Magnetoelastic Nature of the Dodecagonal Anisotropy in Holmium Metal

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We have investigated the magnetoelastic nature of the dodecagonal anisotropy in the magnetic anisotropy energy (MAE) in the basal plane of the hcp crystalline structure in holmium single crystal. We have proved that the origin of the second harmonic of the hexagonal symmetry in MAE clearly lies on a sixth-order magnetoelastic coupling term. The appearance of a 12-fold anisotropy in MAE in a single crystal having hexagonal symmetry provides a new insight on how the magnetic anisotropy can be modified in a magnetic material with giant spin-lattice coupling.

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Magnetoelastic (ME) effects play a crucial role in understanding the electronic and magnetic properties in magnetic materials, being for such a reason the spin-lattice coupling investigated from basic knowledge and exploited to engineer new materials with technological applications [1]. Thus, for instance, it has been proposed that a transition from half-metallic to the semiconductor phase may be driven by applying stress [2] and that the magnetic anisotropy energy (MAE) on synthesized bcc Ni [3] is deeply altered with respect to the anisotropy in the standard fcc phase, mostly due to ME effects. At atomic scale, MAE arises as a consequence of the interaction of the unfilled asymmetric electron clouds and the crystal electric field (CEF), created at the atomic site by the rest of the crystal lattice through the spin-orbit coupling. When considering the distortion of CEF by ME strains, the ME contribution to MAE is obtained. An understanding of how MAE is determined by the symmetry of the point group and the sorting of the magnetic atom and its neighbors is currently a challenging and fundamental quest in magnetism [3,4], since MAE is the key fundamental property that determines the magnetization stability [5], either in bulk or nanostructured materials. In this scenario, two essential factors, a high asymmetry of the $4f$ shells and a giant spin-lattice coupling [6], make of the study of the ME coupling in heavy rare earth (RE) metals still a crucial topic in basic magnetism [7,8]. Thus the influence of ME effects on their electronic and magnetic properties may give rise to remarkable consequences as observed in Ho/Lu superlattices: enhancement of the sixfold anisotropy constant and an unexpected 12-fold anisotropy [9]. Both effects may be explained as the result of the sixfold ME stresses [9,10], but other factors such as broken symmetry at interfaces caused by chemical modulation or the strain state in Ho blocks due to epitaxial growth might provide an alternative explanation, bringing controversy on the physical origin of that 12-fold anisotropy in hexagonal RE metals. In this Letter, we report first on the intrinsic character of both the in-plane field-driven easy axis reorientation (EAR) and the dodecagonal anisotropy in MAE in the Ho single crystal, and second, by direct measurement of the magnetostrictive strain on a sixth-order ME term. Recently, only based on symmetry reasons [9], we proposed as a likely origin for that 12-fold anisotropy the existence of a sixfold modulation for the α strains which belong to the fully symmetric irreducible representation in hexagonal symmetry, Γ^{α}. Now, our experiments have fully confirmed the existence of such a sixth-order spin-lattice coupling term, which is the origin of that second harmonic of hexagonal symmetry, representing a magnetostrictive alteration on MAE never previously reported in the literature.

The holmium single crystal used in these experiments was cut in a disc shape 4 mm in diameter and 1 mm in height, with the **c** axis perpendicular to the disc plane. The character of the magnetic anisotropy within (0001), for temperatures between 12 and 70 K, is investigated by measuring of the magnetic torque, L_k, with a vectorial magnetometer [11]. Experimentally, two anisotropy constants need to be included in the density of magnetic anisotropy energy, e_a, to account for the experimental L_k when the total magnetization, **M**, is within the basal plane (BP) (see Fig. 1). In that way, e_a can be written phenomenologically as follows: $e_a = K_6^6 \cos 6\phi + K_{12}^{12} \cos 12\phi$, being ϕ the azimuthal angle formed among the **a** axis and **M**, and being K_6^6 and K_{12}^{12} the anisotropy constants accounting for the hexagonal symmetry and for its second harmonic, respectively. The theoretical magnetic torque is derived as $L_k(\phi) = -\partial e_a/\partial\phi$, and the experimental one is analyzed making use of two different approaches: for temperatures at which L_k shows a sinusoidal dependence on ϕ we perform a Fourier analysis to obtain the anisotropy constants; on the contrary, when L_k shows a sawtooth dependence we use the maximum torque method [12]. Analyzing L_k, we have obtained $K_6^6(T, H)$ and $K_{12}^{12}(T, H)$ for each pair of T and field strength. Plotting these values

