Anomalous Thermal Expansion and Magnetostriction of Holmium Single Crystals*

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The a-, b-, and c-axis linear strains of single-crystal Ho have been measured from room temperature to 4°K in zero field and in applied fields up to 30 kOe. Pronounced bumps appeared in the thermal-expansion coefficient at the magnetic ordering temperatures of 132 and 20°K. The exchange magnetostriction contribution to the total c-axis strain was isolated and compared to the predictions of the molecular-field theory applied to spiral antiferromagnets. Strain data taken with an applied field show the effects of "fanning" of the moment about the applied-field direction and of the onset of basal-plane anisotropy below 75°K. The dependence of the basal-plane magnetostriction on field angle was measured in the temperature range of magnetic order. Saturation values of the second-order magnetostriction constant were compared with the results of single-ion magnetoelastic theory. A value of 2.5×10^{-3} at $T=0$°K was calculated.

I. INTRODUCTION

RESULTS on the anomalous thermal expansion and magnetostriction of hexagonal close-packed holmium single crystals are presented here.

The giant magnetostrictions reported here as well as those reported for Tb,[1] Dy,[2,3] and Er [4] arise from changes in the balance between elastic and strain-dependent magnetic energies. These rearrangements occur both spontaneously (e.g., anomalous thermal expansion) and on the application of an external field. In the rare earths the magnetostrains may be sorted into those arising principally from the exchange energy and those resulting primarily from the single-ion anisotropy energy. Previous results on Ho[3] revealed field-induced exchange magnetostrictions as large as 0.35% and anisotropic magnetostrictions of order 0.2%. These latter magnetostrains are smaller than those found in Tb and Dy due to the smaller asymmetry of the $4f$ ion cloud in Ho.

Magnetic-moment[5] and neutron-diffraction[6] studies on holmium have established that the metal is paramagnetic above 132°K, and has a spiral antiferromagnetic ordered phase from 132 to 20°K. The moments are constrained to the basal plane by a large axial anisotropy. The interlayer turn angle decreases linearly with temperature from 50° at the 132°K transition to 30° at 20°K and remains essentially constant below 20°K. At 20°K an increase in the fourth- and sixth-order axial anisotropy energy terms produces a transition to a warped conical ferromagnet of mean cone angle 80° from the c axis. Alternate moments assume positions slightly within and outside the surface of this cone. Below 75°K anisotropy is present in the basal plane with the $b(10\bar{1}0)$ axis as the easy magnetic direction

In the spiral region, magnetic fields above a critical value applied in the basal plane produce "fanning" of the magnetic moment about the field direction and still higher fields produce a complete breakdown of the periodic state into ferromagnetic alignment along the field direction. At the lower temperatures intermediate periodic states are stable in particular ranges of applied field. These effects have been discussed in the neutron-diffraction work of Koehler *et al.*[6] and have been calculated theoretically by Nagamiya *et al.*[7]

II. EXPERIMENTAL PROCEDURE

In this experiment crystal strains were measured by a standard procedure using Budd electrical-resistance strain gauges as described previously.[1] The accuracy of the method was checked by measuring the thermal strain of an annealed copper disk from room temperature to 4°K. These tests were made with several different gauges. Comparison of the results with the data of Beenaker and Swenson[8] indicates an over-all accuracy of better than 4%.

The holmium crystals were grown by a thermal strain anneal method.[9] Basal-plane and b-c-axis–plane disk-shaped specimens about 9 mm diam and 1.5 mm thick were spark-cut from the bulk crystals.

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III. THERMAL EXPANSION AND EXCHANGE MAGNETOSTRICTION

Figure 1 shows the a-, b-, and c-axis strains in Ho as a function of temperature from 300° to 4°K. Curves are shown both with and without applied magnetic fields. The temperature derivative or "thermal expansion coefficient" curves for the zero-field a- and c-axis strains are shown in Fig. 2.

Above 132°K, the zero-field curves show a normal anisotropic lattice contraction with decreasing temperature characteristic of hexagonal materials. The basal-plane contraction is isotropic within experimental error. At 132°K helical ordering of the moment begins and an anomalous departure from thermal-like contraction is observed. As discussed below, a rapid expansion along the c axis occurs with an accompanying increased isotropic contraction of the basal plane. At 20°K a sharp slope change occurs as the moments order into the conical ferromagnetic state. The moment and turn angle remain essentially constant during this ordering and thus, in contrast to the ferromagnetic ordering in Dy and Tb, no large discontinuous lattice distortion is observed. This has been shown also in x-ray studies by Darnell.[10]

Because of the dominant magnetic contributions to the strain below the Néel temperature, it is not possible to measure directly the thermal expansion in this region. A reasonable separation of the magnetic and thermal contributions can be effected by extrapolating to low temperatures the thermal strain observed well above the Néel point. Subtraction of this extrapolated thermal strain curve from the total observed zero-field strain yields the magnetostrain contribution. The result of such a separation for the magnetic contribution to the c-axis strain in Ho is shown by the points in Fig. 3. The Grüneisen relation

$$\partial V/\partial T = K\gamma C_v(T) \tag{1}$$

was used to extrapolate the observed high-temperature thermal expansion coefficient below the Néel temperature. The isothermal compressibility K and Grüneisen constant γ were assumed constant. The Debye temperature of 183°K obtained from sound-velocity measurements[11] was used in evaluating C_v.

