large-angle scattering events, $\Delta\rho_e$ is related to the increase in resistivity $\Delta\rho_f$ due to the presence of one Frenkel pair (vacancy and interstitial) by the equation

$$\Delta\rho_e=\sigma_d\Delta\rho_f.$$

The resistivity increase due to a vacancy[12,13] is about $\Delta\rho_v=1.7\times10^{-4}$ Ωcm. The resistivity increase $\Delta\rho_i$ due to an interstitial has not been measured; theoretical estimates of it vary greatly[14] but suggest that $\Delta\rho_i$ is greater than $\Delta\rho_v$. If the resistivity increase due to a Frenkel pair is the sum of the resistivities contributed by a vacancy and an interstitial, we can assume that

$$\Delta\rho_f>1.7\times10^{-4}\ \Omega\text{ cm}.$$

This estimate gives an upper bound for the value of the displacement cross section,

$$\sigma_d<90\text{ b}.$$

Using Fig. 5, we conclude that E_d for Au is presumably greater than 40 eV in agreement with the findings of Lucasson and Walker.[9] Recent experiments[15] suggest that E_d may be less than 40 eV. If this is so, it would appear either that the interstitials make an almost negligible contribution to the Frenkel resistivity, or that near threshold $\Delta\rho_f$ is not simply the sum of $\Delta\rho_v$ and $\Delta\rho_i$, or that the simple theory of the displacement cross section upon which this analysis is based is in need of revision.

ACKNOWLEDGMENTS

We thank R. L. Chaplin, P. E. Shearin, L. Slifkin, and J. B. Ward for valuable suggestions and comments.

---

[12] R. O. Simmons and R. W. Balluffi, Phys. Rev. **125**, 862 (1962).

[13] R. P. Huebener and C. G. Homan, Bull. Am. Phys. Soc. **7**, 543 (1962).

[14] G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957), p. 66.

[15] R. B. Minnix and P. E. Shearin, Bull. Am. Phys. Soc. **8**, 196 (1963).

PHYSICAL REVIEW VOLUME 130, NUMBER 5 1 JUNE 1963

Temperature Dependence of Lattice Parameters for Gd, Dy, and Ho

F. J. Darnell

Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware*

(Received 30 January 1963)

The lattice parameters of single-crystal Gd, Dy, and Ho have been measured over their temperature ranges of magnetic ordering. The *c* axis and volume of all three hexagonal close-packed structures were found to increase with decreasing temperature below their respective Néel or Curie points. The temperature dependence of the *c* axes is in reasonable agreement with the exchange magnetostriction theory of Kittel. Discontinuities in the *c* axes were found for Dy and Ho, and a structure change to orthorhombic was found in Dy, at the antiferromagnetic-ferromagnetic transitions. This structure change is believed to account for the extraordinarily large values of magnetostriction reported for Dy.

INTRODUCTION

THE series of heavy rare earths provide a system exhibiting complex magnetic spin structures with strong dependence on temperature.[1] Spiral configurations of several varieties, and first-order transitions between antiferromagnetic and ferromagnetic states, arise from energy balance among long-range exchange interactions, anisotropy resulting from crystal field–spin orbit effects, and direct exchange. Since indirect exchange in particular may depend strongly on crystal dimensions, and since Kittel has shown[2] that the interplay between exchange and elastic forces can give rise to first-order magnetic transitions when critical lattice dimensions are achieved through normal temperature variations, it is of interest to study the crystal cell dimensions as a function of temperature. This paper reports such studies for Gd, Dy, and Ho and discusses the measurements in terms of the magnetic properties and theories of the heavy rare earth metals.

EXPERIMENTAL DETAILS

The rare earths studied were in the form of single-crystal platelets approximately 0.1 mm thick and 1 mm^2 in area. The plate face was the (001) plane in all crystals examined. The crystals were found by spectrographic analysis to contain a total of 0.1% impurities, consisting mostly of the other rare earths. Lattice parameters were determined from 2θ values measured on a General Electric XRD-5 diffractometer. Scintillation counter output was displayed on a recorder chart together with angle markers, and peak positions were read from the chart to the nearest 0.01 deg. High-order reflections were used, e.g., (00 14) for *c*, and (700) and (440) for *a*.

