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Abstract. The electronic structure of the intermetallic compounds GdCu and GdZn has been calculated using density functional theory and the LMTO method for the ferromagnetic and two different antiferromagnetic orderings of the Gd local moments. The ground state of GdZn is found to be ferromagnetic while GdCu is antiferromagnetic, in agreement with experiment. The reason for the stability of one or other phase is discussed in terms of density of states features near the Fermi level. The effective exchange parameter J_0 is determined from the Green functions corresponding to the calculated magnetic ground states. It is explained why the d-contribution to the Gd magnetic moment is enhanced in ferromagnetic GdZn.

1. Introduction

Binary equi-atomic intermetallic compounds of rare earth (RE) elements and group Ib and IIb metals exhibit a variety of interesting magnetic phases (see, e.g., Takei *et al* 1979, Pinto *et al* 1988). In contrast to these, most of the compounds of REs with Ni have ferromagnetic ground states and they crystallize in the complex FeB-type structure. When Ni is substituted by a group Ib element (Cu or Ag) the structure changes to the cubic CsCl-type structure with an antiferromagnetic ordered ground state. Most compounds with group IIb elements (Zn or Cd) are FM (e.g. GdZn and DyZn, see Oleś *et al* 1976). In many cases non-magnetic compounds (with, e.g., Y or La) exhibit a tendency to transform from a cubic to a tetragonally distorted crystal structure (see Asano and Ishida 1985); this transition can be induced by heating or by applying pressure. Magnetic and structural transformations in RE–transition metal (TM) compounds are closely related, but so far the nature of this connection is not well understood.

Structure-related transitions can often be explained from the energy bands or equivalently the density of states (DOS) near the Fermi level. Asano and Ishida (1985) calculated the electronic structure of LaCd in its cubic (CsCl-type) modification and found a sharp peak in the DOS near the Fermi level. They showed that when the structure changes from cubic to tetragonal (which is the observed structure of LaCd) this peak splits resulting in a lowering of the DOS at E_F. From this they concluded that the tetragonal phase is more stable and this was confirmed by comparing the

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total energies of the two phases. This example, however, refers to a non-magnetic system. The many *magnetic* RE–TM compounds with the cubic CsCl-type structure have not been studied from this point of view and their electronic structures have not been calculated.

The differences in the total energies of magnetic phases are in many cases of the same order of magnitude as characteristic structural energy differences. Therefore a magnetic phase transition can prevent the occurrence of a structural transformation, i.e. it can stabilize a crystallographic modification that would be unstable without the magnetic interaction.

In this paper we present the calculated electronic structures of two magnetic intermetallic RE–TM compounds and we propose that the magnetic structure stabilizes the crystal stucture of the ordered GdCu and GdZn alloys.

2. Method of calculation

The two intermetallic compounds GdCu and GdZn studied in this paper, are antiferromagnetic (AFM) and ferromagnetic (FM) respectively (Takei *et al* 1979). In order to understand why different magnetic structures exist in such similar (with respect to composition and structure) compounds, we performed self-consistent band-structure calculations for the FM and and AFM configurations of both systems. Since the AFM spin structure is not definitely known, in our calculations we studied two types of spin arrangement which are commensurate with the CsCl crystal structure and which may be described as having spin-waves with the wavevectors $q_1 = \pi/a(111)$ and $q_2 = \pi/a(110)$. The orientation of the local magnetic moments of Gd atoms for these two structures (referred to as AFM(I) and AFM(II)) are shown in figure 1.
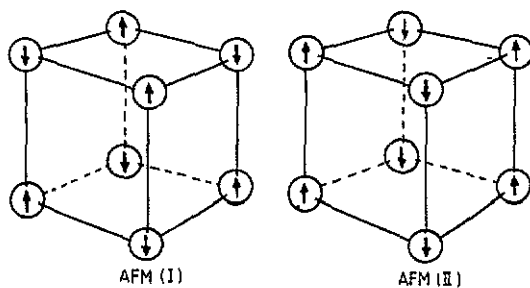

Figure 1. The two types of AFM ordering of the Gd magnetic moments in the CsCl structure considered in this paper.