The analysis of the magnetic exchange energy associated with the spiral structure is clouded by the recent work of Møller and Houman[12] who measured inelastic neutron scattering on terbium and found that the signs of the first two interplanar exchange parameters for the c direction were both positive. It may be argued, however, that the spiral structure is stable in terbium only from 220 to 232°K whereas in holmium

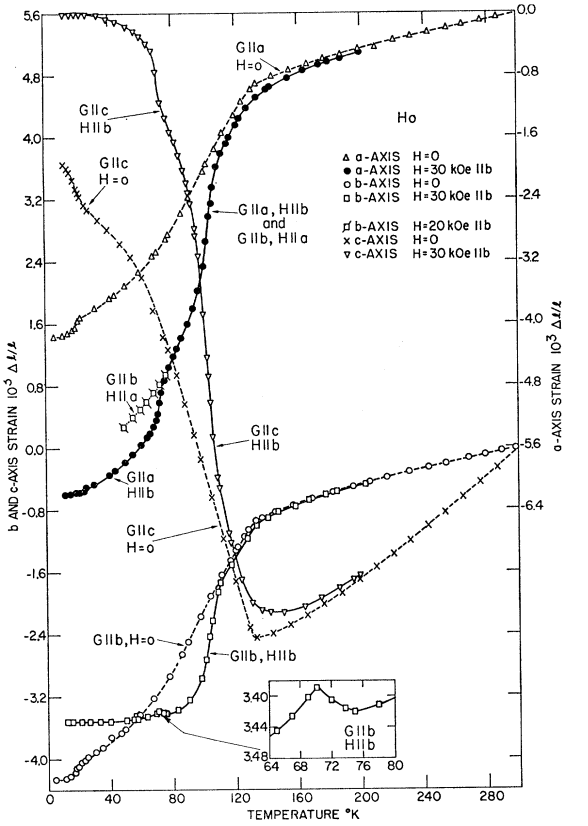

FIG. 1. The a-, b-, and c-axis linear strains as a function of temperature in zero applied field and in fields applied in the basal plane as indicated. G indicates the strain-gauge direction.

the stable range extends from 20 to 131°K, so it is not unreasonable to assume for holmium the simple form:

$$E_{ex} = -M_s^2[J_1 \cos\theta + J_2 \cos 2\theta]. \tag{2}$$

J_1 and J_2 are the corresponding exchange constants for layers whose moment directions are displaced by turn angles θ and 2θ. Under the condition $J_1>0$, $J_2<0$, and $|J_2|>J_1/4$ the spiral is stable and the equilibrium turn angle is given by $\cos\theta_0 = -J_1/4J_2$. The dependence of J_1 and J_2 on the c-axis parameter produces the exchange magnetostriction accompanying changes in θ_0. This effect may be calculated by expanding J_1 and J_2 in a Taylor series, including the contribution of the elastic energy to Eq. (2) and minimizing with respect to the c-axis parameter. The result to first order for the equilibrium c-axis strain is[13]

$$\left.\frac{\Delta l}{l}\right|_c = \frac{cM_s^2}{Y}\left[\frac{dJ_1}{dc}\cos\theta + \frac{dJ_2}{dc}\cos 2\theta\right]. \tag{3}$$

Here M_s is the saturation magnetic moment at temperature T, c the c-axis lattice constant, and Y the elastic constant for the c-axis distortion. In evaluating this