---

* Contribution No. 848.

[1] M. K. Wilkinson, H. R. Child, W. C. Koehler, J. W. Cable, and E. O. Wollan, Suppl. J. Phys. Soc. Japan **17 B-III**, 27 (1962); W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, *ibid.* **17**, 32 (1962).

[2] C. Kittel, Phys. Rev. **120**, 335 (1960).

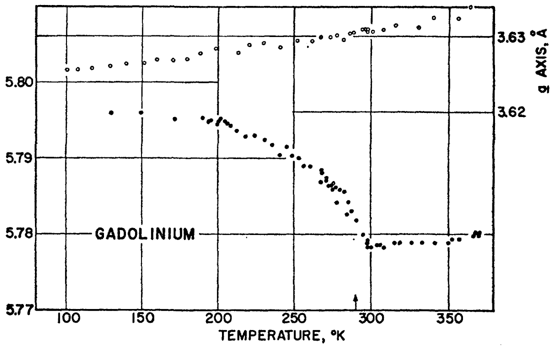

FIG. 1. Lattice parameters of gadolinium vs temperature. ●, c axis; ○, a axis.

The relative values of lattice parameters are believed accurate to ±0.001 Å. Temperatures down to 10°K were achieved by use of cold gases resulting from boiling of liquid nitrogen or liquid helium. The cold gases and protective "curtains" of helium and/or dry nitrogen gases at room temperature were confined by concentric shields of "Mylar" film. The temperature was measured by a copper-constantan thermocouple placed next to the crystal on the goniometer head. Calibration checks were made in liquid nitrogen and liquid helium. The temperatures measured at observed transitions were in agreement with those reported from magnetic and other measurements, with the exception of T_C for Gd.

RESULTS AND DISCUSSION

Although the three rare earths show common features, each will be discussed separately.

Gadolinium

The c axis of Gd (Fig. 1) exhibits below $T_C=298°\text{K}$ the anomalous expansion previously shown by x-ray[3] and single-crystal expansivity[4] measurements, which indicates repulsion along c between ferromagnetic layers lying normal to c. At the same time the a axis shows little deviation from the normal thermal contraction. There is no evidence for a discontinuity in c which would be expected to accompany the first-order antiferromagnetic to ferromagnetic transition proposed by Belov[5] to occur at 210°K. However, a change in interplanar spiral angle of less than ~ 8° would give a change in c which would be obscured by experimental scatter. It should be noted that the Curie temperature observed here is 8 deg above the accepted value of 290°K for Gd.

TABLE I. Experimentally determined quantities involving $\partial\alpha/\partial c$, the change in molecular field constant with c-axis parameter.

	Gd	Dy	Ho
Sublattice magnetization M_0 in emu/cm³	965	1470	1540
$\frac{1}{Y}\frac{\partial\alpha}{\partial c}$ in erg⁻¹ cm² [a]	0.12	0.052	0.057
$\frac{c^2}{Y}\frac{\partial\alpha}{\partial c}M_0^2$ in Å[a]	0.038	0.036	0.042
$(g-1)^2/g^2$	1/4	1/16	1/25
$\frac{1}{Y}\frac{\partial\alpha}{\partial c}$ in erg⁻¹ cm² [b]	0.48	0.58	1.42
$\frac{c^2}{Y}\frac{\partial\alpha}{\partial c}M_0^2$ in Å[b]	0.15	0.83	1.07

[a] From Eq. (1).
[b] From Eq. (2).

For the exchange magnetostriction, or spontaneous deformation of the lattice from its equilibrium dimension c_T in the absence of magnetic force, Kittel derives[2] the expression

$$c-c_T=\frac{c^2}{Y}\frac{\partial\alpha}{\partial c}\mathbf{M}_A\cdot\mathbf{M}_B, \tag{1}$$

where Y is an appropriate elastic constant, and $\partial\alpha/\partial c$ is the change in molecular field constant connecting the *sublattice* magnetizations $\mathbf{M}_A$ and $\mathbf{M}_B$. By assuming values of c_T in line with those observed above the magnetic ordering temperature, and by taking M from magnetization data, it is possible to calculate values for $(1/Y)(\partial\alpha/\partial c)$ as shown in Table I. Since accurate values of saturation magnetization as a function of temperature are not available for Gd, the known