The band-structure calculations were performed by the scalar-relativistic LMTO method (see e.g. Andersen 1975, Andersen *et al* 1985) in the atomic spheres approximation (ASA). The local density prescription by von Barth and Hedin (1972) for the exchange-correlation potential was used and the f states were treated as band states. In general the f states in the RES are not well described by the local density approximation; however, Gd is an exception since the f-shell is half filled (see, e.g., Sticht and Kübler (1985)). The *k*-space integration involved 455 non-equivalent points in

the Brillouin zone for the cubic FM structure and 525 and 540 k-points for AFM(I) and AFM(II), respectively. The k-space integration was performed by the tetrahedron method using an algorithm to generate k-points (Blöchl 1988) based on the ideas proposed by Jepsen and Andersen (1984). According to this algorithm the Brillouin zone is taken as the parallelepiped spanned by the reciprocal lattice vectors. This is first divided into tetrahedra of optimal identical shape, and then after applying the symmetry operations of the crystal a limited set of inequivalent tetrahedra (i.e. those which are not identical by symmetry) is retained and used in the analytical integration. This gives better convergence for the same number of k-points than the algorithm where the k-mesh is generated in the conventional irreducible part of the Brillouin zone.

The atomic sphere radii are listed in table 1 together with our main numerical results which will be discussed in section 3.

Table 1. Atomic sphere radii used in the calculations and main calculation results.

Inter-metallic	Atomic spheres radii (a.u.)	Magnetic phase	Spin magnetic moment per atom (μ_B)		$N(E_F)$ Ryd^{-1}	Total energy /formula unit (Ryd)
			Gd	Me		
GdZn	3.720 (Gd)	FM	7.23	0.03	35.73	−205.3641
	2.876 (Zn)	AFM(I)	7.00	0.00	42.25	−205.3578
		AFM(II)	7.03	0.00	45.19	−205.3577
GdCu	3.720 (Gd)	FM	7.02	0.05	25.65	−179.1631
	2.610 (Cu)	AFM(I)	6.96	0.00	19.32	−179.1630
		AFM(II)	7.05	0.00	19.54	−179.1643

In addition to the usual results obtained in self-consistent band-structure calculations (i.e. DOS, magnetic moments etc) we have evaluated the matrix elements of the Green function and from these calculated the effective exchange parameter J_0. This parameter determines the stability of the colinear local magnetic moment at the zeroth site against small non-colinear deviations. If J_0 is positive the colinear magnetic configuration is stable. J_0 can be expressed in terms of the potential parameters and the scattering path operator as follows (Liechtenstein *et al* 1987):

$$J_0 = -\frac{1}{4\pi} \int^{E_F} \operatorname{Im} \operatorname{Tr}_L [\Delta(T_\uparrow^{00} - T_\downarrow^{00}) + \Delta T_\uparrow^{00} \Delta T_\downarrow^{00}] \, dE \qquad (1)$$

where (in the framework of the LMTO formalism)

$$\Delta_L = p_{\uparrow l}^0 - p_{\downarrow l}^0 \qquad (2)$$

$$T_{LL}^{ii} = \frac{V_l^i - E}{\Gamma_l^i} + \frac{(V_l^i - E)^2}{\Gamma_l^i} G_{LL}^{ii}. \qquad (3)$$

The latter expression was derived by Gunnarsson *et al* (1983) (see equation (2.39) therein) where the scattering path operator was called $\tilde{g}$ instead of the more common designation T which we use in the present paper. On-site matrix elements of the

perfect crystal Green function G_{LL}^{ii} are expressed in terms of the eigenvectors B_{nL}^{tq} of the effective Hamiltonian introduced by Gunnarsson *et al* (1983):

$$G_{LL}^{(tq)(tq)}(E) = \frac{1}{V_{BZ}} \int_{BZ} dk \sum_n \frac{|B_{nL}^{tq}(k)|^2}{E - E_n(k) - i0^+}.$$ (4)

Although the LMTO and KKR first-principles Green function approach as have been used for solving the impurity or embedded-cluster problem in many recent papers the number of metallic systems for which the Green function has been actually calculated have been limited to a few not very complex crystal structures including the FCC and BCC structures (Braspenning *et al* 1984, Ellialtioglu *et al* 1987, Anisimov *et al* 1988, Antropov *et al* 1988), and the CsCl-type structure (Koch *et al* 1986, Stefanou *et al* 1986). The calculation of the Green function elements for the doubled cells of the AFM phases is more complicated due to the presence of several crystallographically equivalent atoms in the unit cell.

