Research articles

Magnetic properties of Gd intermetallics

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ABSTRACT

Using first-principles calculations, based on disordered local moment theory, combined with the self-interaction corrected local spin density approximation, we study magnetic interactions in GdX intermetallics for X = Cu, Zn, Ga, Cd, and Mg. Our predicted magnetic orders and ordering temperatures both at zero and other pressures agree well with experiments including the large increase in the Curie temperature of GdCd under pressure that is shown by our own experimental measurements. From our results it emerges that the Ruderman-Kittel-Kasuya-Yosida interaction on its own can not explain the observed behaviour under pressure, and that the magnetic ordering mechanism is strongly influenced by the occupations of both Gd and anion d-bands.

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1. Introduction

The development of first-principles methodologies based on density functional theory (DFT), in either its local spin density (LSD) approximation or generalized gradient approximation (GGA) to exchange and correlation has resulted in considerable advances in the understanding of transition metal based magnetism, both with respect to ground state properties, and finite temperature fluctuations [1]. When studying rare earth magnetism, model calculations relying on phenomenological parameters have revealed themselves to be very successful in describing the possible mechanisms behind the magnetic ordering, but here fully first-principles calculations remain a challenge due to the strongly correlated nature of the lanthanide 4f-electrons which cannot be described within a standard band picture approach. The reason for this is that LSD does not properly account for the electron–electron interactions which may localize the f-electrons on site. In order to address this shortcoming, additional assumptions or parameters derived from experiment are required.

In the present manuscript, combining the self-interaction corrected (SIC) local spin density with the disordered local moment (DLM) theory, we report our attempts to overcome these hurdles and to predict the magnetic order and transition temperature for a range of binary GdX (X = Cu, Zn, Ga, Cd, and Mg) compounds both

at ambient conditions and under pressure. The DLM theory [1] handles the magnetic fluctuations, whilst the SIC corrects the LSD to provide an adequate description of f-electron correlations [2]. Thus for GdX compounds DLM is meant to describe how valence electrons mediate the interactions between the localized Gd f-electron moments. These interactions may sometimes be described by the Ruderman-Kittel-Kasuya-Yosida (RKKY) [3] model, but can also show strong deviations from this simple picture as we find here. The present DLM + SIC methodology [4,5] has been implemented in the self-consistent field (SCF)-Korringa-Kohn-Rostoker (KKR) multiple scattering theory, which includes the coherent potential approximation (CPA) [6], a mean-field treatment of disorder which performs the ensemble averaging over the alloying constituents, as well as over different local moment orientational configurations [7].

The DLM paramagnetic susceptibility is derived as $\chi(\mathbf{q}, T) = \frac{\mu^2}{3k_B T - S^{(2)}(\mathbf{q},T)}$, where $S^{(2)}(\mathbf{q}, T)$ is the lattice Fourier transform of the spin–spin correlation function [1]. The transition temperature, T_t, can be directly obtained from $T_t = S^{(2)}(\mathbf{q}_{max}, T_t)/3k_B$, with $\mathbf{q}_{max}$ being the wave vector where $S^{(2)}(\mathbf{q}, T)$ is maximal. In this study we focus on a number of Gd intermetallics crystallizing in the CsCl structure, where the Gd ions form a simple cubic lattice, with the anion placed at the centre of the cube. As observed in earlier SIC-LSD calculations on rare earth materials [8], Gd tends to be in the trivalent ground state configuration, $Gd^{3+}(f^7)$, with seven localized f electrons constituting a half-filled shell and this is how it enters all our calculations. In this configuration, spin–orbit

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coupling, quadrupolar and crystal field effects can be safely ignored to first approximation. The Brillouin zone of the primitive cubic CsCl lattice is characterized by three symmetry points corresponding to wave vectors $\mathbf{k} = (0, 0, \frac{1}{2})$, $\mathbf{k} = (0, \frac{1}{2}, \frac{1}{2})$, and $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. For the CsCl lattice only the two first vectors are of relevance for the antiferromagnetic (AF) orderings discussed here [9]. We shall refer to them respectively as AF1 and AF2, with the ferromagnetic (F) order characterized by $\mathbf{k} = (0, 0, 0)$.