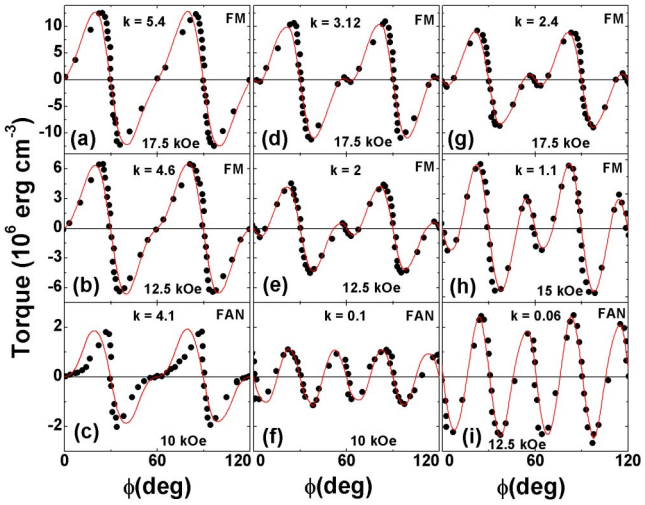

FIG. 1 (color online). Magnetic torque, L_k, versus the azimuthal angle, ϕ, for an applied magnetic field, H, within the basal plane of the hcp crystalline structure in Ho single crystal, at 32.5 K [(a),(b) and (c)], 35 K [(d),(e) and (f)], and 40 K [(g),(h) and (i)]. ϕ is formed between the **a** axis and **M**. The continuous lines are fittings of the experimental data using the following expression: $L_k = 6K_6^6 \sin 6\phi + 12K_{12}^{12} \sin 12\phi$. The ratio among both anisotropy constants, k, at each T and field strength is defined as follows: $k = K_6^6/K_{12}^{12}$. The magnetic phases stabilized by H within BP for each case shown here have been labeled as FM and FAN (the later for the fan phase).

against $1/H$ and extrapolating at $H \rightarrow \infty$ yields the field independent anisotropy constants as usually done. The ME measurements along the **c** axis are carried out by using a high precision capacitive cell with tilted electrodes [13]. Our experimental setup enables us to apply a magnetic field within BP of the single crystal and to measure the magnetostriction along the **c** axis, $\lambda(c)$, as a function of ϕ, namely $\lambda(c, \phi)$. The stability criteria for e_a is straightforwardly obtained from the ratio among both anisotropy constants. Thus, if $k = \mid K_6^6/K_{12}^{12} \mid \leq 4$, L_k simultaneously shows hexagonal and dodecagonal symmetry, being **a** and **b** both simultaneously easy directions, and hard ones do not correspond to crystallographic directions within BP, as shown in Figs. 1(d)–1(i). On the other hand, if $k > 4$, L_k will only show six easy directions within BP even though $K_{12}^{12} \neq 0$ [see Figs. 1(a)–1(c)]. Thus, bearing in mind that easy directions are those ones where L_k crosses through zero with negative slope and those with positive slope correspond to hard directions, for $T \leq 32.5$ K, $k > 4$ for all field strengths tried and therefore, **b** is easy and **a** is hard. In particular, when k gets close to 4, L_k crosses through the **a** axis with nearly null slope. Figures 1(d)–1(i) clearly show 12- fold anisotropy and this becomes predominant at low field when a fan phase is stabilized [14] [see, Figs. 1(f) and 1(i)]. It is worth pointing out that the hexagonal anisotropy reinforces its strength as T decreases, just the opposite behavior of the dodecagonal one, which becomes slightly weaker, as shown in Figs. 1(a), 1(d), and 1(f). Additionally, 12-fold anisotropy is observed independently of the magnetic phase stabilized by the magnetic field, either fan or ferromagnetic (FM) phase. The dodecagonal anisotropy is not observed in L_k below 32.5 K, being the reason that K_6^6 increases much quicker than K_{12}^{12} as temperature decreases and, eventually, when $K_{12}^{12} < K_6^6/4$ the reinforcement of the hexagonal anisotropy at low temperature prevents to observe its second harmonic in L_k, but this does not mean that K_{12}^{12} be negligible or vanishes, simply, it cannot be determined. In fact, at very low temperatures is quite hard to separate apart both contributions to L_k, which may explain the high reported value for K_6^6 in Ho when compared to other heavy RE metals [15]. In previous investigations [9,10], we have observed that K_6^6 is strongly altered by ME effects. Additionally, we satisfactory explained the modifications in the anisotropy energy by introducing a sixfold ME stress, which leads to: K_6^6 comprises a first order ME contribution, $K_{\alpha,6} = B_{\alpha 1}^{66} \bar{\epsilon}_{\alpha 1} + B_{\alpha 2}^{66} \bar{\epsilon}_{\alpha 2}$, and an extra anisotropy emerges in MAE doubling the characteristic hexagonal anisotropy in hcp RE metals, and which may relay on a *self magnetostriction* contribution [K_{12}^{12} is proportional to a $(B_\alpha^{66})^2$ term, see Eq. 2 in Ref. [9]] obtained by minimizing the elastic and ME energy, e_{mel}, with respect to the α strains in hexagonal symmetry, and inserting their equilibrium values in e_{mel} [9]. On the other hand, we have observed by magnetic torque measurements that the field-driven EAR also takes place in the single crystal, which clearly reveals that this transition results from fundamental interactions in holmium.

