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Magnetic structures of hcp bulk gadolinium

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We present results of self-consistent linear-muffin-tin-orbital calculations with the atomic-sphere approximation for hcp bulk Gd, using the local spin-density approximation (LSDA) and gradient correction (GC) for the description of exchange and correlation. In the LSDA calculation antiferromagnetic order is favored over the ferromagnetic, and experimentally observed, structure. The GC weakens the bonding, leading to a higher equilibrium lattice parameter. At the new equilibrium volume the ground state is ferromagnetic. Our results point towards a magnetic phase transition under pressure.

In gadolinium localized $4f$ electrons, exchange and relativistic effects play important roles. Thus, it is a good test case for the applicability of the local spin-density approximation (LSDA) to rare earth systems. It has recently been reported that LSDA calculations for hcp Gd favor a layerwise antiferromagnetic order (AFM) over the ferromagnetic one (FM).[1] This is in contrast to the experimentally observed ground state which is clearly ferromagnetic. Another case where the LSDA does not yield the correct magnetic ground state is Fe.[2] The situation for iron is more complicated, however, since even the ground-state atomic structure found in the LSDA calculation—nonmagnetic fcc—is contradictory to the observed ferromagnetic bcc structure. The application of gradient corrections leads to an ordering consistent with experiment because of a gain in magnetic energy.[3–6] Different atomic structures, namely the hcp, dhcp, and fcc structures, of Gd have been studied in LSDA by Temmerman and Sterne[7] but no evidence for a wrong atomic ground-state structure for Gd was found. Thus, we shall confine our study to the question how different descriptions of exchange and correlation influence the magnetic ordering in hcp Gd.

We perform self-consistent linear-muffin-tin-orbital (LMTO) calculations in the atomic-sphere approximation (ASA).[8] We apply density functional theory using the local spin-density approximation (LSDA) in the formulation of von Barth and Hedin[9] for exchange and correlation and the gradient correction (GC) of Langreth, Mehl, and Hu.[10] Spin-orbit coupling is added to the spin-polarized scalar-relativistic Hamiltonian variationally using the Koelling and Harmon form.[11,7] The basis consists of spherical harmonics with $l_{\max} = 3$ and the $4f$ electrons are treated as intinerant band states as has been argued to be essential for the appropriate description of Gd.[12,13] In another approach[14] the f electrons are treated as core electrons, influencing the valence electrons only as an external potential, leaving out the all important hybridization of the unoccupied f states with the s, p, and d valence electrons.[15]

We use two energy panels in our calculation to allow the spatially far extended $5p$ semicore electrons to relax.[7] All energetically lower lying electrons are kept frozen. The $\mathbf{k}$ space integrals are replaced by sums over 112 $\mathbf{k}$ points in the irreducible part of the volume Brillouin zone and the tetrahedron method is used.[16] The uncertainty of the total energy due to the $\mathbf{k}$-point sampling is less than 0.05 mRy per atom. The c/a ratio was fixed to the experimental value[17] of 1.587 since its optimization (a) is beyond the limits of the ASA and (b) was reported to be problematic even in the full-potential augmented plane wave method[13] due to the softness of Gd. To check the validity of the results obtained with the fixed c/a ratio, we varied the c/a ratio over a range of 5% at the respective equilibrium lattice parameters and found that the conclusions should not be altered by an optimized c/a ratio.

First, we calculated the total energy for FM and AFM hcp Gd as a function of the atomic volume with LSDA. The magnetic moments are alligned parallel to the c axis, which is the easy axis of magnetization at room temperature. In the AFM phase the moments in every second layer are flipped around as shown in Fig. 1. The result for the total energy as a function of the atomic-sphere radius is shown in Fig. 2(a). The equilibrium lattice parameters and bulk moduli are obtained from a fit of the total energies to the Murnaghan equation of state.[18] Zero-point energies are not included. The calculated FM lattice parameter deviates by 0.4% from the experimental value. The good agreement between the experimental and the theoretical values as compared to other calculations[7,12,13,19,20] is due to a slightly different treatment of the $5p$ semicore.[21] The equilibrium lattice parameter of the antiferromagnetic structures is 0.5% smaller than that of the ferromagnetic structure. Consequently, the AFM bulk modulus is about 3% larger than the FM value. At the FM equilibrium volume the total energy of the layerwise antiferromagnetic bulk is 0.55 mRy per atom lower than that of the ferromagnetically ordered. An antiferromagnetic ground state, however, is not ob-

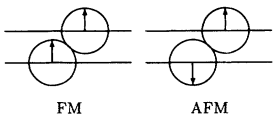

FIG. 1. Schematic picture of the arrangements of the magnetic moments in the two different bulk structures. The lines show (0001) layers.

served experimentally. We note that for $r_{\mathrm{ASA}} > 3.8$ bohr (2% larger than the theoretical equilibrium value) the ferromagnetic solution becomes favorable.