GdCu crystallizes in the CsCl structure at room temperature, and at temperatures below 250 K undergoes a martensitic transition to the FeB structure. It has been shown that in the CsCl phase, antiferromagnetic ordering sets in at $T_N = 145$ K, whilst a further magnetic transition is observed in the FeB structure at $T_N = 45$ K [10]. Here, using the DLM approach we have investigated the onset of magnetism in the CsCl structure. The results are given in Table 1. We predict an AF2 ordering at $T_N = 46$ K, increasing with pressure at a rate of $dT_N/dP = 0.02$ K kbar^{-1}. The theoretical data are qualitatively in good agreement with experiment. We furthermore predict a bulk modulus $B_0 = 82.5$ GPa, compared to the experimental value $B_0 = 69.7$ GPa [11].

Experimentally, under ambient conditions, both GdZn and GdCd are found to be ferromagnetic with rather high ordering temperatures, respectively $T_C = 270$ K for GdZn [13] and $T_C = 265$ K for GdCd [14]. Our DLM + SIC calculations correctly predict both compounds to be ferromagnetic, with Curie temperatures at the theoretical lattice parameter of respectively $T_C = 184$ K for GdZn and $T_C = 234$ K for GdCd (at the experimental lattice parameter the calculations give $T_C = 199$ K for GdZn and $T_C = 205$ K for GdCd) [15]. Although the calculated Curie temperatures are somewhat lower than their experimental counterparts, the overall agreement in absolute terms is rather good. The earlier calculations by Rusz et al. [16], using respectively the mean-field and random phase approximations, underestimate the critical temperature by a factor of 2–3. Buschow et al. [17], using both mean field and spin-fluctuation approaches, estimate critical temperature for GdZn of respectively 1060 K and 410 K.

GdGa crystallizes in the orthorhombic CrB structure, ordering ferromagnetically with a Curie temperature of $T_C = 200$ K [18]. Here, in order to compare to the other compounds, we have modelled GdGa assuming the cubic CsCl structure (as marked by * in Table 1), but using the experimentally observed volume for the CrB structure. For this artificial structure we find GdGa to order antiferromagnetically, namely AF1 with ordering temperature of $T_N = 56$ K as shown in Table 1.

It is generally accepted that the very localized character of the rare earth 4f-electrons implies that the ordering of the corresponding spin moments is driven by indirect coupling. In the case of RKKY [3] this happens through the intermediary of the conduction electrons that locally couple to the 4f-electrons. Assuming free electron behaviour of the valence electrons (isotropic if $L = 0$), the effective interaction strength decays as R^{-3} and for large R is proportional to $\cos(2k_F R)$, oscillating between ferromagnetic and antiferromagnetic ordering as a function of R. For free electrons,

the Fermi momentum is directly related to the density of conduction electrons n, i.e $k_F = (3\pi^2 n)^{1/3}$. Despite its approximations, the simplified RKKY interaction does capture the magnetic properties of rare earth compounds in a great many cases. Here, for the GdCu-GdZn-GdGa sequence, the number of sp-electrons increases from 1 to 3, and the predicted change in magnetic ordering, respectively from AF2 to F to AF1 would seem to indicate that the RKKY interaction is indeed the underlying mechanism for magnetic ordering in these compounds.