Therefore, simply by using symmetry arguments and extending the ME contributions to MAE up to sixth order, the highest compatible with hexagonal crystalline symmetry, it is predicted a ME second-order contribution to MAE. From a microscopic point of view, this contribution would be also expected if the equilibrium strains belonging to Γ^α were obtained making use of the whole ME Hamiltonian, that one including ME parameters and Stevens operators up to sixth degree [1,16]. Reference [17] reports a general expression for the magnetostrictive strain, $\Delta l/l$, for hexagonal crystals in terms of the phenomenological magnetostrictive constants. The ME sixth-order terms can be measured for **M** within BP ($\theta = \pi/2$). In that way, a phenomenological expression is obtained, $\Delta l/l = \lambda(c, \phi) = \lambda(c, 0) + \lambda_{66}^\alpha \cos 6\phi$, where $\lambda(c, 0)$ is a combination of isotropic coefficients and $\lambda_{66}^\alpha = \lambda_{1,66}^\alpha + 3\lambda_{2,66}^\alpha$ is a linear combination of irreducible magnetostrictive sixth-order constants, accounting for the isotropic, $\lambda_{1,66}^\alpha \propto B_{\alpha 1}^{66}$, and tetragonal deformations, $\lambda_{2,66}^\alpha \propto B_{\alpha 2}^{66}$ [18]. Therefore, in order to complete the puzzling picture of the ME effects in MAE and to shed some light on the physical origin of the dodecagonal anisotropy in holmium, we have performed systematic measurements of $\lambda(c)$ as a function of T and field strength and orientation within BP. Our measurements

have shown that $\lambda(c, \phi) > 0$, which implies that the hexagonal cell is compressed within (0001) by simply making use of Poisson's ratio. As expected, $\lambda(c)$ isotherms are strongly dependent on the magnetic phase stabilized by H and their character changes with T. Below Curie temperature, $T_C = 18$ K, and for zero field, the magnetic structure in Ho is FM along the **c** axis and helix within BP, with the magnetic moments forming a cone structure, disappearing the FM component above T_C and remaining the helix structure up to the Néel temperature, $T_N = 132$ K [14]. By applying a magnetic field within BP, different magnetic structures are stabilized depending on T and field strength (ferrocone, helifan, and fan) before reaching a FM structure [16,19]. For $T < T_C$, $\lambda(c)$ shows an abrupt increase at low field as result of the onset of a FM phase stabilized by H, reaching the same value at saturation for H along both in-plane directions, **a** and **b** [see Fig. 2(a)]. Above T_C, the most striking result is that $\lambda(c)$ saturates at different values depending on whether H is along the **b** or **a** axis, namely $\lambda(c, b)$ and $\lambda(c, a)$, respectively. Additionally, it remains negligible, whereas H does not turn the helix phase into a FM one, as shown in Figs. 2(b) and 2(c), where $\lambda(c)$ abruptly increases when the transition takes place. Notice that this happens at lower magnetic field when H is along the **a** axis for $T > T_C$. It is also observed that $\lambda(c, a)$ presents a kink before reaching the major jump, revealing

