to intrinsic, i.e., where the concentration of the minority carriers is changing rapidly with respect to the majority carriers. In order to expect agreement in this region, one must assume an unusually high degree of uniformity and perfection of the crystal. The extrinsic region, or lower temperature region of Fig. 8, has already been discussed. The value of $N_v^{\frac{2}{3}}m^*/m=0.75$ for both holes and electrons gives a reasonable fit at 300°K. An assumption of $N_v^{\frac{2}{3}}m^*/m=1.0$ would decrease the absolute value of the 300° points by 0.011 volt whereas an assumption of $N_v^{\frac{2}{3}}m^*/m=0.55$ would increase them by 0.015 volt.

The "density of states" effective mass parameter $N_v^{\frac{2}{3}}m^*/m$ is related to the inertial effective mass parameter, m^*/m, by the statistical factor which we have called $N_v^{\frac{2}{3}}$, N_v would be the number of equivalent valleys or edges in a band with no spin-orbit splitting. The theoretical problem is discussed in some detail by Herring.[4] It suffices here to point out that while our result is not directly comparable with a number of recent experiments[16] that determine inertial effective mass, a comparison of the values may give further information about the band structure.

We are indebted to our colleagues F. J. Morin, J. A. Burton and C. Herring for many helpful discussions.

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Structure of Gd, Dy, and Er at Low Temperatures*

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The crystal structures of gadolinium, dysprosium, and erbium metals have been determined over a wide temperature range. The metals are hexagonal close packed and the a_0 unit axis contracts nearly linearly with decreasing temperature, whereas the c_0 unit axis exhibits an abnormal expansion with decreasing temperature below magnetic transformations of the metals. The c_0 behavior is believed to be associated with the magnetic properties of the metals.

I. INTRODUCTION

MAGNETIC transformations in metals are usually accompanied by crystal structure changes which may be of different types.[1] In view of the fact that some of the rare earth metals have been reported to be ferromagnetic it was felt that an x-ray study of the structures of these over a wide temperature range should be made. This report covers such studies for gadolinium, dysprosium, and erbium.

Gadolinium has been reported[2–5] to have a ferromagnetic Curie point of 16°C. Dysprosium exhibits[6–9] a magnetic anomaly at about 175°K and a ferromagnetic Curie point near 90°K. Erbium has recently been found[10] to have a magnetic susceptibility anomaly of the dysprosium type near 80°K, and it is further reported that the susceptibility becomes strongly field-dependent below 55°K.

Dilatometric studies on gadolinium and dysprosium have been reported by Trombe and Foex.[11,12] For gadolinium they report an abrupt decrease in the coefficient of thermal expansion below the Curie point. A similar phenomenon was displayed by dysprosium below the magnetic anomaly near 175°K.

The electrical resistivities[4] of the three metals also exhibit peculiarities near the temperatures cited above, showing the influence of the transformations on the conduction process. This is also in evidence in the study of the Hall effect as reported by Kevane *et al.*[13]

II. EXPERIMENTAL METHODS

The metal samples used were prepared by methods reported earlier.[14,15] Metal filings annealed under vacuum at 550°C for about 30 hours were mixed with pulverized

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NaCl crystals which served as an internal standard for the exposures. The mixed samples were placed in thin-walled glass capillaries approximately 0.035 cm in diameter. A Debye-Sherrer powder camera capable of operating at various temperatures was used for the exposures. A temperature-controlled, helium gas stream flowing past the sample was used to obtain the different temperatures. The temperature fluctuation during a given exposure was less than four degrees and mean temperatures for exposure have been used in reporting the results. Cu-α radiation was employed in the study and long exposure times gave negatives suitable for analysis.

The metal samples used showed the following impurities as determined spectrographically: for gadolinium, 0.02 percent Ca, 0.05 percent Nd, 0.1 percent Sm and 0.02 percent Tb; for dysprosium, Ca detectable, 0.01 percent Ho, 0.07 percent Y, traces of Fe, Ta, and Mg; for erbium, less than 0.02 percent Ho, less than 0.02 percent Y, traces of Ca, Fe, Mg, and Si.