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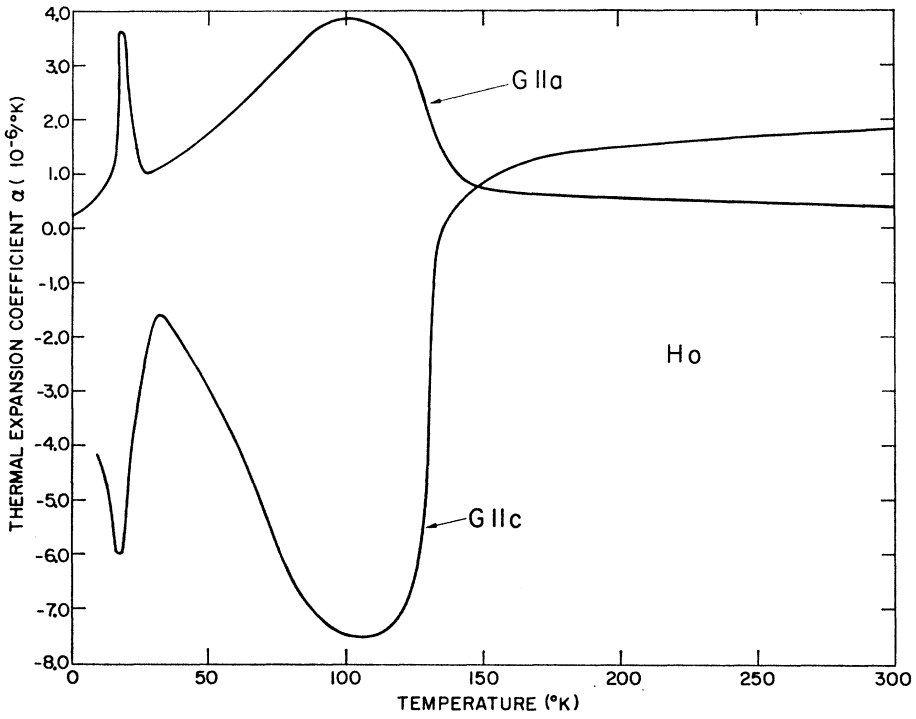

FIG. 2. Anomalous thermal-expansion coefficients for the a- and c-axis directions obtained from the data of Fig. 1. The a- and b-axis values were equal within experimental error. G indicates the strain-gauge direction.

expression for Ho, the 4°K value of the magnetic moment used was from Strandburg *et al.*[5] with the temperature dependence established by Koehler *et al.*[6] from neutron diffraction. The magnetic values could not be used directly because of the lack of complete ferromagnetic alignment above 50°K in the fields used. The temperature dependence of the lattice constant[10] c appearing on the right side of Eq. (3) is small compared to experimental error and was not included. Values of the single-crystal elastic constants are not yet available for Ho. Equation (3) was fit to the experimental data at 30 and 90°K which yielded values of

$$\frac{1}{Y}\frac{dJ_1}{dc}=0.023 \text{ cm}^2/\text{erg},$$

$$\frac{1}{Y}\frac{dJ_2}{dc}=-0.013 \text{ cm}^2/\text{erg}.$$

The resulting strain curve, calculated using Eq. (3), is shown by the solid line in Fig. 3 for the range 20 to 120°K. It should be noted that the major temperature dependence arises from M^2 and that the above numbers can only give an indication of the magnitude of the c-axis derivative of the exchange constants. The degradation of the fit at the higher temperature can be ascribed to uncertainties in extrapolation of the thermal-expansion data, to possible errors in the value of the magnetization, and to inadequacies in the molecular-field approximation.

IV. MODIFICATION OF STRAIN BY APPLIED FIELDS

Above 132°K the strain data (shown in Fig. 1) obtained in the presence of a magnetic field show small departures from the zero-field curves which were proportional to H^2 at the higher temperatures as expected for a paramagnet from thermodynamics. The application of a field in the spiral magnetic region produces distortions of the interlayer turn angles from their equilibrium values ("fanning") and a corresponding additional exchange magnetostriction which can be obtained by averaging Eq. (3) over the perturbed moment directions. The observed effect in the region between 132 and 75–80°K is shown by the data in Fig.

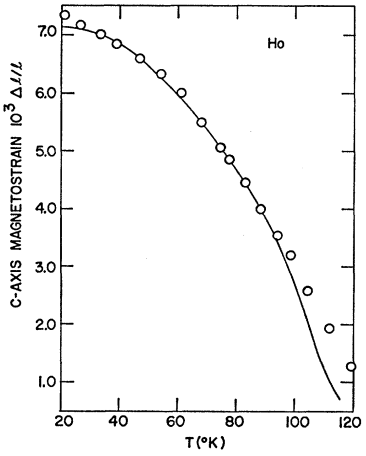

FIG. 3. Magnetic contribution to the total c-axis strain in zero field. The circles are values obtained from the data of Fig. 1. The solid line represents a molecular-field expression for the strain (see text).

1. Below the latter temperatures it is estimated from magnetization data[5] that complete magnetic alignment is achieved in the 30-kOe applied field. The giant 0.77% positive c-axis magnetostriction below the Néel temperature which arises from changes in the inter-layer exchange energy assisted by the applied field and anisotropy is the largest such distortion of the three spiral rare earths Dy, Tb, and Ho.