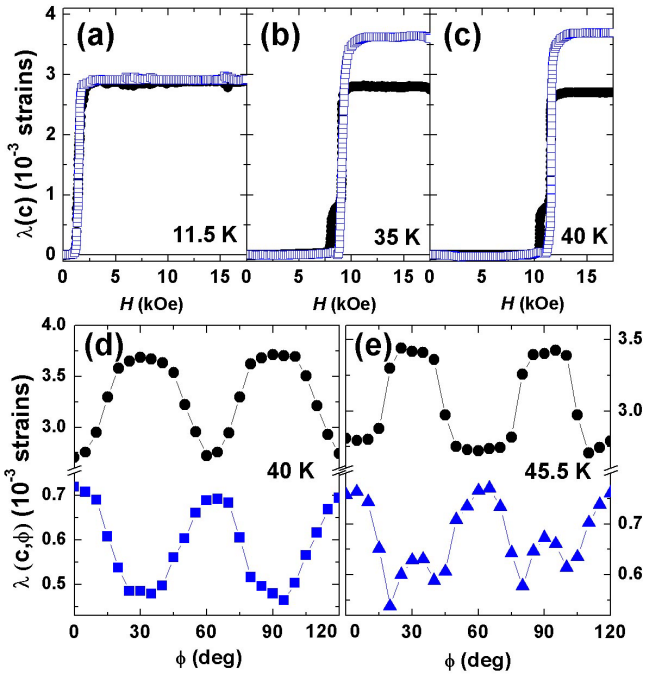

FIG. 2 (color online). Magnetostriction isotherms [(a),(b) and (c)] along the **c** axis, $\lambda(c)$, for H along the **a** axis (black circles) and the **b** axis (blue squares). Magnetostriction along the **c** axis versus ϕ, angle between the **a** axis and **M**, for 17.5 kOe [(d) and (e), black circles], for 11.25 kOe [(d), blue squares], and for 12.25 kOe [(e), blue triangles]. The continuous lines are guides to the eye.

that a fan phase is stabilized by H, whereas that when H is applied along the **b** axis, the transition from helix to FM phase takes place through no intermediate magnetic phases. That additional kink is simultaneously observed in $\lambda(c, b)$ and $\lambda(c, a)$ for higher T. Our ME measurements at saturation were checked against previous electron diffraction experiments [20] and we found that the values for $\lambda(c, b)$ at high field agree quite well. We have plotted $\lambda(c, \phi)$ at maximum magnetic field for each field orientation to find out its dependence on ϕ. We have found a well-defined sixfold modulation in $\lambda(c, \phi)$ for temperatures above about 27.5 K, as presented in Figs. 2(d) and 2(e). Below about 27.5 K, we have not observed any dependence on ϕ in $\lambda(c, \phi)$, but as T increases, it gradually appears a smooth sixfold term becoming stronger and approaching to a sinusoidal dependence on ϕ [see Figs. 2(d) and 2(e)]. At low temperature, the sixfold anisotropy is so high that it anchors the magnetic moments along the **b** axis for H along the **a** axis even at high field and, therefore, there is no difference in the reached value for $\lambda(c)$ when H is applied along different in-plane directions. As T increases, K_6^6 strongly decreases and, it is then, when H is able to pull magnetic moments out from easy directions (**b** axis), allowing the sixfold anisotropy to be observed in $\lambda(c, \phi)$. In fact, the ME isotherms shown in Figs. 2(b) and 2(c) are well saturated at high field. Therefore, in sight of the magnetostriction measurements, we claim that the sixth-order ME term $\lambda_{66}^{\alpha} = (\lambda(c, a) - \lambda(c, b))/2$, does exist and the experimental data make clear that λ_{66}^{α} emerges as consequence of the intrinsic dependence of the α strains on the direction cosines of **M**. We have also found that λ_{66}^{α} changes its sign as a function of the field strength for $T \geq 35$ K as shown in Figs. 2(d) and 2(e). We strongly believe that the field-induced EAR from **a** to **b** axis [9] is the origin of that change in sign shown by λ_{66}^{α}. Additionally, for $T \geq 45$ K and at low field, λ_{66}^{α} shows small extra bumps around **b** axis [see Fig. 2(e)]. This is not fully clear yet, but it seems to be the onset of magnetic structures like helifan phases, appearing about this range of T and for low field [19], that could play their role when H is rotated around **c** giving rise to those extra bumps along **b** axis in $\lambda(c)$. The thermal dependence presented by $\lambda(c, b)$ is clearly non-monotonous in temperature, showing a decreasing behavior either at low or at high T, as shown in Fig. 3(a), which shows that several competing terms contribute with a different thermal dependence in a complex way [18]. On the other hand, $\lambda(c, a)$ is strongly affected by the high hexagonal anisotropy mainly below 30 K, tending to overlap with $\lambda(c, b)$ as a result of the lack of field strength. Above 50 K and for 17.5 kOe, $\lambda(c, a) > \lambda(c, b)$ as consequence of the EAR from **a** to **b** axis. In Fig. 3(b) are shown the thermal dependencies for λ_{66}^{α} and K_{12}^{12}, presenting both a similar variation with T, making clear that their thermal dependence matches each other as consequence of they both are correlated. λ_{66}^{α} reaches a maximum value of