Thus, Gd is another case for which LSDA does not describe the magnetic ground state properly. We will try to improve the description of exchange and correlation by the use of gradient corrections.[3–6] We use the gradient correction of Langreth-Mehl-Hu[10] which is merely an addition of gradient terms to the von Barth-Hedin functional we used before. Figure 2(b) shows the total energy of both magnetic structures as a function of atomic-sphere radius with the c/a radius fixed as before. For both structures the equilibrium lattice parameter is increased by about 4% compared to the LSDA result and the bulk moduli are consequently smaller. This behavior obeys the common trend in GC results as compared to L(S)DA.[22] It is due to a redistribution of charge caused by stronger exchange repulsion in some parts of space. This can be seen in Fig. 3 where the differences between the self-consistent total radial charge densities of GC and LSDA calculations are shown for the FM phase in the upper and the AFM phase in the lower panel for the two different equilibrium ASA radii. Within the bonding region the changes for both phases are similar and therefore lead to comparable lattice expansion. The elastic

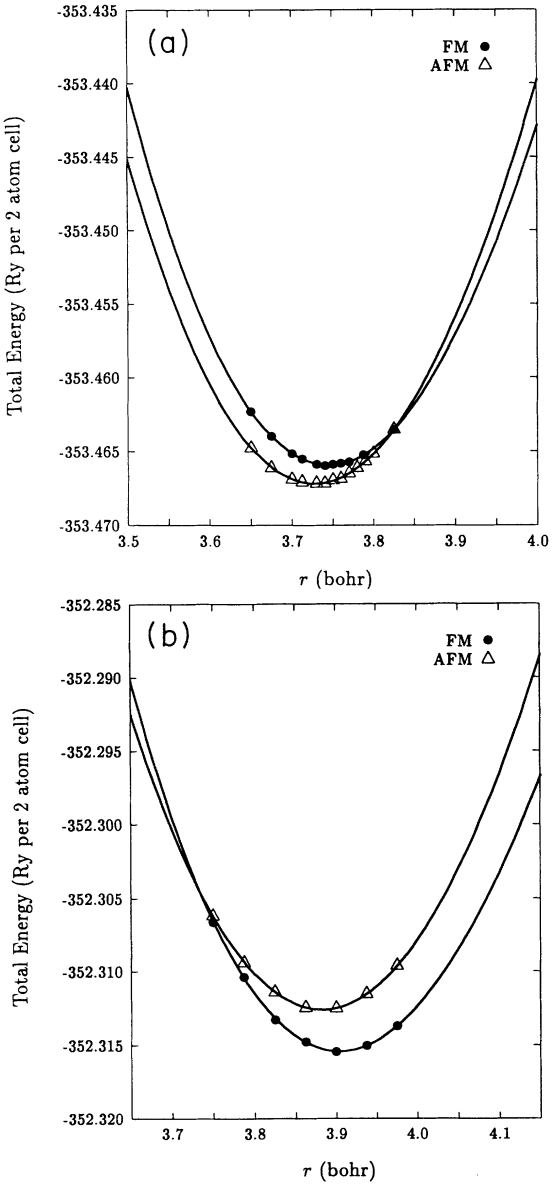

FIG. 2. Total energy of hcp Gd two atom unit cell as a function of the atomic sphere radius from the (a) LSDA and (b) GC calculations. The c/a ratio was fixed to the experimental value of 1.587 for both structures. Symbols show the calculated values and the lines are obtained from the fit to the Murnaghan equation of state.

