Origin of Magnetic Anisotropy of Gd Metal

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Using first-principles theory, we have calculated the energy of Gd as a function of spin direction, θ, between the c and a axes and found good agreement with experiment for both the total magnetic anisotropy energy and its angular dependence. The calculated low temperature direction of the magnetic moment lies at an angle of 20° to the c axis. The calculated magnetic anisotropy energy of Gd metal is due to a unique mechanism involving a contribution of 7.5 μeV from the classical dipole-dipole interaction between spins plus a contribution of 16 μeV due to the spin-orbit interaction of the conduction electrons. The $4f$ spin polarizes the conduction electrons via exchange interaction, which transfers the magnetic anisotropy of the conduction electrons to the $4f$ spin.

The magnetic anisotropy energy (MAE) of the rare earth metals normally arises from the interaction between the crystalline electric field and the electric multipole moments of the $4f$ charge cloud [1]. Typical anisotropy energies of rare earth metals are of the order of meV/atom. Since the electric multipole moments of an ion in a pure S state are zero, Gd metal is an exception. Its measured anisotropy energy is 2 orders of magnitude smaller than that of a typical rare earth metal but is the same order of magnitude as the $3d$ transition metal Co, which also crystallizes in the hexagonal closed-packed structure. However, the origin of the MAE of Gd has never been understood [2]. Dipole-dipole interactions between the large spins are known to make a significant contribution [1,3,4], and they contribute an anisotropy energy of the form $K_1^0 \sin^2\theta$ where θ is the angle between the magnetic moment and the c axis with $K_1^0 = 7.5$ μeV/atom. However, the total measured MAE from experiment is 35.4 μeV/atom [5,6], requiring a contribution of 28 μeV/atom that must originate elsewhere. The easy direction is observed to lie at an angle of about 20° to the c axis at low temperatures [7], which would not be possible without $\sin^n\theta$ contributions ($n > 2$) to the MAE.

Since the Gd f^7 configuration fills the spin-up shell, the spin density is spherical and higher magnetic multipole interactions between the f spins may be ruled out [8]. One possibility is that the Gd ion is not in a pure S state. The quantum numbers L and S are not exactly good quantum numbers due primarily to spin-orbit interaction and configuration interaction although J remains a good quantum number if the crystal field is weak, as is the case for heavy rare earths. We calculate [9] that the ground state is better than 97% pure. However, even if the exact ground state were known, it would not be possible to calculate the magnetic anisotropy without knowledge of the crystal field.

We propose instead that conduction electron MAE is the dominant contribution. Conduction electron magnetic anisotropy is small in $3d$ transition metals and is known to be due to the spin-orbit interaction of the $3d$ electrons [10–21]. The MAE is considerably larger in magnetic actinide compounds where the spin-orbit interaction of the $5f$ states is large [22,23]. The rare earth metals are $5d$ transition metals, where the $5d$ states are more than 10 eV broad and would not by themselves be magnetic. They are, however, polarized through exchange interactions with the $4f$ states and the conduction electron moment reaches a maximum calculated value for Gd at about $0.65\mu_B$/atom [24–27]. This provides a new mechanism for the magnetic anisotropy. A magnetic field, applied away from the easy axis, interacts with and rotates both $4f$ and conduction electron magnetic moments. However, the exchange field of the $4f$ spin is much larger than any applied field, and it also polarizes the conduction electron moment parallel to the applied field. The spin-orbit splitting of the conduction electrons provides the magnetic anisotropy that, since any applied field couples mainly to the $4f$ spin, would *appear* to be a magnetic anisotropy of the localized $4f$ states if they are described by a spin Hamiltonian.