The role of s-electrons in mediating the effective interaction between f-electrons in GdX was also highlighted in an early study by Grechnev et al. analyzing the effect of pressure on the susceptibility of Gd compounds [19]. However in a couple of follow-up articles [17,20] the authors pointed out that the different values of T_C for isoelectronic GdZn and GdMg could be hardly explained in the framework of RKKY. In their LMTO calculations, treating the 4f-electrons as part of the core, they observe that the density of states (DOS) at the Fermi level is characterized by the Gd 5d electrons, whereas there are almost no s-electrons, and that there tend to be more or less noticeable deviations from the predicted RKKY behaviour that require a more exact treatment of the actual band character of the conduction electrons. Consequently they concluded that, in line with a mechanism proposed earlier by Campbell [21], a local 4f-5d interaction at the Gd site mediated by the direct overlap of the 5d-states on neighbouring Gd sites, could be acting as competing (ferromagnetic) mechanism for magnetic ordering in compounds where the rare earth ions are close. Postnikov et al. [22] in their LSD based electronic structure calculations on GdZn observed the DOS at the Fermi level to be strongly influenced by the Gd 5d-states, and conjectured the ferromagnetic
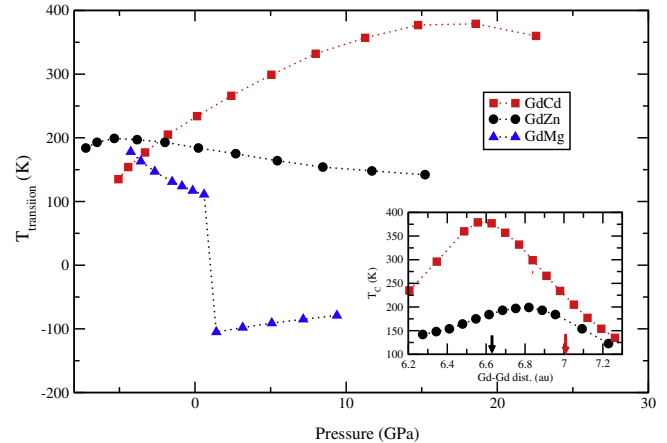

Fig. 1. Calculated transition temperatures as a function of pressure for GdCd (red squares), GdZn (black circles), and GdMg (blue triangles). Positive values refer to Curie temperatures, negative values refer to Néel temperatures for AF1 GdMg. (Inset) Curie temperatures of GdCd and GdZn as a function of Gd-Gd distance. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
A comparison of calculated and experimental data for a number of GdX compounds. Column 1: Compound, Columns 2–5 and 6–9: respectively experimental and theoretical values for volume (Å^3), magnetic order, transition temperature (K), and pressure derivative of transition temperature (K kbar^{-1}).

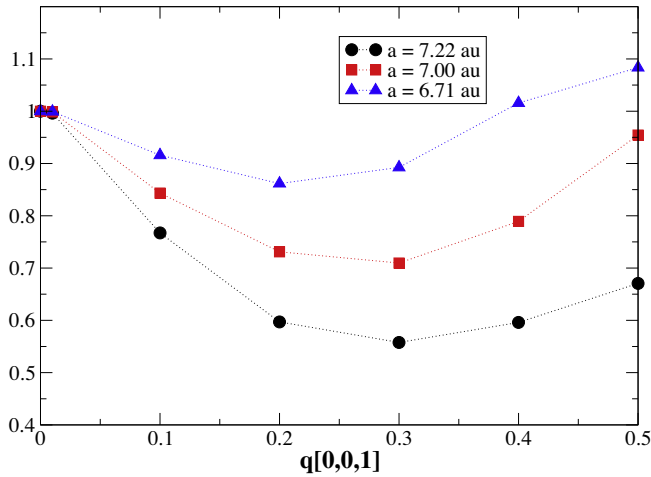| GdX	Experiment				Theory			
	V	order	T	$\frac{dT}{dP}$	V	order	T	$\frac{dT}{dP}$
GdCu	43.69	AF2	150	0.27 [12]	40.42	AF2	46	0.02
GdZn	46.80	F	270	−0.13	43.00	F	184	−0.45
GdGa*						AF1	56	
GdCd	52.81	F	265	1.60	50.39	F	234	1.50
GdMg	55.22	F	120		50.89	F	117	

Fig. 2. The calculated paramagnetic susceptibility ratio $\frac{\chi(\mathbf{q},T)}{\chi(\mathbf{q}=(0,0,0),T)}$ at $T = 300$ K for $\mathbf{q}$ along [001] for three a values for GdMg. It shows the competition between ferromagnetic (FM) and antiferromagnetic (AF1) correlations in GdMg's paramagnetic state.

ordering in GdZn to be stabilized by the relatively low DOS at the Fermi level.