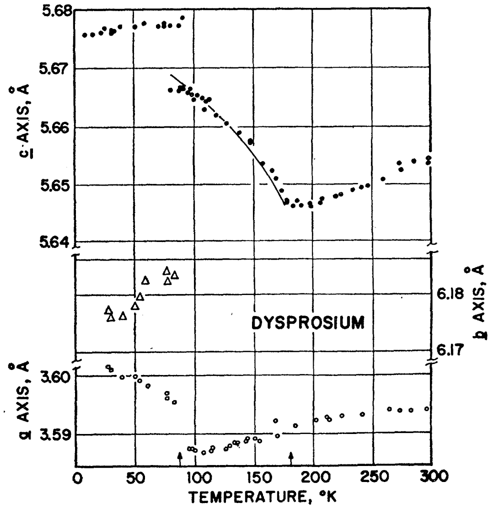

FIG. 2. Lattice parameters of dysprosium vs temperature. ●, c axis; ○, a axis; △, b axis. Above 86° structure is hexagonal close-packed; below 86° it is orthorhombic. Solid line shows calculation of Eq. (1) using constants of Table I.

---

[3] J. R. Banister, S. Legvold, and F. H. Spedding, Phys. Rev. 94, 1140 (1954).

[4] R. M. Bozorth and T. Wakiyama, J. Phys. Soc. Japan 17, 1669 (1962); Suppl. J. Appl. Phys. 34, 1351 (1963).

[5] K. P. Belov and A. V. Ped'ko, Zh. Eksperim. i Teor. Fiz. 42, 87 (1962) [translation: Soviet Phys.—JETP 15, 62 (1962)].

moment[6] at $T=0$, $M=965$ emu/cm^3, was used with the temperature dependence established for Dy (see below). This calculation assumes that the magnetic interactions can be treated in terms of molecular fields, with the sublattice moment M determining the interaction energy. In the case of the rare earths the dominant exchange arises from indirect interactions through the conduction electrons.[7] For such exchange interactions we may write an energy of the form $-\sum \mathbf{S}_i \cdot \mathbf{S}_j$, the product of the localized f-shell electron spins. The spins are related to the total angular momentum $\mathbf{J}$ by $\mathbf{S}=(g-1)\mathbf{J}$; $g\mathbf{J}$ corresponds to the observed magnetization. Comparable values of $\partial\alpha/\partial c$ for the rare earths should then be sought by rewriting the lattice deformation expression as

$$c-c_T=\frac{c^2}{Y}\frac{\partial\alpha}{\partial c}\left(\frac{g-1}{g}\right)^2 \mathbf{M}_A\cdot\mathbf{M}_B. \tag{2}$$

Values of $(1/Y)(\partial\alpha/\partial c)$ obtained by fitting Eq. (2) to the observed c parameter dependences are also listed in Table I, and are discussed below. A more detailed theory might include explicitly the nearest- and next-nearest-neighbor interactions which stabilize the spiral spin configurations,[8] and their separate dependences on lattice parameter.

The expansivity for the c axis is easily calculated and is in agreement below T_C with the single-crystal data of Bozorth,[5] showing a maximum $\gamma_c=(1/l)(dl/dt) = -100\times10^{-6}$ just below the Curie temperature. Above T_C, however, we find $\gamma_c>0$ in the range 300–370°K, with a value $\gamma_c=4\times10^{-6}$. In the range 300–340°K Bozorth finds a negative expansivity, $\gamma_c\sim -30\times10^{-6}$. The rather abrupt changes in easy direction of magnetization shown from anisotropy measurements[9] are not reflected in the lattice parameter data. This is consistent with a dominant indirect exchange interaction of the form $\mathbf{M}_A\cdot\mathbf{M}_B$ which depends on the *relative* orientation of magnetic sublattices.

