Temperature dependence of the ferromagnetic order parameter in Gd, Tb, and Dy

M. D. Kuz'min,[1] A. S. Chernyshov,[2] V. K. Pecharsky,[2] K. A. Gschneidner, Jr.,[2] and A. M. Tishin[3]
[1]*Leibniz-Institut für Festkörper-und Werkstoffforschung, IFW Dresden, PF 270116, D-01171 Dresden, Germany*
[2]*Ames Laboratory and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-3020, USA*
[3]*Department of Physics, M.V. Lomonosov Moscow State University, 119992 Moscow, Russia*
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Temperature dependence of spontaneous magnetization, $M_s(T)$, corresponding to the single-domain ferromagnetic state, has been studied experimentally using high-purity single crystals of Gd, Tb, and Dy. The resulting $M_s(T)$ curves follow the "3/2−5/2−1/3 law." Anomalies due to the crystal-field gap and to the helix-ferromagnet transition in Tb and Dy are practically indiscernible.

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Ever since the initial success of Weiss's molecular field theory nearly a century ago[1] progress toward an adequate quantitative description of ferromagnetism has been slow. Satisfactory agreement between theory and experiment has been achieved in certain particular cases, but no general equation of state of a ferromagnet has been found. After decades of oblivion, the prospects of reaching this goal look bright again after the recent announcement of a formula accurately describing spontaneous magnetization M_s at arbitrary temperature:[2]

$$\frac{M_s(T)}{M_s(0)} = \left[1 - s\left(\frac{T}{T_C}\right)^{3/2} - (1-s)\left(\frac{T}{T_C}\right)^{5/2}\right]^{\beta}, \qquad (1)$$

It is worth noting that in the past,[3,4] $M_s(T)$ has been modeled by various empirical functions employing as many as five fitting parameters. In Eq. (1), the number of adjustable parameters is reduced to a minimum: Two scale factors, $M_s(0)$ and T_C, and a single dimensionless parameter s determining the shape of the curve. The critical exponent β proved to be close to 1/3 in ferromagnetic metals,[2,5] whereas ferromagnetic insulators appear to be better described with $\beta=0.369$,[6] which is the theoretical value characteristic of the three-dimensional (3D) Heisenberg universality class.[7]

Equation (1) has been verified for a rather limited number of ferromagnets for which the necessary experimental data were available in the literature. One exception—iron—follows a law similar to Eq. (1) but the exponent in the last term in square brackets is 4 rather than 5/2.[2] It is therefore critical to extend the analysis to a greater number of ferromagnets. Unfortunately, the use of spectroscopic data instead of spontaneous magnetization or low sample quality may result in artifacts. The best way forward is to conduct needed experimental studies of magnetization using high-purity single crystals. Elemental solids are preferred to binary or ternary compounds because disorder and impurities are easier to minimize.

Here, we concentrate on heavy lanthanides Gd, Tb, and Dy. When magnetically ordered, they are either collinear ferromagnets (Gd) or nearly ferromagnets (Tb and Dy): Even when the ferromagnetic state is not the ground state, it lies only slightly above the (helical) ground state and collinearity is attainable in moderate magnetic fields, i.e., ~1–2 T for Dy (Ref. 8) and as little as 0.02 T for Tb.[9] Therefore, these systems are no different from ordinary ferromagnets as far as experimental determination of M_s is concerned, Dy being equivalent to a high-coercivity case. Magnetic fields $\lesssim$5 T, available in most commercial magnetometers, are sufficient in order to determine M_s.

From the conceptual point of view, one should note that the spontaneous magnetization vector in the helical phase is, of course, zero when averaged over the volume of a macroscopic sample. However, averaging the magnetic moments of all atoms in the nth layer yields a nonzero vector $\mathbf{M}_n$, its magnitude being independent of n. Thus, in the helical phase, the quantity M_s should be understood as $M_s = \langle|\langle\mathbf{M}\rangle_{n\text{th layer}}|\rangle_n$, rather than just $\langle\mathbf{M}\rangle_{\text{volume}}$. This situation is, in a way, similar to that in a multidomain state of an ordinary ferromagnet.

The so-defined quantity M_s owes its importance to the fact that, when magnetic ordering takes place, it can be regarded as an order parameter, or a measure of the *degree* of the magnetic order in a system.[10] The *kind* of the magnetic order can then be described by the helix wave number k, relevant to the energetically weaker order-order transitions between the ferromagnetic ($k=0$) and helical ($k\neq 0$) phases. Such transitions are expected to have no significant effect on $M_s(T)$.