To obtain the lattice constants of the NaCl, the calculated a_0's were extrapolated to $\theta=90°$. The values so obtained were found to be commensurate with the values which would be anticipated from the thermal expansion coefficient of sodium chloride. The $\sin^2\theta$ values for the metal were then modified by using the correction curve obtained by comparing the observed and calculated $\sin^2\theta$'s for the NaCl lines. Lattice parameters of the metals were calculated using the corrected $\sin^2\theta$ of the reflections and expressions derived by minimizing the sum of the squares of the deviations of the calculated angles from the observed angles. The calculation was checked, and errors estimated by substituting the calculated values back in the $\sin^2\theta$ of the individual reflections.

TABLE I. Variation of the lattice constants of gadolinium and sodium chloride with temperature.

Temperature (°K)	Gadolinium a_0(A)	Gadolinium c_0(A)	Sodium chloride a_0(A)
106	3.629±0.002	5.796±0.004	5.603±0.001
175	3.630±0.002	5.798±0.005	5.614±0.001
183	3.631±0.002	5.786±0.005	5.615±0.001
216	3.629±0.002	5.780±0.005	5.623±0.001
231	3.633±0.002	5.782±0.005	5.625±0.001
283	3.633±0.002	5.776±0.005	5.636±0.001
285	3.633±0.002	5.781±0.005	5.637±0.001
298	3.635±0.002	5.776±0.005	5.641±0.001
299	3.633±0.002	5.771±0.005	5.640±0.001
300	3.636±0.002	5.779±0.005	5.641±0.001
324	3.634±0.002	5.778±0.005	5.645±0.001
349	3.639±0.002	5.777±0.005	5.653±0.001

III. RESULTS AND DISCUSSION

Gadolinium

It was difficult to obtain clear negatives for the gadolinium analysis. It appeared that the absorption coefficient of gadolinium metal for Cu-α radiation was very high. Exposure times of twenty to forty hours gave from seven to thirteen readable metal lines for the analysis.

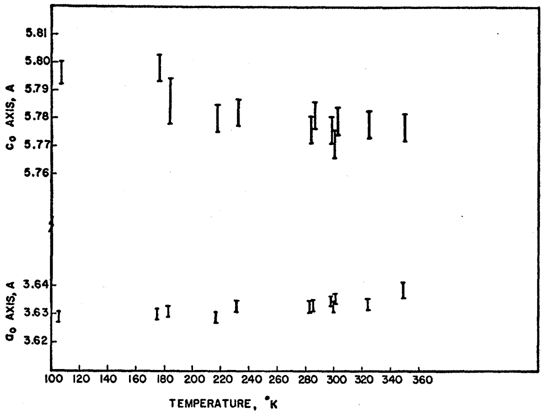

FIG. 1. Variation of the lattice parameters of gadolinium with temperature.

At room temperature, gadolinium was found to have a hexagonal, close-packed structure as was noted by Klemm and Bommer.[16] It was found, however, that the lattice constants were appreciably larger than those found by them. The largest part of this difference may be accounted for by the upward revision of the wavelength values in angstroms since their study.

It was found that there was no gross change in the structure of gadolinium across the Curie point, but it was noted that the c_0 unit axis increased with decreasing temperature in the region between the Curie point and 175°K as seen in Table I and in Fig. 1. The behavior of the a_0 unit axis appeared to be normal, within experimental error, showing an increase with increasing temperature. Assuming linear trends above and below the Curie temperature, the macroscopic coefficient of thermal expansion may be estimated as -2×10^{-6} per degree K below the Curie point and about 10×10^{-6} per degree K above the Curie point. This is in rough agreement with the dilatometric study of Trombe and Foex.[11]

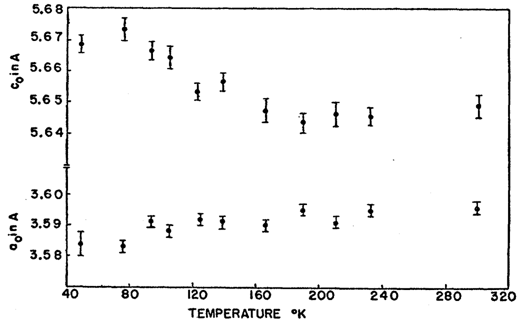

FIG. 2. Variation of the lattice parameters of dysprosium with temperature.

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TABLE II. Dysprosium and sodium chloride lattice constants.