In Gd metal the spin-up $4f$ states are all occupied and, when spin polarized, lie well below the Fermi energy. In the absence of spin-orbit interaction it makes little difference whether these states are treated as part of a spin-polarized core or as part of the band structure. There is a problem with the empty spin-down states [28–33]. For example, Harmon [29] has argued that the empty $4f$ spin-down states are a few eV above the Fermi energy, hybridize with the conduction electrons, and change the Fermi surface. Since the calculated MAE unforgivingly reflects the quality of the electronic structure calculations, we have calculated the MAE with the $4f$ states treated both as spin-polarized conduction electrons and as

TABLE I. Calculated and experimental de Haas–van Alphen frequencies for Gd (in 10^7 G). In brackets calculated frequencies with spin-orbit interaction are given. The FP-LMTO results are the present work, atomic sphere approximation (ASA) results are from [27]. MY stands for Mattocks and Young [34].

MY identification	Exp. [34]	Calc. FP-LMTO	Calc. [27] ASA
α_1	4.0	5.05 (5.13)	5.47 (5.36)
α_2	1.35, 1.63	1.89 (1.92)	2.19 (2.05)
γ_1	6.9	6.01 (5.98)	7.77 (7.44)
α_3	2.45	2.41 (2.41)	3.66
γ_2	8.7	7.77 (7.81)	10.20
β_1	4.5	4.45 (4.37)	5.80 (5.51)

spin-polarized core states. When the $4f$ states are treated as spin-polarized conduction electrons the calculated maximum value of E_A at $\theta = 90°$ is 571 μeV/atom, an order of magnitude larger than experiment [5]. The large calculated MAE is due to the effect of spin-orbit interaction on the $4f$ states when the f states are in bands, which is eliminated when the $4f$ spin density is derived from an S state within the standard model for the rare earths. Further evidence in favor of the standard model is provided by the calculated Fermi surface. With the $4f$ states part of a localized core, we calculated some of the Fermi surface sheets (α_1, α_2, α_3, γ_1, γ_2, and β_1) and found excellent agreement with the experiment of Mattocks and Young [34] (MY) as illustrated in Table I. Therefore, in what follows we always refer to calculations with the $4f$ states in a self-consistent spin-polarized core and absent from the band structure [35].

In Fig. 1 the calculated E_A is plotted together with the curve for the measured low temperature E_A. The latter is derived from the regular part of the magnetic torque obtained from [5], Eq. (4). The irregular part of the
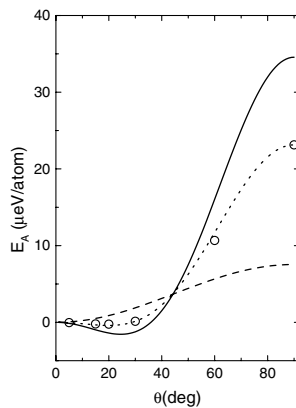

FIG. 1. Calculated energy of Gd metal as a function of angle from the c axis. The full line is the experimental E_A from data in Ref. [5], Eq. (4). The open circles are the calculated total MAE results for the electronic structure plus dipole contribution. The dashed line is the dipole contribution. The dotted line is a fit to the calculated results using $-11.568(\cos 2\theta - 1) + 3.765(\cos 4\theta - 1)$.

magnetic torque shifts the minimum in E_A to 20°. The calculations were made with a relativistic, full-potential linear muffin-tin orbitals method (FP-LMTO) [36]. The conduction band basis set included a double basis set [36] of $5s$, $5p$, $6s$, $6p$, and $5d$ states. The self-consistent calculations were made in the local spin density approximation [37] with the band contribution to E_A evaluated from the force theorem [13,38,39].