Herein, we report a designed experimental verification of Eq. (1). Apart from the already mentioned noncollinearity of the ground state, Eq. (1) also disregards the crystal-field gap in the magnon dispersion relation. This neglect did not lead to serious consequences in the case of a hard magnetic material, YCo_5.[2] Here, we intend to test if the same is true in relation to Tb and Dy.

The single crystals of Gd, Tb, and Dy investigated in this work were prepared by the Materials Preparation Center at the Ames Laboratory using the strain-anneal method. The starting polycrystalline metals were 99.89 at. % (99.98 wt. %) pure. The contents of major impurities in Gd/Tb/Dy were as follows (in ppm atomic): O—658/357/600, C—197/713/190, F—110/3/110, Fe—7.6/7/60, and N—67/23/50. The specimens for the magnetization measurements were cut using the spark erosion technique from large grains and shaped as parallelepipeds with the following dimensions (in mm): 1.8×1.8

$\times 7.9$ (Gd), $1.8\times 1.8\times 10$ (Tb), and $2\times 2\times 4$ (Dy). The magnetic field was always applied along the longest edges of the samples, which were parallel to the easy magnetization axes, i.e., to the $[10\bar{1}0]$, $[11\bar{2}0]$, and [0001] directions in the case of Dy, Tb, and Gd samples, respectively. The crystallographic directions were determined using the Laue backreflection technique. The combined accuracy of orientation with respect to the magnetic field was $\pm 5°$.

The magnetization was measured using an extraction magnetometer (Lake Shore, Model No. 7225) in static magnetic fields ranging from 0 to 5.6 T and in the temperature interval from 4.5 to 300 K. The absolute accuracy of the magnetic measurements was checked against the Pt standard and found to be better than 5%, the relative accuracy being about 1%. All magnetization data were corrected for demagnetization. The demagnetizing factors used in the case of Gd, Tb, and Dy were 0.1, 0.09, and 0.2, respectively.[11]

The spontaneous magnetization was determined following Belov and Goryaga,[12,13] i.e., presenting the magnetization isotherms as B/M versus M^2 and extrapolating the linear high-field sections to $B/M=0$ in order to extract the intercept, M_s^2. Extrapolation from the high-field region, free from magnetic domains, is essential for the correct determination of $M_s(T)$. We note that the so-called kink method,[14] based on an oversimplified molecular field model,[15] is not a valid alternative. Operating at small fields, it simply ignores the existence of a hysteresis loop, which leads to uncontrolled systematic errors.

The so-determined and normalized to unity at $T=0$ spontaneous magnetization is plotted against reduced temperature in Fig. 1, where all relevant normalization constants are given. The data points were fitted to Eq. (1) with $\beta=1/3$, solid lines, the best-fit values of s being indicated in the drawings. In the case of Tb and Dy, T_C in Eq. (1) was replaced with T_N. Attempts to use larger values of β ($0.35 \leqslant \beta \leqslant 0.4$) produced fits of inferior quality.

Upon examining Fig. 1, one concludes that there is excellent agreement between Eq. (1) and the experimental data. For Gd, our results are consistent with the fit in Ref. 2 of earlier data:[16] $M_s(0)$ and s are the same, while our T_C is marginally lower, 289 versus 291 K. This is in line with the assertion[2] that s is an intrinsic property—sample quality plays no important role here. In the case of Tb and Dy, the possible deviations at low temperature due to the crystal-field gap and at the helix-ferromagnet transition points (the latter are indicated with arrows) are too small to be visible on the scale of Fig. 1. The apparent insignificance of the above effects does not warrant, in our view, the use of expressions more complicated than Eq. (1).

Clearly, the shape parameter s decreases as one moves from Gd to Tb and Dy, and the corresponding curves in Fig. 1 gain in squareness. According to the ideas advanced in a recent communication,[17] the smaller values of s should indicate the strenthening of long-range ferromagnetic exchange. This is in contrast to the growing tendency of noncollinearity and falling ordering temperatures toward the end of the lanthanide series. That is, while the curves take a more distinctly "ferromagnetic" shape, the general behavior becomes less ferromagnetic.