Temperature (°K)	Dysprosium a_0(A)	Dysprosium c_0(A)	Sodium chloride a_0(A)
48– 50	3.584±0.004	5.668±0.003	5.596±0.001
75– 77	3.583±0.002	5.673±0.004	5.597±0.001
92– 94	3.591±0.002	5.666±0.003	5.601±0.001
103–107	3.590±0.002	5.664±0.004	5.602±0.001
122–124	3.595±0.002	5.653±0.003	5.604±0.001
138–140	3.591±0.002	5.656±0.003	5.607±0.001
165–167	3.595±0.002	5.647±0.004	5.613±0.001
188–192	3.595±0.002	5.643±0.003	5.617±0.001
210–212	3.591±0.002	5.646±0.004	5.620±0.001
231–235	3.595±0.002	5.645±0.003	5.627±0.001
299–301	3.595±0.002	5.657±0.006	5.641±0.001
298–302	3.596±0.002	5.649±0.003	5.641±0.001

TABLE III. Erbium and sodium chloride lattice constants.

Temperature (°K)	Erbium a_0(A)	Erbium c_0(A)	Sodium chloride a_0(A)
42.5–43.5	3.558±0.001	5.590±0.002	5.595 ±0.001
64 –66	3.562±0.002	5.582±0.003	5.597 ±0.001
83 –87	3.561±0.001	5.582±0.002	5.798 ±0.001
102 –104	3.563±0.001	5.581±0.002	5.601 ±0.001
151 –153	3.563±0.001	5.586±0.002	5.6095±0.0015
199 –201	3.565±0.001	5.591±0.002	5.6195±0.001
300 –302	3.562±0.002	5.602±0.003	5.641 ±0.001

Dysprosium

The x-ray negatives obtained using dysprosium samples showed some background, but were considerably clearer than the negatives for gadolinium. From eight to fourteen metal lines were observable on the negatives with exposure times of twelve to twenty hours. The lines indicated a hexagonal, close-packed structure for all exposures. This is in fair agreement with results reported by Klemm and Bommer[16] when account is taken of the wavelength revision reported above.

Results are summarized in Table II and Fig. 2. If linear trends above and below 190°K are assumed, a least mean square analysis gives a macroscopic coefficient of expansion of 9×10^{-6} per degree K above 190°K, and 0.5×10^{-6} per degree K below that temperature. This is comparable with the dilatometric result of Trombe and Foex.[11]

Erbium

The negatives for erbium had little background. Exposure times of eleven to twenty hours gave from twelve to twenty-three detectable metal lines. The structure of erbium metal was hexagonal, close-packed for all exposures. This structure has also been reported by Klemm and Bommer.[16] Their lattice constants, when revised as indicated previously, are in fair agreement with the values reported here.

Results of the x-ray exposures are summarized in Table III and Fig. 3. Assuming linear trends and using a least mean square analysis, the macroscopic coefficient of thermal expansion may be estimated as about 10×10^{-6} per degree K above 100°K, and about zero below that temperature.

In general, it would appear that the unusual behavior of the c_0 parameter below the Curie point or magnetic anomaly is probably due to the internal fields of the domain and may be regarded as a form of magnetostriction due to that field. It also suggests that there is a correlation between the crystal directions and the directions of easy magnetization. This effect has been observed in other ferromagnetic elements. If the rare earth metals are similar to the hexagonal, close-packed phase of cobalt at room temperature, the direction of easy magnetization would be parallel to the c_0 axis.

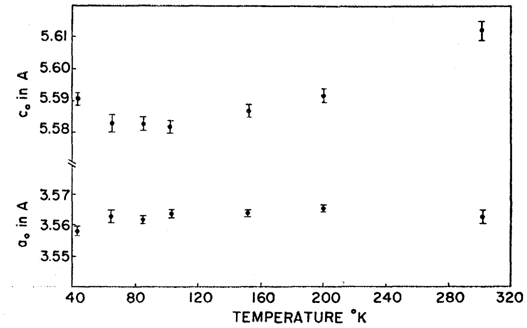

FIG. 3. Variation of the lattice parameters of erbium with temperature.

It should be noted that sodium chloride might be useful as a temperature index as well as an internal standard because of its large and relatively uniform expansion coefficient.

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