Dysprosium

The variation of lattice constants previously reported[10] for Dy is plotted in Fig. 2. The hexagonal axis shows in the antiferromagnetic state the type of expansion found for Gd. The temperature dependence of this expansion is in agreement with Eq. (1) for $(1/Y)(\partial\alpha/\partial c)$ given in Table I. Figure 2 shows the c calculated from Eq. (1). The magnetization assumed was that reported by Behrendt *et al.*[11] from 0 to 120°K and by Wilkinson *et al.*[12] from 120 to 180°K. The interplanar angle θ is from Wilkinson *et al.* The discontinuity at 86°K, $\Delta c=0.010$, is larger, however, than would be predicted by Eq. (1) on the basis of the change in θ. The disagreement is due to the distortion of the structure to orthorhombic below 86°. The orthorhombic a and b lattice parameters are shown in Fig. 2; above 86° the orthorhombic a and hexagonal a axes are identical.

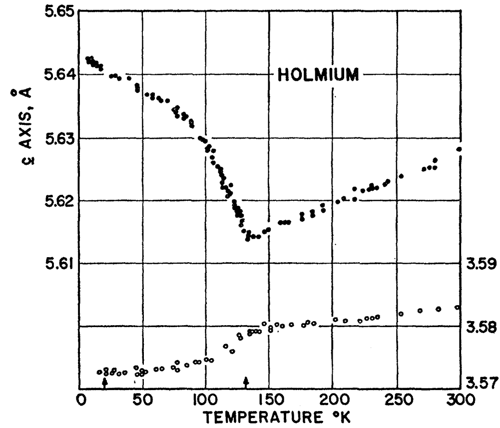

FIG. 3. Lattice parameters of holmium vs temperature. ●, c axis; ○, b axis.

The driving force which causes the orthorhombic distortion arises from the same type of magnetoelastic coupling that causes the c expansion below the magnetic ordering temperatures of Gd, Dy, and Ho. In all three cases the interplanar angle is less than 90°, and the same sign for $\partial\alpha/\partial c$ and for $c-c_T$ would be expected. In the antiferromagnetic region, however, the spiral spin arrangement does not permit distortion in any one direction of the hexagonal basal plane; only in the ferromagnetic state is the necessary uniaxis established to allow the spontaneous distortion.

Measurements[13] of magnetostriction, λ, on polycrystalline Dy have given values as high as 2.4×10^{-3} in the antiferromagnetic state. Study of the field dependence of λ shows that these values occur only when the applied field exceeds the critical field H_c which causes transition to the ferromagnetic state. The observed extraordinarily large magnetostriction values thus would seem to be only a measure of the lattice structure change to orthorhombic, a change which involves linear distortions of +0.2, −0.5, and +0.3% in the a, b, and c directions, respectively. Magnetostriction measurements on single crystals will be helpful in clearing up this point. In the ferromagnetic region λ decreases but remains large because the existence of magnetic domains causes formation of equal volumes distorted along each of the three equivalent easy

---

[6] W. E. Henry, J. Appl. Phys. **29**, 524 (1958).

[7] P. G. de Gennes, Compt. Rend. **247**, 1836 (1958); S. H. Liu, Phys. Rev. **121**, 451 (1961).

[8] U. Enz, Physica **26**, 698 (1960); R. J. Elliott, Phys. Rev. **124**, 346 (1961); T. A. Kaplan, *ibid.* **124**, 329 (1961).

[9] C. D. Graham, Jr., J. Phys. Soc. Japan **17**, 1310 (1962); Suppl. J. Appl. Phys. **34**, 1341 (1963).

[10] F. J. Darnell and E. P. Moore, Suppl. J. Appl. Phys. **34**, 1337 (1963).

[11] D. R. Behrendt, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 1544 (1958).

[12] M. K. Wilkinson, W. C. Koehler, E. O. Wollan, and J. W. Cable, J. Appl. Phys. **32**, 48S (1961).

[13] K. P. Belov, R. Z. Livitin, S. A. Nikitin, and A. V. Ped'ko, Zh. Eksperim. i Teor. Fiz. **40**, 1562 (1961) [translation: Soviet Phys.—JETP **13**, 1096 (1961)]; **15**, 279 (1962); E. W. Lee and L. Alperts, Proc. Phys. Soc. (London) **79**, 977 (1962).

crystallographic directions.[10] Application of a field creates a unique direction and gives a large magnetostriction which again is a reflection of the spontaneous orthorhombic distortion.