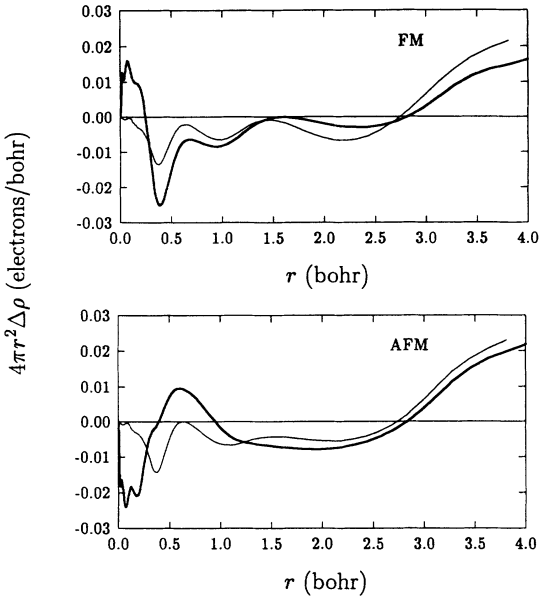

FIG. 3. Difference in the radial charge between GC and LSDA results for the two equilibrium volumina. The upper panel shows the result for the FM phase, the lower panel for the AFM phase. Thin lines are used for $r_{\mathrm{ASA}} = 3.75$ bohr and thick lines for $r_{\mathrm{ASA}} = 3.90$ bohr.

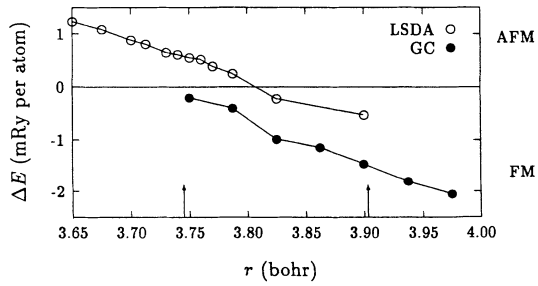

FIG. 4. Total energy difference between the ferromagnetic and antiferromagnetic phase as a function of the atomic sphere radius. The arrows indicate the two equilibrium radii of the FM phase.

TABLE I. Elastic properties of the ferromagnetic (FM) and layerwise antiferromagnetic (AFM) phases of hcp Gd. The experimental values for the bulk modulus were extrapolated to 0 K.

		r_{ASA} (bohr a.u.)	a_0 (Å)	B_0 (GPa)
LSDA	FM	3.745	3.620	40.9
	AFM	3.727	3.603	42.0
GC	FM	3.903	3.773	35.0
	AFM	3.882	3.753	35.8
Expt.	FM		3.6336[a]	41.3[b], 39.9[c]

[a]Reference 23 at 24 °C.
[b]Reference 24.
[c]Reference 25.

properties for both sets of calculations are summarized in Table I. At the new equilibrium volume the ordering is now reversed and the ferromagnetic structure is favored over the antiferromagnetically ordered one by 1.46 mRy per atom. The difference in the total energies of the two magnetic structures is shown in Fig. 4. Both the LSDA and GC curve show that for larger volumes the FM solution is preferred and that for smaller volumes the AFM solution wins. However, for the GC case the onset of the FM solutions occurs at smaller ASA radii. An indication for the reason of this shift can be seen in the polarization ζ, which is defined as the difference in charge density of spin up minus spin down divided by the total charge density. ζ for LSDA and GC at the two equilibrium volumes are depicted in Fig. 5. For the AFM phase we show the atom with total spin down (lower panel). In the upper panel the results for the FM phase are shown. The polarizations from the LSDA calculations are smaller for both ASA radii and their changes larger for the GC. For the AFM phase the polarization is not affected much by either description of exchange and correlation or the variation in volume. The stronger polarization of the FM phase in GC as compared to the LSDA result leads to a slight stabilization of the FM against the AFM phase for the same volume. Similar observations have been reported for Fe.[5] The magnetic moments are summarized in Table II. The total magnetic moments are smaller in the AFM phase than in the FM phase and do hardly vary with lattice parameter or description of exchange and correlation. In the FM phase we observe an increase in the spin moment upon GC which is partially compensated by a decrease of orbital moment. It is clear from Table II, however, that the magnitude of the magnetic moment depends mainly on the lattice parameter and not on the description of exchange and correlation. The calculated value near the experimental lattice parameter agrees reasonably well with other calculations[7,12,13,19,20] and so does the g factor. The values at the equilibrium volume of the GC calculation are by about $0.2\mu_B$ larger. The agreement with the experimental value[26] of $7.63 \pm 0.01\mu_B$ is better for the moment calculated at the LSDA equilibrium conditions (-1% deviation) than for the GC value ($+2\%$ deviation).