3. Results and discussion

3.1. GdCu

The DOS of the FM and AFM(II) structures of GdCu are shown in figures 2 and 3 respectively. The DOS for the AFM(I) phase are hardly visually distinguishable from those of the AFM(II) phase. The main numerical results are summarized in table 2 for all the structures considered here. We shall now discuss the most important features of the DOS.

Table 2. Partial populations of the valence band states according to LMTO calculations.

Intermetallic	Atom	s↑	s↓	p↑	p↓	d↑	d↓	f↑	f↓
GdZn									
FM	Gd	0.332	0.318	0.372	0.302	0.977	0.646	6.984	0.173
	Zn	0.548	0.564	0.463	0.429	4.947	4.937	0.007	0.003
AFM(I)	Gd	0.349	0.308	0.334	0.339	0.891	0.698	6.983	0.216
	Zn	1.109		0.888		9.876		0.009	
AFM(II)	Gd	0.333	0.321	0.356	0.318	0.907	0.706	6.983	0.200
	Zn	1.107		0.885		9.874		0.009	
GdCu									
FM	Gd	0.379	0.358	0.378	0.327	0.931	0.746	6.983	0.222
	Cu	0.397	0.411	0.238	0.219	4.726	4.681	0.004	0.002
AFM(I)	Gd	0.390	0.354	0.358	0.357	0.911	0.763	6.982	0.210
	Cu	0.807		0.465		9.400		0.005	
AFM(II)	Gd	0.379	0.359	0.385	0.332	0.941	0.737	6.982	0.214
	Cu	0.805		0.464		9.400		0.005	