Technically the most challenging aspect of our calculations is the large number of k points needed to converge E_A. We tried to solve this problem initially by using the Gaussian smearing method of Methfessel and Paxton [40] to its lowest order for calculating the distribution function, together with a very large number of k points. We tested several densities of k-point sampling until convergence was achieved. The largest number considered was 65 536 k points in the Brillouin zone and it yielded a MAE that deviates less than 1% from the MAE using 27 648 k points. The calculated energy difference between basal plane and c-axis magnetization directions was about 40 μeV. The shape of the E_A curve was reproduced less accurately with this Brillouin zone sampling since its functional dependence was approximately $\sin^2\theta$ and there was no minimum off the c axis. The modified tetrahedron method [41], which employs quadratic interpolation of the band structure, should be more accurate, and when we applied it we obtained results that are both qualitatively and quantitatively different from those obtained from the Gaussian smearing method [40] in its lowest order. Although higher order sinusoidal contributions started to be appreciable with a 27×10^3 k-points mesh, 3.2×10^5 k points were required in order to achieve convergence. Values of $E_A(\theta)$ obtained with the largest considered mesh (3.2×10^5) deviated from values calculated with the next largest (2.33×10^5) by less than 10% for $\theta \leq 20$ and by less than 3% for larger angles. We obtain a minimum in the electronic structure contribution of -1.75 μeV at 30° which leads to a minimum in the total calculated E_A of -0.24 μeV at 20°.

The huge number of k points needed to converge the eigenvalue sum and MAE, and the fact that the lowest order in the expansion of the Gaussian smearing
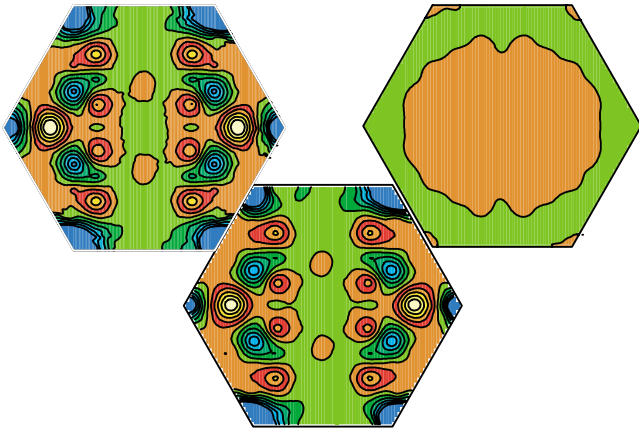
FIG. 2 (color). Calculated E_A (band) of Gd metal for different k points in the k_x-k_y plane ($k_z = 0$) (top left). The central figure reports contributions from all states with energy ϵ ($E_F - 1.714$ eV $\leq \epsilon \leq E_F$), while the top-right figure refers to contributions from states with energy $-\infty \leq \epsilon \leq E_F - 1.714$ eV. E_F indicates the Fermi energy. The color scale (blue, green, brown, yellow) represents an increasing MAE going from $\leq -5000\ \mu$eV/atom (blue) to $\geq +5000\ \mu$eV/atom (yellow). The transition from negative to positive contributions occurs between green and brown coloration.

method [40] yields results that contain no contribution higher than $\sin^2\theta$ to the MAE, suggests that the MAE is extremely sensitive to the fine structure close to the Fermi surface. As is shown in Fig. 2 contributions to the MAE are concentrated in a region in k space close to the Fermi energy with contributions from single k points bigger than the total (but with differing signs). This is consistent with the observation made by Franse and Gersdorf [5] that 21 parameters are required in the expansion of the torque curve in sinusoidal functions in order to obtain a satisfactory fit but that this number could be reduced to only 4 if one took into account Fermi surface effects with a simple model as proposed in the same paper.

In conclusion, we have shown that the MAE of Gd metal is due to a combination of the dipole-dipole interaction and the MAE of the conduction electrons. Since contributions to the conduction electron MAE of higher order than $\sin^2\theta$ occur only when quadratic interpolation of the energy bands is used rather than Gaussian smearing these higher order contributions must be due to extremely fine band structure effects close to the Fermi energy. The $4f$ spin polarizes the conduction electrons via exchange interaction, which transfers the MAE of the conduction electrons to the $4f$ spin. This mechanism for the MAE must be present in all of the rare earth metals and the heavy actinides but, since it is far smaller than the MAE arising from the interaction between the crystalline electric field and the electric multipole moments of the $4f$ charge cloud, it is particularly important for S-state ions.

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