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CRYSTAL STRUCTURE OF HOLMIUM AND ERBIUM BETWEEN 77° AND 300°K

V. A. FINKEL' and M. I. PALATNIK

Physico-technical Institute, Ukrainian Academy of Sciences

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The crystal structures of holmium and erbium are measured by means of low-temperature x-ray diffraction between 77° and 300°K. It is shown that an anomalous expansion of the hexagonal close-packed lattices occurs along the hexagonal axis below T_N (132.5°K for Ho and 84°K for Er). Discontinuous changes of the linear expansion coefficients for holmium and erbium occur at T_N ($\Delta\alpha_\perp > 0$, $\Delta\alpha_\parallel < 0$). At T ~ 120°K a peak is observed in the temperature curve of the atomic volume of holmium; this peak is associated with a change in the Fermi surface topology.

EARLIER studies of the crystal structure of rare earth metals (REM—gadolinium,[1] terbium,[2] and dysprosium[3]) at low temperatures have revealed the existence of several common structural effects despite differences in the magnetic structures of REM. Thus, at the transition from the paramagnetic state to the ferromagnetic state (of Gd) and to the antiferromagnetic state (of Tb and Dy) λ anomalies of the thermal expansion coefficients were observed that are characteristic of second order phase transitions; below the temperatures of the second order phase transitions the parameter c of the hcp lattices increased rapidly with decreasing temperature; for all the investigated REM in a magnetically ordered state a peak was observed on the temperature curves of the atomic volume [V(T)]. The last effect was associated with a change in the topology of the Fermi surface as this surface intersected the boundary of the first Brillouin zone.[4]

The present work, a natural continuation of the REM structural studies,[1-3] is a precision investigation of the crystal structures of Ho and Er at 77°–300°K by means of low-temperature x-ray diffraction.

Ho is known to be paramagnetic below 133°K, antiferromagnetic at 20°–133°K, and ferromagnetic below 20°K.[5] The helicoidal antiferromagnetic structure of Ho can be described in first approximation as a highly distorted simple spiral (SS) in which the helicomagnetic turn angle (θ) decreases monotonically from 50° at T_N to ~36° at 35°K, after which it drops steeply to 30° at T_c; below T_c there appears a constant component of the magnetic moments along the c axis of the hcp lattice, i.e., a ferromagnetic spiral (FS) is formed.[6] The measured parameters of the Ho lattice at low temperatures indicate anomalous behavior of the a(T) and c(T) curves below T_N,[7] in qualitative agreement with dilatometric measurements on Ho single crystals.[8] The Néel temperature of polycrystalline Ho is lowered as the pressure is increased ($dT_N/dp = -0.40$ deg/kbar).[9]

Three regions of magnetic ordering have been observed in Er below T_N (80°–85°K).[10] From 52°K to T_N the components of the magnetic moments in the basal planes of the hcp lattice are in a way disordered; the components along the principal axis are modulated sinusoidally with the period 3.5 c—this kind of antiferromagnetic structure is called a linear static spin wave (LSW). In the range 20°–52°K helicoidal ordering of the spin projections in the basal planes is observed, but the sinusoidal modulation of the longitudinal component of the magnetic moment is preserved—the complex spiral (CS) type of antiferromagnetic structure is formed. Below T_c (20°K), as in the case of holmium, there is a stable ferromagnetic spiral (FS). X-ray diffraction[11] has shown the anomalous behavior of the a(T) and c(T) curves below T_N, in agreement with dilatometric measurements.[12] With increasing pressure the Néel temperature of Er is lowered ($dT_N/dp = -0.26$ deg/kbar).[13]

In our present work we used polycrystalline samples of Ho (99.5% pure) and Er (99.4% pure). The samples were first annealed for 10 hours at ~10^{-6} Torr and 1000°C. The technique of low-temperature x-ray investigation of Ho and Er was essentially the same as that described in [3]. Diffraction patterns were obtained with an URS-50I diffractometer that was equipped with a cryostat. Diffraction peaks were registered coming from the (300) planes (reflection angle θ ~ 70°) and (105) planes (θ ~ 66°) of the hcp lattices of Ho and Er. These conditions permitted us to measure the lattice constants with quite high accuracy: $\Delta a \sim 1.0 \times 10^{-4}$ Å, $\Delta c \sim 2.7 \times 10^{-4}$ Å (with $\Delta\theta \sim 0.5'$ as the maximum error of the reflection angles). The temperatures were measured with ~0.2°K accuracy.