(i) *The Gd 4f states are split by about 0.38 Ryd by the intra-atomic exchange interaction into two narrow peaks, the lowest-lying of them (for spin-up electrons) being completely filled. The overall shape and positions of these peaks are practically unaffected by the magnetic structure or the 3d element (Cu or Zn) involved. Smaller*
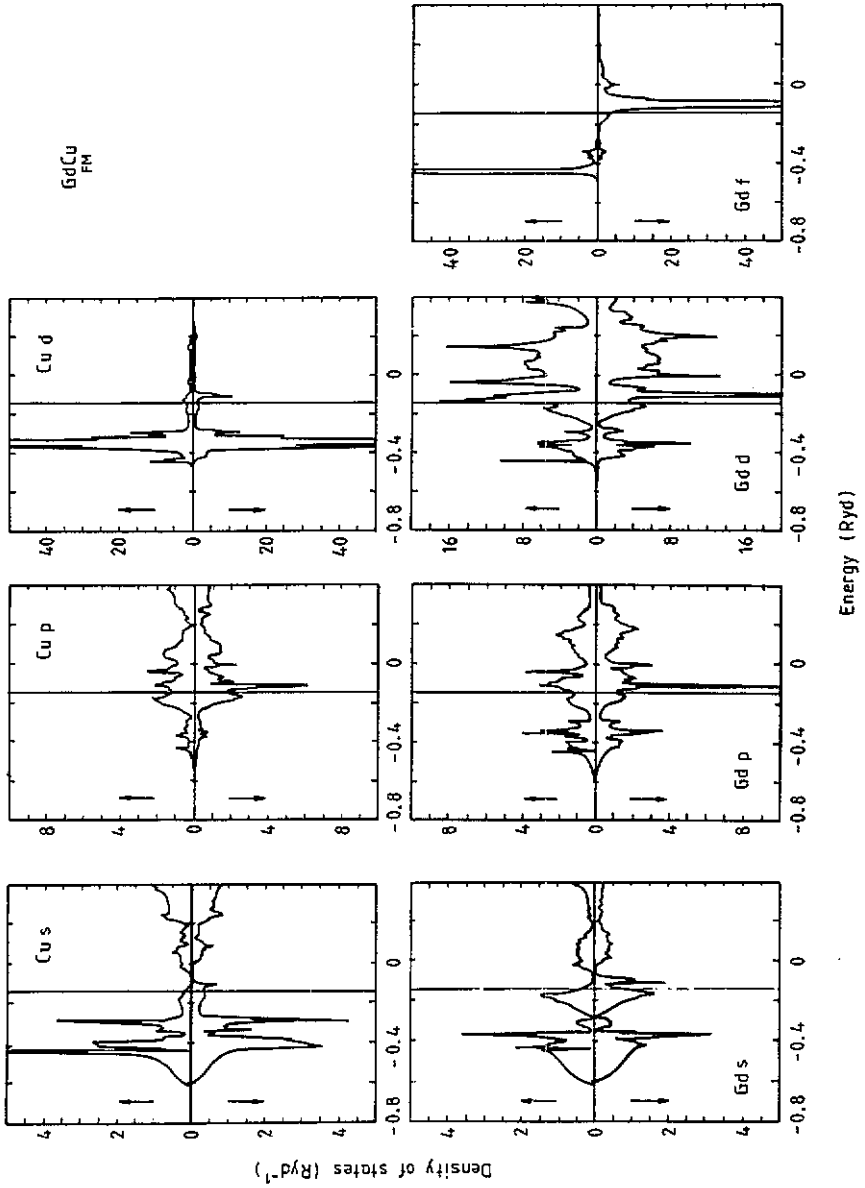
Figure 2. Spin and orbital projected DOS in GdCu for the FM phase. The Fermi level is indicated by the vertical line.
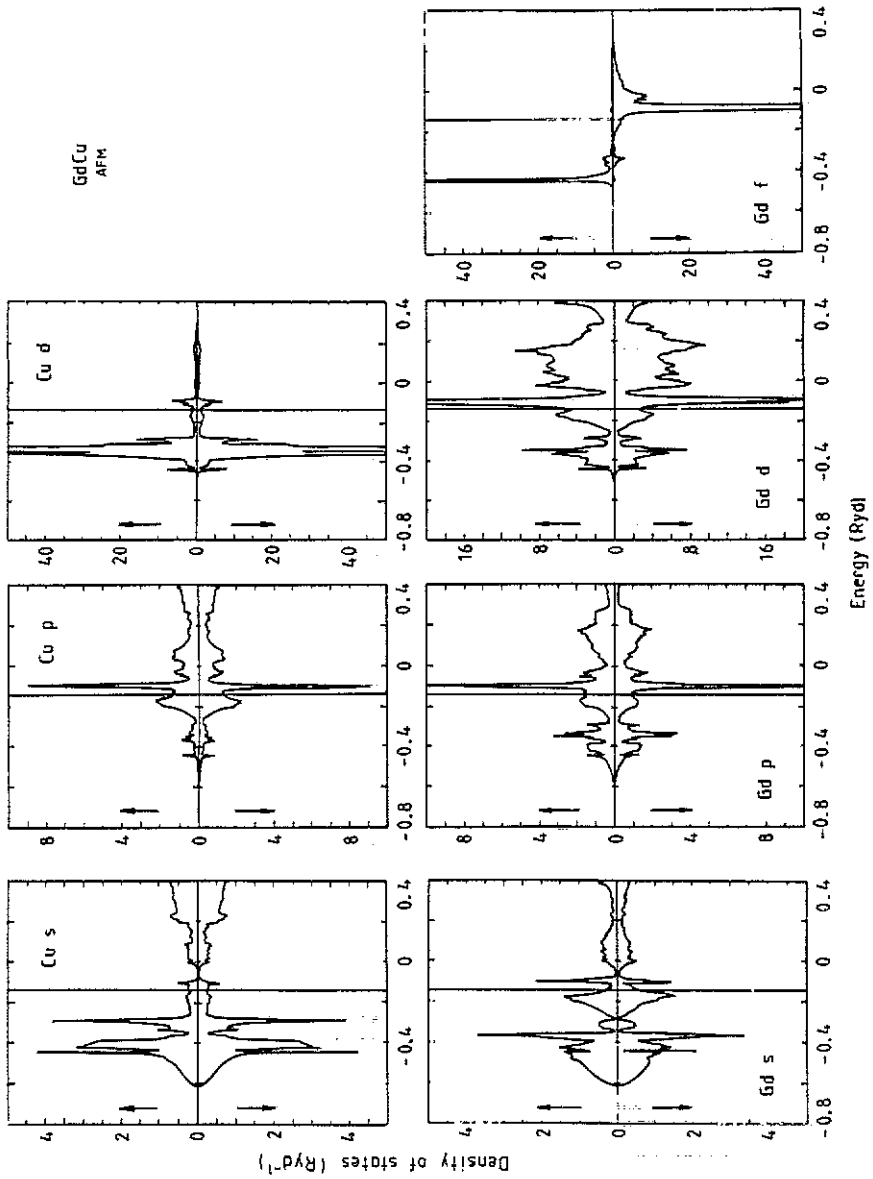
Figure 3. Spin and orbital projected DOS in GdCu for the AFM phase. The Fermi level is indicated by the vertical line.

