PHYSICAL REVIEW VOLUME 132, NUMBER 3 1 NOVEMBER 1963

Lattice Parameters of Terbium and Erbium at Low Temperatures

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

(Received 20 June 1963)

Lattice parameters have been determined for terbium between 300 and 77°K and for erbium between 300 and 10°K. The temperature dependences of the hexagonal c axis for both elements are in qualitative agreement with a strain-dependent on $\mathbf{M}\cdot\mathbf{M}$, the scalar product of the moments of adjacent planes of ferromagnetically coupled spins. Below its temperature of ferromagnetic ordering, 220°K, terbium shows an orthorhombic distortion similar in magnitude to that observed previously for dysprosium. The distortion corresponds to an expansion along b or $[10\bar{1}0]$, the easy direction in terbium.

INTRODUCTION

The complex spin arrangements which exist in the ordered states of the heavy rare-earth elements have been determined in detail by neutron-diffraction[1] and magnetization[2] studies. The large magnetocrystalline anisotropy in these metals demonstrates a strong coupling between the magnetic moments and the lattice. It is, therefore, to be expected that the lattice parameters will strongly reflect changes in magnitude and direction of the magnetic moment. Such coupling has been demonstrated by dilatometric studies[3] on many of the rare earths and by recent x-ray studies on gadolinium,[4] dysprosium,[4,5] and holmium.[4] The present paper describes x-ray determinations of the crystal-cell parameters for terbium and erbium and discusses their relation to the known magnetic structures.

EXPERIMENTAL METHODS

The x-ray diffraction studies were carried out on small single crystals. The terbium sample was cut from a large crystal, consisting of two or three grains, which had been grown by annealing an arc-melted button. The erbium sample was formed during reduction of the metal chloride. Both samples had estimated purities of approximately 99.9%, with the major impurities consisting of other heavy rare earths. As described[4,5] previously, diffractometer data were taken in the back-reflection region, with 2θ values measured to the nearest 0.01°. Estimated errors in lattice parameters are ± 0.001 Å. A major source of error is the temperature, which was determined by a copper-Constantan thermocouple placed in contact with the sample. Temperatures are believed accurate to $\pm 2°$ at the higher temperatures and $\pm 4°$ at the lowest temperatures. The known magnetic transitions were used as internal standards to adjust the measured temperatures. Cooling was accomplished by directing onto the sample a stream of helium or nitrogen gas resulting from boiling of the corresponding liquid.

RESULTS AND DISCUSSION

Terbium

The lattice parameters for terbium as a function of temperature are displayed in Fig. 1. Below the ferromagnetic ordering temperature, 220°K, the $h00$ and $hh0$ reflections are each split into two components with intensity ratios of the lower 2θ to the higher 2θ peaks of 1:2 and 2:1, respectively. These components may be indexed on an orthorhombic cell corresponding to expansion along the b or $[10\bar{1}0]$ direction and contraction along the a or $[2\bar{1}\bar{1}0]$ direction. Such distortion, although opposite in sign to that found[5] for dysprosium, is in accord with the positive magnetostriction[6] and easy

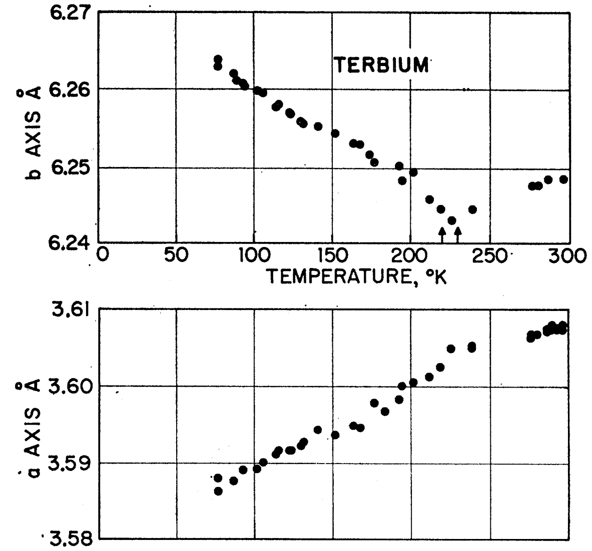

FIG. 1. Crystallographic cell parameters for Tb versus temperature. Above 220°K, a represents an hexagonal cell and $b=\sqrt{3}a$. Below 220°K, a and b correspond to an orthorhombic cell.