We observed no diminishing of symmetry in the Ho and Er hexagonal lattices. Figures 1 and 2 show the lattice constant measurements and the temperature dependences of the linear expansion coefficients ($\alpha_\perp = a^{-1}da/dT$ and $\alpha_\parallel = c^{-1}dc/dT$) obtained by numerical differentiation of the a(T) and c(T) curves. Two different segments of

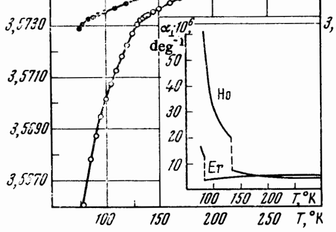

FIG. 1. Temperature dependence of the lattice constant a and $\alpha_\perp$ for Ho and Er.

REM	T_N, °K	V, Å^3	ΔC_p [16] cal/deg-mol	$\Delta\alpha \times 10^6$, deg^{-1} Along a b axes $(\Delta\alpha_{11})$	Along c axis $(\Delta\alpha_{33})$	$\Delta\alpha_V$	$\frac{dT_N}{d\sigma_{11}}$, deg/kbar	$\frac{dT_N}{d\sigma_{33}}$, deg/kbar	$\frac{dT_N}{dp}$, deg/kbar	Note
Ho	132.5	30.96	5.5	12.9	—53.3	—26.3	0.14	—0.57	—0.29	dT_N/dp = —0,40 [9]
Er	84	30.37	1.9	12.3	—29.7	—8.1	0.24	—0.57	—0.16	dT_N/dp = —0,26 [13]
Dy	178						0.36	—0.94		From [17]

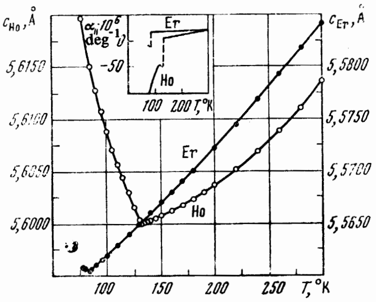

FIG. 2. Temperature dependence of the lattice constant c and of $\alpha_{\|}$ for Ho and Er.

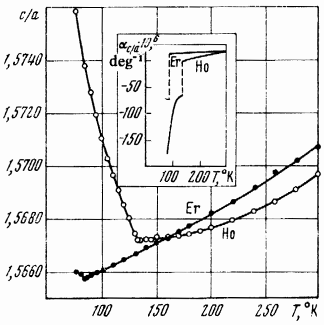

FIG. 3. Temperature dependence of the axial ratio c/a and of the thermal expansion coefficient $a_{c/a}$ for Ho and Er.

the a(T) and c(T) curves are observed for both metals: 77°–132.5°K and 132.5°–300°K for holmium, 77°–84°K and 84°–300°K for erbium, corresponding to the antiferromagnetic and paramagnetic states. The temperature curves of the lattice constants have very different slopes below and above T_N, but no discontinuous changes of a and c were observed at T_N. As in the cases of other REM, in a magnetically ordered state c increases anomalously with decreasing temperature. However, for Ho the c(T) curve in the antiferromagnetic region is very much steeper than for Er ($\alpha_{\|}^{Ho} < \alpha_{\perp}^{Er}$). Below T_N the a(T) curves behave normally except that their slope is steeper than in the paramagnetic region.

