinai, Theory of Phase Transitions: Rigorous Results, Pergamon Press, Oxford, 1982.

[8] I. Turek, J. Kudrnovský, G. Bihlmayer, S. Blügel, J. Phys.: Condens. Matter 15 (2003) 2771.

[9] I. Turek, V. Drchal, J. Kudrnovský, M. Sob, P. Weinberger, Electronic Structure of Disordered Alloys, Surfaces and Interfaces, Kluwer, Boston, 1997.

[10] K.H.J. Buschow, Rep. Prog. Phys. 42 (1979) 1373.

[11] I. Turek, J. Kudrnovský, M. Diviš, P. Franek, G. Bihlmayer, S. Blügel, Phys. Rev. B 68 (2003) 224431.

[12] J. Rusz, I. Turek, M. Diviš, Phys. Rev. B 71 (2005) 174408.