Holmium

The expansion of c below $T_n = 132°\text{K}$ is shown more markedly by Ho (Fig. 3) than for Gd or Dy, and the simultaneous contraction along a is also more clearly observed. Constants containing $(1/Y)(\partial\alpha/\partial c)$ are given in Table I; calculations were based on the assumption that the sublattice magnetization behavior was the same as for Dy. The angle θ was taken from Wilkinson *et al.*[1,14] At the 20° transition a slight discontinuity in c is observed. Neutron diffraction measurements[14] have shown that at this transition the interplanar angle θ, as seen in projection on the basal plane, decreases by no more than 3°. At the same time all the moments tilt about 20° out of the plane to give a ferromagnetic moment along c. This tilt involves a slight decrease in the true interplanar angle even though the c plane projection shows no change. The Δc calculated from Eq. (1), using the constants of Table I and a possible total angular change of 5°, is 0.001 Å; this is equal to the change observed, which is just at the edge of the present experimental error. The magnetization at the transition is believed[1] to undergo no change.

The values of $(1/Y)(\partial\alpha/\partial c)$ calculated from either Eq. (1) or from Eq. (2) are not as nearly equal as might be expected *a priori*. This may be due in large measure to the necessary assumptions regarding c_T and $M(T)$. If we calculate the quantities $(c^2/Y)(\partial\alpha/\partial c)M_0^2$, however, we do find nearly equal values for the three elements, as shown in Table I, when Eq. (1) is used. The values involving $\partial\alpha/\partial c$ calculated on the basis of molecular field approximations thus appear slightly more consistent than those calculated on the basis of spin-spin interactions. It is possible that the anomalous c expansion arises at least in part not from the indirect $\mathbf{S}\cdot\mathbf{S}$ interactions but from exchange involving the total moment, e.g., dipole-dipole interactions.

SUMMARY AND CONCLUSIONS

Accurate measurements of the lattice parameters of Gd, Dy, and Ho show, in detail, the anomalous expansion along the hexagonal c axes with decreasing temperature in their magnetically ordered regions. The dependence of the expansion on magnetization and spin configuration is in reasonable agreement with the theory of exchange magnetostriction developed by Kittel, and shows the strong inter-relation between magnetic and elastic forces.

In the case of Dy the antiferromagnetic to ferromagnetic transition is proven to be first order, with a distortion of the normal hexagonal close-packed crystal structure to orthorhombic below 86°K. The driving force for this distortion is believed to be the same type of magnetoelastic coupling that gives rise to the anomalous c axis expansion. The unusually large magnetostriction observed for Dy is a result of this spontaneous structure change.

In Ho the antiferromagnetic to ferromagnetic transition is accompanied by a barely observable discontinuity in the c axis, in agreement with the change in spin configuration observed by neutron diffraction.

On the basis of the present measurements we may predict the behavior of the lattice constants for the remaining heavy rare earths. Tb is expected to show c expansion[15] below $T_n = 232°\text{K}$ and a discontinuity in c with the transition to ferromagnetism at 221°K. A distortion to orthorhombic will probably occur, by analogy with Dy. The c dimensions of Er[4] and Tm should show expansion below their respective Néel temperatures of 84° and 53°, and discontinuous expansions in c should take place at the transitions to ferromagnetic ordering. No distortion from hexagonal is expected since the spin ordering does not change at the transition in a way to give the necessary single axis in the basal plane. Exchange magnetostriction associated with the ferromagnetic cone can only provide distortion along the already present hexagonal axis.

ACKNOWLEDGMENTS

The single crystals of the rare earth metals were kindly supplied by Dr. J. L. Moriarty of the Lunex Company, Pleasant Valley, Iowa. The x-ray data were taken largely by E. P. Moore. The author is indebted to Professor E. F. Bertaut, Professor B. Dreyfus, Professor M. J. Buerger, Dr. P. Arthur, Jr., Dr. H. S. Jarrett, and Dr. C. T. Prewitt for discussions of the work.

---

[14] See reference 1. Sample A showed an interplanar angle of ~37°, constant through the transition; sample B showed a change from 33° in the antiferromagnetic state to 30° in the ferromagnetic state.

[15] F. Barson, S. Legvold, and F. H. Spedding, Phys. Rev. **105**, 418 (1957).