---

* Contribution No. 897.

[1] For Tb, W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, J. Phys. Soc. Japan **17**, Suppl. B-III, 32 (1962); for Er, M. K. Wilkinson, H. R. Child, W. C. Koehler, J. W. Cable, and E. O. Wollan, *ibid.* **17**, 27 (1962); these papers include work and references also on Dy, Ho, and Tm.

[2] For Tb, D. E. Hegland, S. Legvold, and F. H. Spedding, Phys. Rev. **131**, 158 (1963); for Er, R. W. Green, S. Legvold, and F. H. Spedding, *ibid.* **122**, 827 (1961).

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

[4] F. J. Darnell, Phys. Rev. **130**, 1825 (1963).

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

[6] K. P. Belov, R. Z. Levitin, and S. A. Nikitin, Izv. Akad. Nauk SSSR, Ser. Fiz. **25**, 1328 (1961) [translation: Bull. Acad. Sci. USSR, Phys. Ser. **25**, 1394 (1962)]; S. A. Nikitin, Zh. Eksperim. i Teor. Fiz. **43**, 31 (1962) [translation: Soviet Phys.—JETP **16**, 21 (1963)].

$[10\bar{1}0]$ direction[2] reported in the literature. The data show somewhat greater scatter than similar x-ray measurements on other rare earths due to a greater degree of strain in the terbium sample, and due to overlapping of orthorhombic components in the region near the ordering temperature. In the case of dysprosium the first-order transition, below which the orthorhombic distortion appears, occurs approximately 90° below the Néel temperature. The sublattice magnetization has then become large, and the resulting distortion clearly separates the orthorhombic components of the diffraction lines. In the case of terbium the first-order transition is approximately 10° below the Néel temperature. The resulting orthorhombic distortion is small since the sublattice magnetization is small, and the orthorhombic components are less clearly resolved.

The orthorhombic distortion, which amounts to several tenths of 1% in linear dimension, is in essence a measure of the magnetostriction which normally is not large enough in ferromagnetic materials to be observed by x-ray measurement. The distortions observed here have been used to calculate single-crystal magnetostriction constants for the ferromagnetic state of terbium as a function of temperature.[7] As in the case of dysprosium, the orthorhombic distortion continues to increase as the sublattice magnetization increases with decreasing temperature. The ratio b/a, which is 1.732 for the hexagonal structure, becomes $b/a=1.746$ for terbium at 77°; for dysprosium at 77°, $b/a=1.720$.

The expansion of the c axis below the Néel temperature (Fig. 2) is in agreement with similar findings[4,5,8] for the other heavy rare earths. It may be understood semiquantitatively in terms of the coupling between the elastic and magnetic energies described in the exchange magnetostriction theory of Kittel.[9] This approach gives a lattice constant equal to the nonmagnetic phonon dimension plus a term proportional to $\mathbf{M}\cdot\mathbf{M}$. Expansion in both the antiferromagnetic and ferromagnetic states corresponds to a positive value of $\partial J/\partial c$, an increase in the exchange with expansion along the hexagonal axis. Although $c-c_T$, the difference between the actual lattice parameter and the lattice parameter in the absence of magnetic forces, increases rapidly below 220°K and is roughly proportional to M^2, at the lower temperatures a contraction term is evident, presumably due to the continuing expansion of the a-b plane. An average value for $(c^2/Y)(\partial J/\partial c)M_0^2$ in the range 160 to 220°K is ≈ 0.04 Å. This is in the narrow range 0.036 to 0.042 Å found[4] for Dy and Ho. Here Y is an elastic modulus, J is the molecular-field constant, and M_0 is the *sublattice* magnetization equal 1335 emu/cm^3 for Tb.