peaks arising from the hybridization with the Gd 4f states also appear in other partial DOS, in particular in the Gd d and Cu d states.

(ii) A relatively narrow band, mostly Cu 3d in character, is situated about 0.2 Ryd below the Fermi level. Its spin-down and spin-up components are practically identical, exhibiting no spin splitting even for the FM structure. Due to Cu d and Gd d hybridization these states give a pronounced structure to the Gd d DOS.

(iii) The two-peak structure within ± 0.1 Ryd around the Fermi level may be seen in several partial DOS but it is most pronounced in the Gd d DOS. A structure like this was also found in the calculation by Hasegawa and Yanase (1977) for YZn and by Asano and Ishida (1985) for LaCd.

Although the intra-atomic exchange interaction in the Gd 4f shell sustains the magnetic moment which is highly localized and practically independent of the magnetic structures considered (see table 1), the relative energies of the different phases are sensitive to the detailed behaviour of the DOS, especially near the Fermi level. An important difference between the FM and AFM structures is that in the former the effective field splits the bands and hence the peaks in the DOS while in the AFM case, the spin-up and spin-down peaks do not exhibit any such splitting and differ only in their relative intensity. An additional feature of the AFM phase is the absense of local magnetic moments on the Cu atoms. The populations of the partial states of Cu atoms summed over the two spin directions are practically equal in both magnetic structures, therefore the Gd d states which are dominant at the Fermi level and behave differently in the FM and AFM phases are primarily responsible for their relative stability.

In the AFM structure, the Fermi level falls between two peaks in the DOS while the FM splitting shifts the dominant peak in the spin-up DOS towards the Fermi level, thus leading to an increase in $N(E)$. This situation is known to be relatively unfavourable for the stability of a crystal phase. A comparison of the total energies which are listed in table 1 shows that AFM(II) has the lowest energy of all three structures. The energy difference is 1.2 mRyd (per formula unit) or 190 K in temperature units compared with the FM phase. This difference in energies is not directly related to the Neél temperature which is 144 K for GdCu (Sekizawa *et al* 1970), but it is worth noticing that the two temperatures are close.

Our results show that of the two AFM structures considered, the AFM(II) is the true ground state. This is consistent with the results of Takei *et al* (1979) who studied the magnetic structure of the AFM alloy $GdCu_{0.45}Zn_{0.55}$ by neutron diffraction. The fact that the AFM(I) phase has slightly higher energy than that of AFM(II) (in fact it is equal to that of the FM state, see table 1) is somewhat surprising since, as previously mentioned, they have very similar partial DOS and, in particular, the two-peaked structures near the Fermi level are practically identical. This may be explained by the considerably reduced Gd magnetic moment in the AFM(I) structure (table 1) due to the reduction in the Gd d and p contributions to the moment (see table 2) while the net Gd f contribution is identical in all structures. With this reduced magnetic moment, the inter-atomic exchange on the Gd atom fails to lower the total energy of the AFM(I) phase below that of the FM phase.