As a consequence of the described behavior exhibited by the temperature curves of the Ho and Er lattice constants, the linear expansion coefficients undergo abrupt changes at T_N (positive for $\alpha_{\perp}$ and negative for $\alpha_{\|}$), as shown in the small graphs of Figs. 1 and 2. The λ anomalies of the thermal expansion coefficients at the paramagnetic to antiferromagnetic transition (P → SS for Ho and P → LSW for Er) indicate that these transformations are second order phase transitions.[14]

According to the Ehrenfest relation[4]

$$\Delta\alpha_V = \frac{\Delta C_p}{T_N V}\frac{dT_N}{dp} \qquad (1)$$

the sign of the discontinuity in the volume expansion coefficient ($\alpha_V = 2\alpha_{\perp} + \alpha_{\|}$ [15]) at second order phase transitions is determined by the sign of dT_N/dp, i.e., by the character of the pressure dependence of the Néel point (the heat capacity discontinuity ΔC_p is positive for transformations at T_N or at T_C). It is easily shown that in the case of uniaxial stresses applied to single crystals of hexagonal metals along the a(σ_{11}) and c(σ_{33}) axes we can obtain relations analogous to (1) for the hydrostatic case:

$$\Delta\alpha_{11} = \Delta\alpha_{\perp} = \frac{\Delta C_p}{T_N V}\frac{dT_N}{d\sigma_{11}}, \qquad \Delta\alpha_{33} = \Delta\alpha_{\|} = \frac{\Delta C_p}{T_N V}\frac{dT_N}{d\sigma_{33}}. \qquad (2)$$

Using (2), the measured values of $\Delta\alpha_{\perp}$ and $\Delta\alpha_{\|}$ at T_N, and values given in the literature[16] for ΔC_p at the Néel points of Ho and Er, we are able to evaluate $dT_N/d\sigma_{11}$ and $dT_N/d\sigma_{33}$. Unfortunately, the results (given in the table) cannot be compared with direct measurements of T_N shifts induced by uniaxial stresses parallel and perpendicular to the hexagonal axis, since measurements of the type mentioned have been performed only on Dy.[17] The table shows that for all three helicoidal antiferromagnets (Dy, Ho, Er) $dT_N/d\sigma_{11} > 0$ and $dT_N/d\sigma_{33} < 0$, the absolute values being fully comparable.

In (1) the terms $\Delta\alpha_V$ and dT_N/dp are, respectively, the traces of the matrices of discontinuities in the linear expansion coefficients ($\Delta\alpha_{ii}$) and of shifts of T_N induced by normal stresses ($dT_N/d\sigma_{ii}$); both matrices have been converted to the same principal axes.[15] We can therefore calculate

$$\frac{dT_N}{dp} = \mathrm{Sp}\frac{dT_N}{d\sigma_{ii}}$$

from the experimental values of $\Delta\alpha_V = \mathrm{Sp}\,\Delta\alpha_{ii}$ and known values of the other quantities. The values of dT_N/dp calculated for Ho and Er agree fairly well with direct determinations of Néel temperature shifts under hydrostatic pressure (see the table).

The sharply anisotropic temperature shift, observed here, of the transition to a magnetically ordered state, induced by uniaxially oriented stresses, is evidently associated with varying dependence of the exchange interaction integrals[1)] on interatomic separations. It appears that a similar effect can occur in many noncollinear magnetic materials having noncubic crystal structure.

The temperature dependence of the axial ratio c/a behaves in an identical manner for both investigated metals: c/a increases with temperature in the paramag-

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[1)] For the simple spiral (SS) case we here refer to I_0—the exchange integral between atoms in the basal plane (001), I_1—between atoms in neighboring basal planes, I_2—between atoms in next to nearest layers etc. [18]

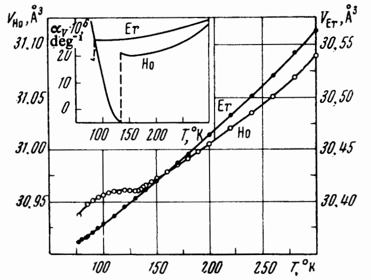

FIG. 4. Temperature dependence of the atomic volume (V) and of the volume expansion coefficient (d_V) for Ho and Er.