TABLE II. Magnetic moments per atom in units of the bohr magneton μ_B. The first lines show the spin and second the orbital contributions. The experimental value for the magnetic moment is $7.63 \pm 0.01\mu_B$ (Ref. 26).

	s	p	d	f	sum	total	g
FM							
r_{ASA} = 3.75 bohr a.u.							
LSDA	0.016	0.146	0.425	6.776	7.363		
	0	-0.004	-0.033	0.232	0.195	7.56	2.055
GC	0.016	0.153	0.433	6.783	7.385		
	0	-0.004	-0.032	0.214	0.178	7.56	2.051
r_{ASA} = 3.90 bohr a.u.							
LSDA	0.014	0.181	0.500	6.765	7.459		
	0	-0.006	-0.038	0.331	0.287	7.75	2.079
GC	0.014	0.193	0.525	6.771	7.502		
	0	-0.006	-0.038	0.320	0.276	7.78	2.076
AFM							
r_{ASA} = 3.75 bohr a.u.							
LSDA	0.031	0.036	0.346	6.734	7.147		
	0	-0.020	0.145	0.172	0.297	7.44	2.086
GC	0.030	0.037	0.341	6.739	7.147		
	0	-0.019	0.146	0.162	0.289	7.44	2.083
r_{ASA} = 3.90 bohr a.u.							
LSDA	0.031	0.041	0.344	6.727	7.143		
	0	-0.020	0.132	0.227	0.339	7.48	2.097
GC	0.030	0.041	0.333	6.732	7.136		
	0	-0.019	0.134	0.212	0.327	7.46	2.094

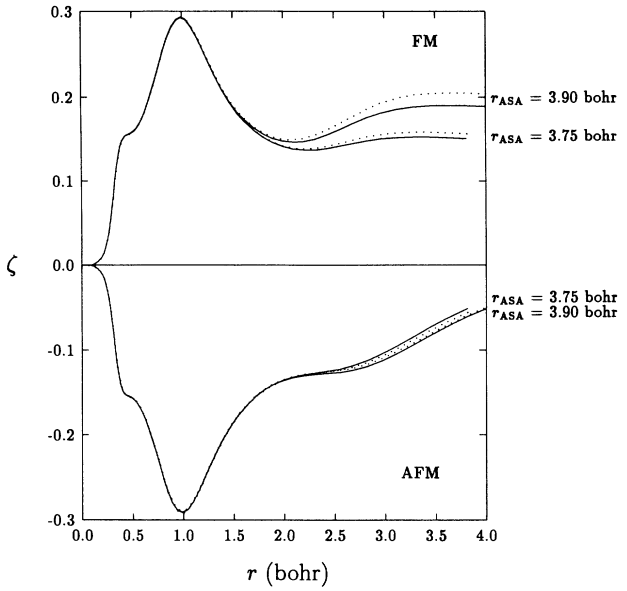

FIG. 5. Polarization ζ as a function of the distance from the atomic origin. Solid lines represent results from the LSDA calculations, dotted lines GC results. For description see text.

In conclusion we find that a layerwise antiferromagnetic (AFM) hcp Gd bulk structure is favored over the ferromagnetic (FM) structure in a LSDA description. This contrasts with the experimentally observed ground state for bulk Gd which is ferromagnetic. The description of the elastic properties is in good agreement with experiment in the LSDA picture. The use of the Langreth-Mehl-Hu GC increases the equilibrium lattice parameter for both structures by about 4% and finds a FM ground state starting from smaller ASA radii than LSDA. The magnetic ground state at the GC equilibrium lattice parameter is FM. We find a transition from the AFM to the FM state for r_{ASA} = 3.83 (LSDA) and 3.73 (GC) bohr radii. The transition pressure is estimated to be of the order 4–5 GPa from the GC results.[27] Such a structure has not been observed experimentally but there is a transition from the ferromagnetic hcp into a metastable antiferromagnetic Sm-type rhombohedral structure at pressures in the range of 1.5–2.7 GPa.[28] The Sm-type rhombohedral structure is the energetically next atomic structure in the transition row hcp → Sm-type → dhcp → fcc observed for the rare earths under pressure.[28] Its energy difference to that of the hcp structure should therefore be smaller than the dhcp-hcp difference of 0.92 mRy as calculated by Temmerman and Sterne[7] which brings it in the same energetical range as the differences between FM and AFM hcp structures and this might well be the reason why the AFM hcp structure has never been experimentally observed. Since the Sm structure is structurally still quite similar to the hcp structure we believe, however, that our results indicate that the magnetic ordering is reasonably described with GC.[27]

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