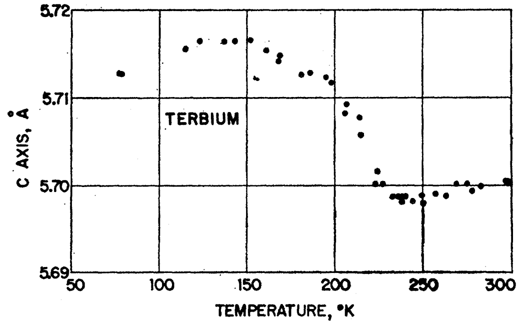

FIG. 2. Crystallographic cell parameter c for Tb versus temperature. Above 220°K, structure is hexagonal; below 220°K, structure is orthorhombic.

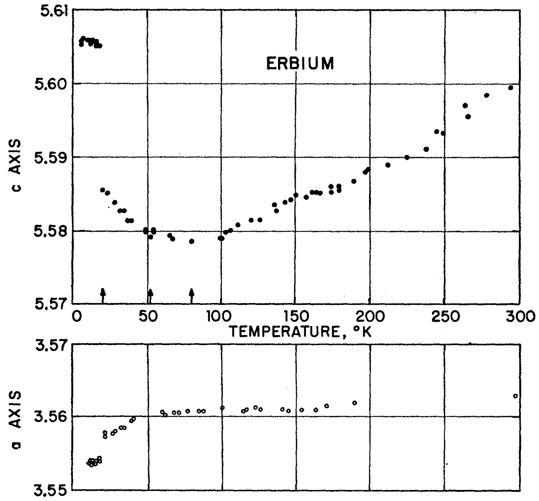

FIG. 3. Crystallographic cell parameters c and a for hexagonal Er versus temperature.

Erbium

The c and a lattice parameters determined for erbium are shown in Fig. 3. The several states of magnetic ordering for erbium are clearly reflected in the lattice parameters; the coupling between elastic and magnetic forces may again be understood qualitatively in terms of an $\mathbf{M}\cdot\mathbf{M}$ interaction. Above the Néel temperature, $T_N=80$°K, the c axis contracts in a more or less normal fashion. Between 80° and 52°, where erbium exhibits[1] a sinusoidally varying z component of magnetization, the thermal contraction is overcome and the c axis begins to expand slightly with decreasing temperature. Between 52 and 20°K, where an additional ordering in the a-b plane is present, the additional contribution to the $\mathbf{M}\cdot\mathbf{M}$ interaction gives rise to an increase in the rate of c expansion with decreasing temperature. With the first-order transition at 20°K, there is a large discontinuous increase in the c dimension corresponding to collapse of the sinusoidal z variation and formation of a conical spin configuration with consequent increase in the $\mathbf{M}\cdot\mathbf{M}$ interaction. There is believed[1,2] to be no change in M at the transition. All of these c dimension changes are reflected inversely in the a axis. Expansion

---

[7] F. J. Darnell, Phys. Rev. **132**, 128 (1963).

[8] R. M. Bozorth and T. Wakiyama, J. Phys. Soc. Japan **17**, 1669 (1962).

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

of the c axis at low temperatures had been previously observed by Banister *et al.*[10] No orthorhombic distortion is observed in the ferromagnetic state since the sinusoidal variation in the a-b plane is retained. Application in the ferromagnetic state of fields sufficient to collapse the helical component should lead to orthorhombic distortion comparable to that observed for terbium.