3.2. GdZn

The most evident difference between the DOS in GdZn (figures 3 and 4) and GdCu is the lower position and smaller width of the Zn d band which therefore exhibits only weak hybridization with other states. As in GdCu these d bands are completely filled

and the different positions do not seem to affect the states near the Fermi level where a two-peaked structure as in GdCu may be seen. The position of the Fermi level is, however, shifted upwards with respect to the peaks, because the conduction bands must now accommodate the additional electron supplied by Zn. We may therefore discuss the changes in terms of a rigid-band picture.

In contrast to GdCu where the AFM ordering of local moments was a mechanism to prevent the exchange splitting of the conduction bands as a whole and to pin the Fermi level in a 'gap' region, the AFM structure of GdZn looks unstable because the conduction band is now filled up to the sharp peak just above the 'gap', thus resulting in a relatively high DOS at the Fermi level (see table 1). In this case, an FM splitting of the bands moves the peak in at least one spin sub-band (the minority spin) away from the Fermi level. The total energy per formula unit of FM GdZn is 6 mRyd lower than that of both AFM structures (the total energy of AFM(I) and AFM(II) are practically equal for this compound).

These simple rigid-band-based considerations seem applicable to a series of pseu-dobinary alloys $GdCu_{1-x}Zn_x$ where a transition from AFM to FM ordering occurs as x approaches 65 at.% (Takei et al 1979). Some important details, however, cannot be understood in the framework of the rigid-band picture, among them the anomalous polarization of the Gd d states in FM GdZn. The magnitude of the d-component of the Gd magnetic moment is 1.5 times higher in FM GdZn than in all other phases considered here (where it has almost the same magnitude); the d-moment is also much higher than in pure Gd (Sticht and Kübler 1985) where the total magnetic moment per atom is relatively high ($7.5 \mu_B$). This may be explained as follows: The Gd f level for the minority-spin state is situated immediately above the Fermi level and manifests itself in the Gd d-DOS as a narrow peak owing to d–f hybridization. For the spin-down states, it remains pinned at the position of the f_1 state when the conduction band is being filled. The corresponding peak in the spin-up density of Gd d states is, however, free to move downwards as the exchange field appears in the FM crystal. When moving through and below the Fermi level, this spin-up peak moves farther down and absorbs more electrons in GdZn than in GdCu. The reason is not that there is an additional electron in the conduction band of GdZn (because this mostly increases the population of the Zn s, p and d states as may be seen from table 2), but rather that the hybridization of the Gd d states with those of the 3d metal is different. In GdCu, the hybridization with the energetically close Cu d states leads to their DOS being reproduced as a compact sub-band in the Gd d DOS near the bottom of the band formed by the proper Gd d states. This is filled by both spin-up and spin-down electrons. In GdZn, the much lower lying Zn d band appears as a minor feature in Gd d-DOS which therefore can only contain a small number of electrons. Gd d electrons therefore have to fill the spin-up peak close to the Fermi level. The increase in the Gd local moment in FM GdZn enhances the exchange energy gain and stabilizes this phase as the ground state.

We shall now discuss the possible effects of magnetic interactions on the structural stability.