As shown in Fig. 1, for temperatures down to 75°K the transverse basal-plane magnetostrictions (i.e., $G\|a$, $\mathbf{H}\|b$ and $G\|b$, $\mathbf{H}\|a$, where G represents the strain-gauge direction) are identical indicating negligible basal-plane anisotropy. Below 75°K a rapid increase in basal-plane anisotropy occurs as is evidenced by the increased strain appearing in the transverse magnetostriction observed with the field applied along the easy magnetic direction over that found with the field applied in the hard (a axis) direction. A corresponding anomaly is also observed in the c-axis strain in the same temperature region.

For data taken in the presence of a field, no sharp change is observed at 20°K as the additional field energy precludes the formation of the warped conical state.

V. ANISOTROPIC MAGNETOSTRICTION

The expression for the a-, or b-axis strain accompanying a rotation of the magnetization through an angle θ in the basal plane is given to lowest order by

$$\left.\frac{\Delta l}{l}\right|_{a,b} = \pm\lambda^{\gamma,2}\sin^2\theta, \tag{4}$$

using the notation of Callen and Callen.[14] Theta is referred to the b-axis direction. The magnetostriction constant $\gamma^{\gamma,2}$ represents a coupling between the strain and a second-order spin operator. The contributions of fourth- and sixth-order hexagonal spin operators have been calculated and produce terms proportional to $\sin^2 2\theta$. Their contribution was experimentally evaluated in the study of the magnetostriction of Tb.

The Callens[14] have shown on the basis of a classical single-ion model that the temperature dependence of the second-order magnetostriction constant $\lambda^{\gamma,2}$ is represented by

$$\lambda^{\gamma,2}(T)=\lambda^{\gamma,2}(T=0)\frac{I_{3/2}[\mathfrak{L}^{-1}(m)]}{I_{1/2}[\mathfrak{L}^{-1}(m)]}, \tag{5}$$

where I is a modified Bessel function of the second kind, $\mathfrak{L}^{-1}$ is the inverse of the Langevin function, and m is the reduced magnetization. This expression closely represents the temperature dependence of the basal-plane magnetostriction in Tb and Dy from 4°K to above room temperature.

Figure 4 shows the anisotropic magnetostrain which accompanies the rotation of the applied magnetic field through 180° in the basal plane. The algebraic signs of the a-axis strains at 74.6°K have been reversed for comparison to the b-axis curves shown for 141.3, 100.2, 80.6, and 70.2°K. At 118°K (not shown) the magnetostriction was zero within 1 part in 10^7. Above 75°K the data show negligible departures from $\sin^2\theta_b{}^1$ behavior indicating again the absence of appreciable basal-plane anisotropy above this temperature. The sharp increase of the anisotropy is indicated by the extreme distortion of the 70.2°K curve. These distortions become more pronounced for lower temperatures and lower fields as expected.

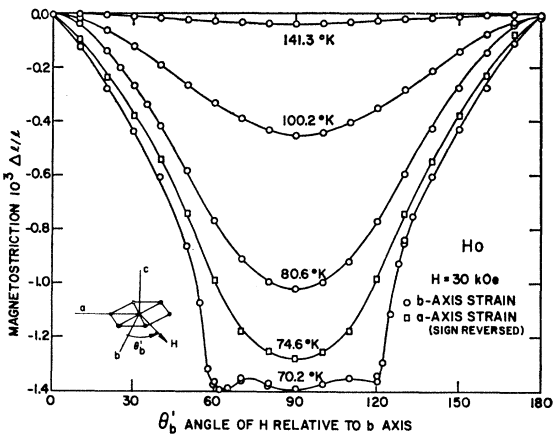

FIG. 4. Basal-plane strain as a function of the angle of the field applied in the basal plane relative to the b axis. The algebraic sign of the 74.6°K a-axis strain curve has been reversed for comparison to the b-axis results.

The strong influences of basal-plane anisotropy and of exchange "fanning" of the moment makes it impossible, with the available fields, to determine true saturation values of $\lambda^{\gamma,2}$, over the entire temperature range of magnetic order. It is thus not practical to attempt a comparison of the temperature dependence of the experimental magnetostriction to the single-ion theory. However, from the values of $\lambda^{\gamma,2}$ obtained in the temperature range 70–80°K where the above effects are minimal, an anticipated $T=0$°K value of $\lambda^{\gamma,2}(0)=2.5\times10^{-3}$ was calculated. This is less than one-third that obtained for Tb(8.7×10^{-3}) and Dy(8.4×10^{-3}) due to the smaller single-ion anisotropy produced by the more symmetric $4f$ charge distribution in Ho as shown by Tsuya *et al.*[15]

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