CONCLUSIONS

Expansion of the hexagonal axis with decreasing temperature observed for terbium and erbium, and for the other heavy rare earths, demonstrates a positive sign for the rate of change of the effective exchange integral with distance. The magnitude of $\partial J/\partial c$ for terbium is of the same order as that found for dysprosium and holmium. The temperature dependences of the c axes may be semiquantitatively explained by an interaction of the form $\mathbf{M}\cdot\mathbf{M}$, in agreement with ideas of coupling between magnetic and elastic forces proposed by Kittel and by Rocher[11]. The magnitude of $\partial J/\partial a$ for terbium is found to be comparable to $\partial J/\partial c$.

The orthorhombic distortion or magnetostriction of terbium is found to be easily observable by x rays. The changes in linear dimensions at 77° are -3.2×10^{-3} for $\Delta a/a$ and 4.6×10^{-3} for $\Delta b/b$.

ACKNOWLEDGMENTS

It is a pleasure to thank E. P. Moore for performing the diffraction measurements and calculating the lattice constants. The Tb single crystal was supplied through the courtesy of Professor F. H. Spedding of Iowa State University; Er single crystals were kindly furnished by Dr. J. L. Moriarty of the Lunex Company.

---

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

[11] Y. A. Rocher, J. Phys. Chem. Solids, **23**, 759 (1962); Advan. Phys., **11**, 233 (1962).

PHYSICAL REVIEW VOLUME 132, NUMBER 3 1 NOVEMBER 1963

Extension of the Statistical Model of the Atom

VICTOR A. ERMA*
Giannini Scientific Corporation, Santa Ana, California

(Received 11 August 1961; revised manuscript received 25 June 1963)

The statistical model of the atom is extended within the semiclassical framework to include the correlation energy of the electron gas, obtained by an interpolation formula which reproduces the known high- and low-density limits exactly. The basic equations of the model are derived, and general theoretical results valid for all free atoms and ions are obtained. These include the determination of the electron density at the edge of the atom, a virial theorem for the atom, and a treatment of the Fermi-Amaldi correction. The equations of the model are solved in terms of a Thomas-Fermi-Dirac-like approximation, in terms of a semiconvergent expansion for the potential near the nucleus, and numerically on a computer for the atoms argon, chromium, krypton, xenon, and uranium. The solutions of the model are illustrated in detail for the case of argon, including a calculation of the energy terms of the argon atom. Finally, the application of the extended model is illustrated by a calculation of atomic polarizabilities and diamagnetic susceptibilities and the results are compared with experiment.

I. INTRODUCTION

THE so-called semiclassical statistical model of the atom, originated independently by Thomas[1] and Fermi,[2] has proved to be a simplified, albeit fruitful and versatile approach to the many electron system of the atom, and has been made the basis for the calculation of a large variety of atomic properties. Comprehensive reviews of the theory and applications of the statistical model have been given by Corson,[3] Gombas,[4] and March.[5]

The model is based on a number of simplifying assumptions which we shall sketch briefly. To begin with, it is assumed that the electrons surround the nucleus with a spherically symmetric density distribution. The basis of the model lies in assuming further that the volume of the atom can be divided into subvolumes $4\pi r^2dr$ over which the potential is approximately constant, but which still contain a sufficiently large number of electrons. Finally, the electrons occupying each subvolume at a distance r from the nucleus are considered to constitute a totally degenerate gas at zero temperature, whose energy density ϵ depends solely on the

---

* The present paper is based on part of a Doctoral Dissertation at the California Institute of Technology, 1961 (unpublished).

[1] L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).

[2] E. Fermi, Z. Physik **48**, 73 (1928).

[3] M. Corson, *Perturbation Methods in the Quantum Mechanics of n-Electron Systems* (Hafner Publishing Company, Inc., New York, 1950).

[4] P. Gombas, *Die statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Vienna, 1949). A more up-to-date, though more abbreviated version of the same work is contained in P. Gombas, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 36, p. 109.

[5] N. H. March, Suppl. Phil. Mag. **6**, 1 (1957).