GdMg crystallizes in the CsCl structure and is isoelectronic with both GdZn and GdCd but with no filled 3d or 4d bands. At zero pressure, our calculations predict a transition to ferromagnetic order at $T_C = 117$ K in good agreement with the experimentally determined value of $T_C = 120$ K. To further investigate the role of d-electrons, we compare the behaviour under pressure of the magnetic ordering in GdZn, GdCd, and GdMg. The resulting change in transition temperature under pressure is shown in Fig. 1. Most notably, for GdMg this change comprises a transition from ferromagnetic to antiferromagnetic ordering, which in Fig. 1 is indicated

by the change from positive to negative transition temperatures. The pressure data for GdZn and GdCd on the other hand show no sign of transition towards an antiferromagnetic phase even at large pressures, thus indicating a dramatically changed magnetic ordering behaviour brought about by the presence of the anion d-bands, and that can not be explained within the limits of a simple RKKY mechanism.

The transition from F to AF1 can also be observed in the calculated susceptibilities for GdMg, depicted in Fig. 2 along the AF1 symmetry direction for three different lattice parameters. As a function of $\mathbf{q}$, the calculated $\chi(\mathbf{q})$ has maxima at both $\mathbf{q} = 0$ and $(0, 0, \frac{1}{2})$ of similar height and consequently competing F and AF correlations in the PM state of this alloy. Which ones are stronger depends on the value of a used in the calculation. At the theoretical lattice parameter ($a = 7.00$ a.u.), $\chi(0, 0, 0) > \chi(0, 0, \frac{1}{2})$, indicating dominant ferromagnetic fluctuations. Reducing the Gd-Gd separation weakens the FM aspects. Eventually the AF1 component starts to dominate, i.e. $\chi(0, 0, 0) < \chi(0, 0, \frac{1}{2})$ and, for example, a 4% decrease of the lattice parameter leads to an AF1 state instead below the Néel temperature $T_N = 87$ K.

The GdMg findings are in good agreement with experiment including, as shown in our earlier study, a further second order transition into a canted magnetic ordered state at $T_F = 85$ K [15]. When Mg is replaced by isoelectronic Zn or Cd, low-lying, nominally filled d-shells ($3d^{10}$ and $4d^{10}$ respectively) are added to the valence electrons of the nonlanthanide. We find that the weak interaction of Gd d-electrons with these states is enough to perturb their influence on the Fermi surface (FS), so that these compounds remain ferromagnetic to $T = 0$ K and their Curie temperatures, T_C, are much higher than GdMg's.