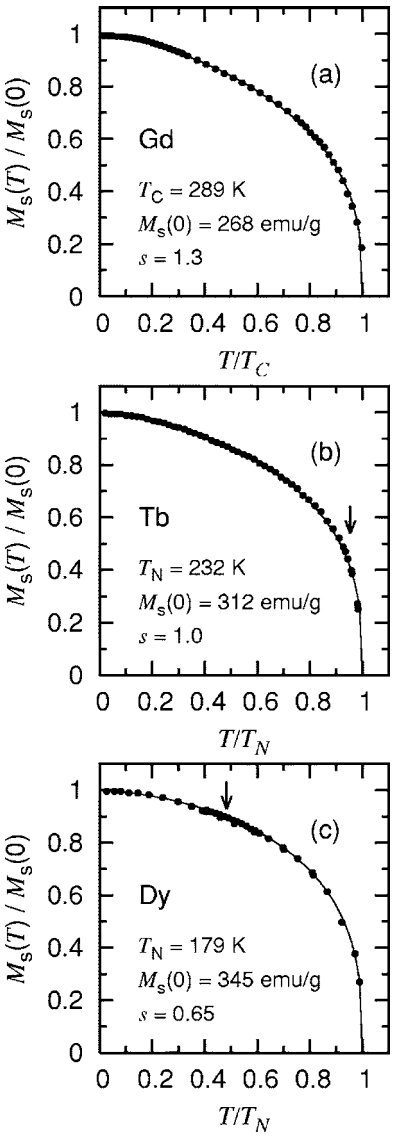

FIG. 1. Reduced spontaneous magnetization versus reduced temperature. The continuous curves were calculated using Eq. (1) with $\beta=1/3$ and the parameters indicated in the drawing. The arrows in the case of Tb (b) and Dy (c) mark the position of the helix-ferromagnet transition points.

The two apparently conflicting trends can be reconciled if one takes into consideration the anisotropic nature of the hexagonal close-packed structure characteristic of the heavy lanthanide metals, Fig. 2. This anisotropy and the resulting competition between several interlayer exchange interactions (links shown as dashed lines in Fig. 2) give rise to the helical magnetic structure. For the simplest description, it is sufficient to consider only two of them: The (oblique) ferromagnetic nearest-neighbor links and the (vertical) antiferromagnetic next-nearest-neighbor links.

The presumably much stronger ferromagnetic in-plane exchange (horizontal links in Fig. 2) is not involved in the formation of the helicoid. Nor is it *per se* capable of providing high magnetic ordering temperatures on account of the well-known fact that—within the Heisenberg model—magnetic ordering is only possible in a three-dimensional

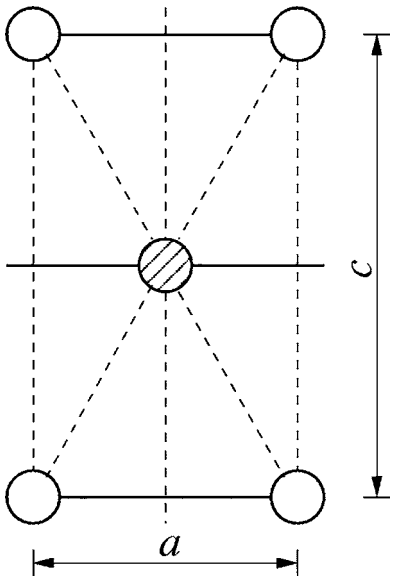

FIG. 2. Side view of the hcp unit cell (the hatched atom does not lie in the plane of the drawing). The dashed lines are the exchange links involved in the formation of the helical magnetic structure.

lattice. The in-plane exchange appears to affect the shape of the temperature dependence of the ferromagnetic order parameter, expressed by the quantity s. The curves in Fig. 1 become more square and more ferromagneticlike for heavier lanthanides, despite the apparent weakening of ferromagnetism. It is quite extraordinary that such a property is latent in systems that are no longer truly ferromagnetic. One has to admit at this stage that the mechanisms governing the shape parameter s are not fully understood.

Summarizing, the temperature evolution of the ferromagnetic order parameter $M_s(T)$ in the heavy lanthanide metals Gd, Tb, and Dy has been found to follow Eq. (1) with $\beta = 1/3$. No systematic deviation from Eq. (1) has been detected in Tb or Dy, either due to the noncollinear ground state or to the crystal-field gap; this deviation must be $\lesssim 1\%$. The latter estimate is in line with what was earlier found by Niira:[18] The crystal-field gap anomaly in Dy results in a less than 1% deviation, and therefore, it is not only invisible on the scale in Fig. 1 but has virtually no effect on the quality of the fit employing Eq. (1). The ferromagnetic component of the interlayer exchange interaction weakens in the heavier lanthanides, giving way to helical antiferromagnetism. On the contrary, the in-plane exchange becomes more ferromagnetic in character, as manifested by the observed systematic decrease of the shape parameter s.

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