As mentioned in the introduction, the stabilization of the tetragonal phase in LaCd (Asano and Ishida 1985) could be explained by the splitting of the peak in the DOS at the Fermi level which reduces the total energy of the system. The magnitude of the splitting was about 0.03 Ryd which is of the same order of magnitude as the exchange splittings in the FM structures considered earlier. Moreover, the difference between the total energies of the cubic and tetragonal phases is 9 mRyd per formula unit
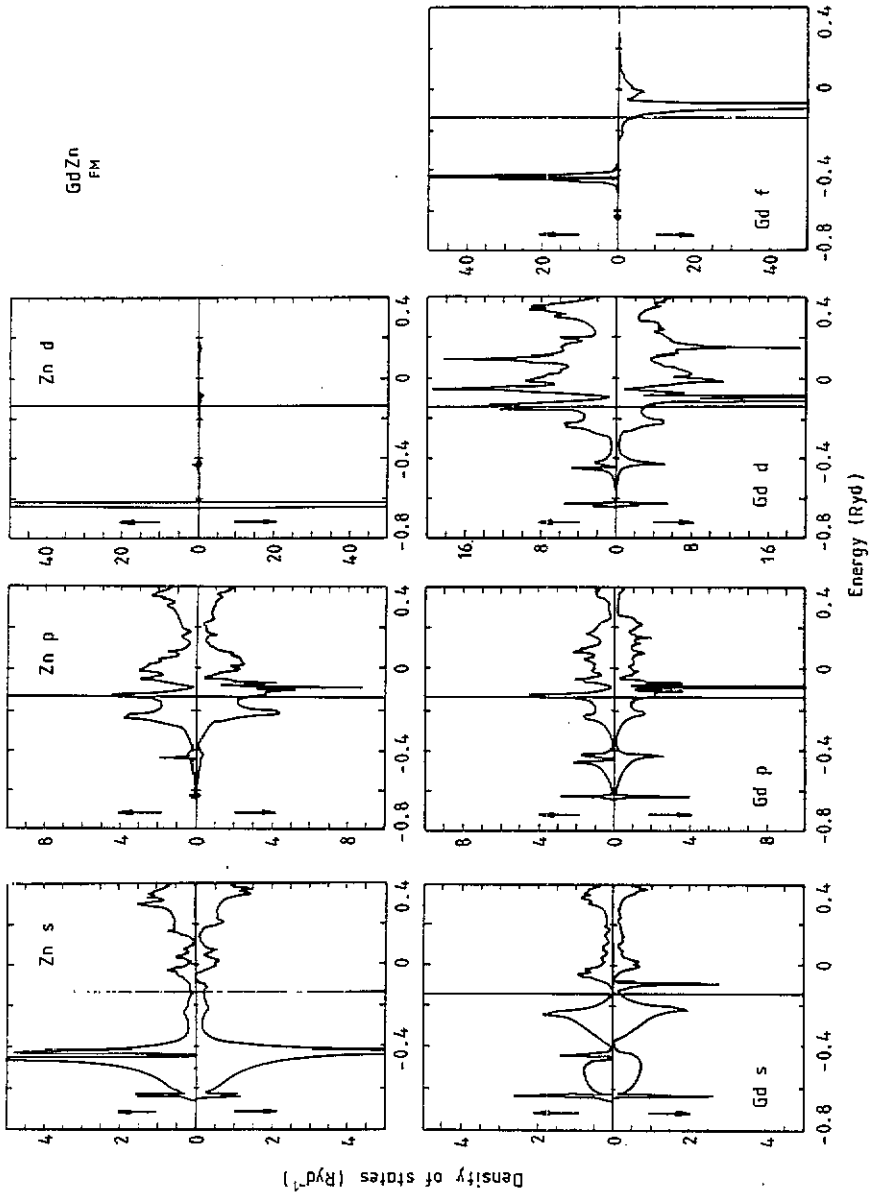
Figure 4. Spin and orbital projected DOS in GdZn for the FM phase. The Fermi level is indicated by the vertical line.
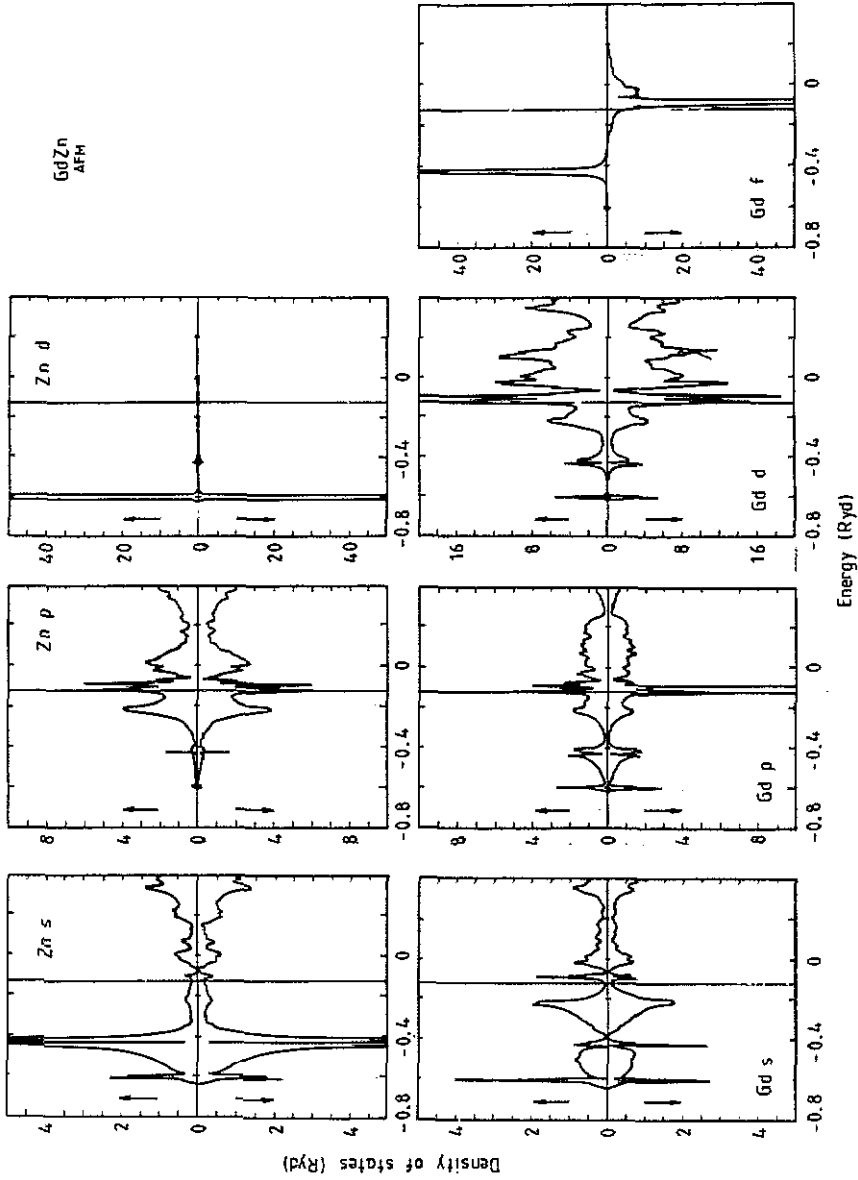
Figure 5. Spin and orbital projected DOS in GdZn for the AFM phase. The Fermi level is indicated by the vertical line.