From Fig. 1 we observe that both GdZn and GdCd remain ferromagnetic under pressure, with the T_C of GdCd increasing rather dramatically reaching a maximum value of around 375 K for pressure of 15 GPa, whilst the T_C of GdZn decreases gradually from
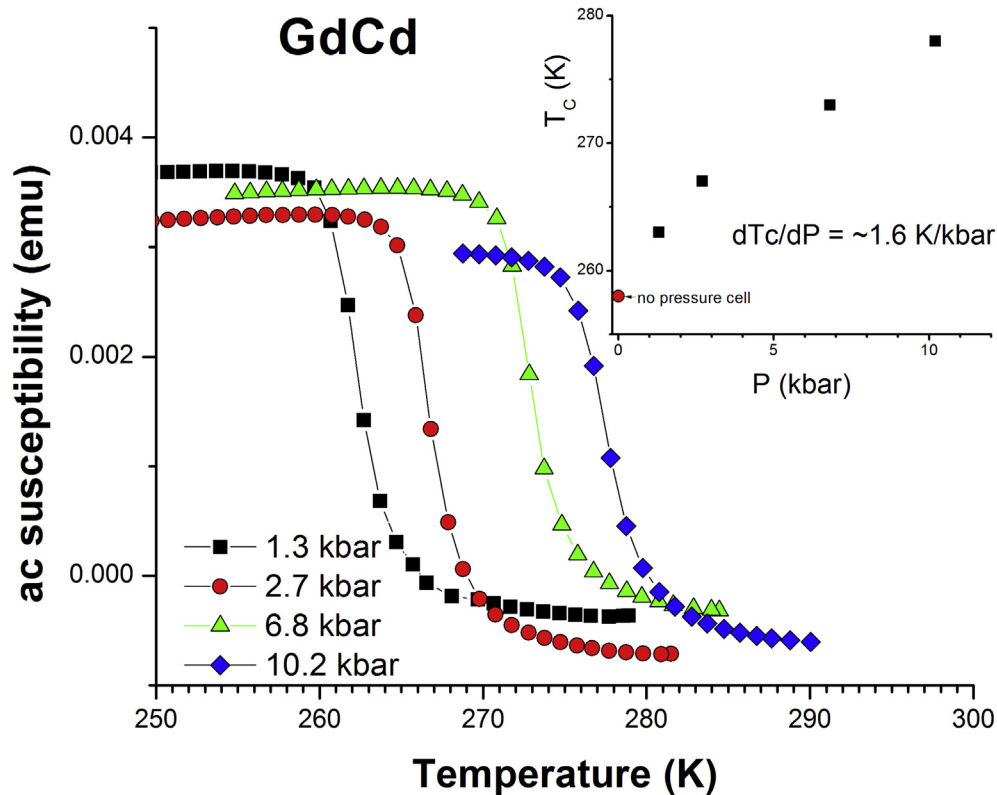

Fig. 3. Pressure-dependent ac susceptibility measurements of GdCd as a function of temperature. (Inset) Curie temperature as a function of pressure.

184 K at zero GPa to around 150 K at 15 GPa. The experimentally determined value for the pressure derivative of the GdZn critical temperature, $dT_C/dP = -0.13$ K kbar^{-1} [23], compares well with our calculated value of -0.45 K kbar^{-1}. For GdCd, owing to the paucity of reliable published experimental pressure data, we have carried out our own pressure-dependent ac susceptibility measurements to test the prediction. The results are shown in Fig. 3. The ambient pressure point has been obtained without pressure cell and is not shown in the figure. A clear increase of the magnetic ordering temperature (T_C) with applied pressure was observed with an approximate rate of change of 1.6 K kbar^{-1}. The $T_C(P)$ dependence is not perfectly linear and a slight tendency to saturation is seen in the inset of Fig. 3. The experimental measurement of $\frac{dT_C}{dP} = 1.6$ K kbar^{-1} reproduces an earlier measurement under gas pressure that finds $\frac{dT_C}{dP} = 1.1$ K kbar^{-1} and is in excellent agreement with the theoretical prediction of 1.5 kbar^{-1}.

The different signs of respectively the GdZn and GdCd pressure derivatives, $\frac{dT_C}{dP}$, would appear to be at odds with the rather noticeable similarity in electronic structure. When plotting T_C as a function of the Gd-Gd distance (see inset of Fig. 1) instead, we observe that both curves behave qualitatively in a very similar way. Starting from large values, T_C initially increases with decreasing Gd-Gd distance for both GdZn and GdCd, reaching a maximum whence it starts decreasing with further reduction of the Gd-Gd distance. The $\frac{dT_C}{dP}$'s shown in the main figure originate from where the two compounds have their equilibrium lattice spacings, marked by black (GdZn) and red (GdCd) arrows in the inset. The observed trend in T_C as a function of Gd-Gd distance could be interpreted in terms of an RKKY like mechanism, but one should note that the oscillation does not go all the way to an AF1 state even at very high pressures. The quantitative differences in the calculated T_C's on the other hand are a result of the different degrees of hybridization of respectively the $3d$ of Zn and the $4d$ of Cd with the $5d$ of Gd, a further indication of the role played by d-states in mediating the magnetic interaction.

To conclude, the successful capturing of these unusual temperature and pressure trends of the Gd intermetallics' magnetism is a consequence of the theory's detailed description of the valence electrons. The theory includes both the response of these electrons to the magnetic ordering of the f-electron local moments as well as their effect upon it.

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