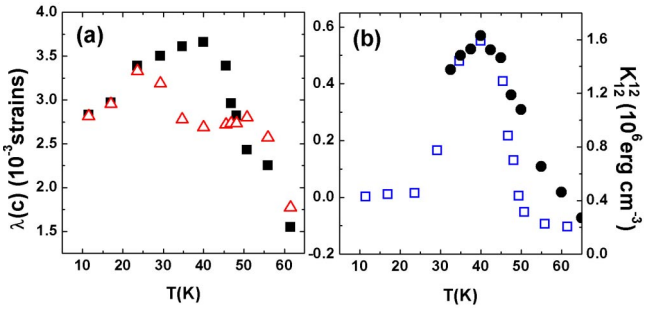

FIG. 3 (color online). Thermal dependence (a) for $\lambda(c)$ at 17.5 kOe for H along the **b** axis (black squares) and along the **a** axis (red triangles) in Holmium single crystal and (b) for the dodecagonal anisotropy constant, K_{12}^{12}, (black circles), and for the sixth-order ME term, λ_{66}^{α}, at 17.5 kOe (blue squares).

560×10^{-6} strains and K_{12}^{12} presents a maximum value of 1.6×10^{6} erg cm^{-3} both ones at 40 K [see Fig. 3(b)]. The later is nearly 10 times smaller than $K_6^6(0\ \mathrm{K}) = 1.7 \times 10^7$ erg cm^{-3} [18]. A rough estimation for K_{12}^{12} at 0 K would give a value of 1.0×10^6 erg cm^{-3} or even less [10,18], which indicates a slight variation with respect to its largest value, and therefore, showing a variation similar to that of $\lambda(c, b)$ for temperatures below about 40 K. This value for K_{12}^{12} may explain a 9% in excess reported on K_6^6 at 0 K in the case of Ho [15], when assumed that at very low T both anisotropies, sixfold and 12-fold, are inseparable each other.

It is well known that the temperature dependence is a fingerprint of the microscopic origin of a magnetic anisotropy constant [16,18]. As K_{12}^{12} only comprises sixth-order ME constants (see Ref. [9]), that means that, microscopically, only sixth-degree Stevens operators assign its temperature dependence. Thus, to explain its nonmonotonous thermal variation competing sixth-order single- and two-ion ME contributions may be considered. Our experiments clearly set out that sixth-order ME interactions within BP generate magnetostrictive deformations in the crystalline structure preserving the hexagonal symmetry. The ME constants $B_{\alpha 1}^{66}$ and $B_{\alpha 2}^{66}$ correspond to the hexagonal magnetoelastic coupling within the basal plane and which give rise to a sixfold component in the magnetoelastic strains belonging to Γ^{α}, ϵ_{α_1} and ϵ_{α_2} [9]. As a consequence of their sixfold intrinsic dependence on the direction cosines of the total magnetization, reflecting the symmetry of the D_{3h} point group in hcp RE metals, these magnetostrictive strains present a dynamic character when **M** is rotated around the **c** axis, which leads to modify the CEF generated by the surrounding ions due to the modulation of the position of the atomic sites on the crystalline structure. Thus, and resulting as a magnetoelastic second-order effect, an extra anisotropy which doubles the hexagonal one appears in MAE. The EAR from **a** to **b** axis permits to observe a mandatory 12-fold anisotropy at that particular values of temperature and magnetic field for which $K_6^6 \simeq 0$. In summary, the magnetoelastic nature of a 12-fold anisotropy in MAE in a single crystal having hexagonal crystalline symmetry has been proved. We have experimentally determined the sixth-order ME term, which is responsible of that second-order ME contribution to MAE. This ME modification on MAE gives a new insight on how magnetic anisotropy can be altered in rare earth metals and, more generally, in all those magnetic materials with giant spin-lattice coupling.

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