according to Asano and Ishida (1985) which is close to the energy difference between the FM and AFM phases in our calculation. It shows that the magnetic polarization effects and structural distortions can compete as mechanisms for reducing the total energy of the system, and their interplay can determine the relative stability of one or other phase.

In order to check whether the self-consistent solutions found for the FM and AFM structures of GdZn and GdCu are stable against non-colinear deviations of the magnetic moments, we calculated the exchange parameter J_0 per Gd atom according to equation (1). For GdZn in the FM modification and for GdCu in the AFM(II) modification, the exchange parameters were found to be 22 and 16 mRyd i.e. positive and with the f contribution dominating. For GdZn in the AFM(II) phase, the corresponding value was negative (-9 mRyd) which is consistent with the conclusion following from a comparison of total energies that this phase is not stable.

The fact that the absolute values of J_0 are very different in FM and AFM GdZn reveals the, at least partially, delocalized nature of the Gd magnetic moments (for completely localized moments in the Heisenberg model, J_0 would merely change sign when switching from FM to AFM ordering). The most delocalized part of the Gd moment comes from the 5d contribution which is enhanced in GdZn as previously mentioned.

In conclusion we have found that in GdZn the FM ordering reduces the DOS at the Fermi level, and therefore stabilizes the cubic crystal structure of the CsCl type. The enhancement of the magnetic moment on Gd atoms is another mechanism that works in favour of the stability of this phase. In GdCu, the structural stabilization is achieved by establishing the tetragonal AFM phase AFM(II) which does not result in energetically unfavourable (for this compound) band splittings and at the same time allows high magnetic moments on Gd atoms.

Acknowledgments

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