netic region and decreases in the antiferromagnetic region (Fig. 3). The corresponding thermal expansion coefficients

$$\alpha_{c/a} = \left(\frac{c}{a}\right)^{-1}\frac{d(c/a)}{dT} = \alpha_\parallel - \alpha_\perp$$

behave similarly (insert in Fig. 3). Extrapolation of c/a = f(T) to the Curie temperature yields $(c/a)_{T_C} \sim 1.58$ for Ho; this extrapolation is impossible for Er. It is of interest that for all REM where at T_C the simple spiral type of antiferromagnetic structure is destroyed (Tb,[2] Dy,[3] Ho) the values of $(c/a)_{T_C}$ coincide; for other types of magnetic structure $(c/a)_{T_C}$ differs from 1.58.2) These observations are consistent with ideas developed in [19] to the effect that c/a not only characterizes the lattice anisotropy but also serves as a measure of exchange energy in hexagonal rare earth magnets, and that the temperature dependence of the axial ratio evidently determines the character of changes in REM magnetic structure.

The temperature dependences of the atomic volume

$$V = {}^1/_4 a^2 c\sqrt{3}$$

and the volume expansion coefficient

$$\alpha_V = V^{-1}\frac{dV}{dT} = 2\alpha_\perp + \alpha_\parallel$$

of Ho and Er are shown in Fig. 4. The V(T) curve for Ho behaves as for other REM: in the paramagnetic region the atomic volume increases with temperature, a sharp minimum is observed at T_N, and below T_N a broadened peak (T_{max}) is observed at ~120°K. The minimum of V(T) corresponds to a negative discontinuity of α_V; α_V vanishes at T_{max}, of course, and no singularities are then observed on the $\alpha_V(T)$ curve. The maximum of the V(T) curve for Ho is not so distinct as for Gd, Tb, and Dy,[1-3] obviously because T_{max} and T_N lie close together. This circumstance hampers the observation of anomalies of various physical properties at T_{max} in the case of Ho, although the existence of peaks of electrical resistivity[5] and of H_{cr} 3) [20] at 120°K is not doubted.

The positive slope of V(T) for Er in the antiferromagnetic region ($\alpha_V > 0$) obviously excludes the possibility that a maximum of the atomic volume will appear for $T < T_N$ (at any rate, in the range where LSW structure exists). The volume expansion coefficient of Er possesses a considerably smaller discontinuity than that of Ho. In the paramagnetic region no essential differences are observed in the behavior of the V(T) curves for Ho and Er.

Thus the difference in the character of helicoidal antiferromagnetic order (SS for Ho and LSW for Er) correlates with small quantitative differences in the thermal expansion of these metals ($\alpha_\perp^{Ho} > \alpha_\perp^{Er}$, $\alpha_\parallel^{Ho} < \alpha_\parallel^{Er}$). These differences lead, in turn, to a qualitative difference in the behavior of the curves representing the temperature dependence of the atomic volume in the magnetically ordered state. Both the changed type of helicoidal magnetic ordering and the absence of the anomaly of volume thermal expansion that characterizes other REM apparently result from the fact that Er has a considerably smaller lattice than lighter REM (the so-called lanthanide contraction). In particular, the situation where the shortest distance from the center to the boundary of the Brillouin zone equals the radius of the Fermi surface may not be realized in the case of Er.

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CONCLUSIONS

1) A precision investigation of the crystal structures of Ho and Er was carried out in the temperature range 77°–300°K. The hcp lattices of these metals are stable in the entire region.

2. At 132.5°K for Ho and 84°K for Er kinks of the temperature curves of the lattice constants are observed, which are associated with second order antiferromagnetic-paramagnetic phase transitions.

3. Discontinuities of the linear expansion coefficients of Ho and Er at T_N reveal strong anisotropy ($\Delta\alpha_\perp > 0$, $\Delta\alpha_\parallel < 0$) resulting from different dependences of exchange integrals on interatomic separations.

4. The temperature curve of the atomic volume of Ho possesses a peak at ~120°K, whereas the volume expansion of Er behaves normally.

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2) Thus, for the direct transition of Gd from the paramagnetic to the ferromagnetic state $(c/a)_{T_C} \sim 1.59$, [1] while for Er we have $(c/A)_{T_C} \sim 1.57$. [11]

3) H_{cr} is the magnetic field strength at which antiferromagnetic structure is destroyed.

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