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HIGH TEMPERATURE ALLOTROPY AND THERMAL EXPANSION OF THE RARE-EARTH METALS*

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SUMMARY

By means of high temperature X-ray techniques the crystal structure of lanthanum, cerium, praseodymium, neodymium, ytterbium, and possibly gadolinium was found to be body-centered cubic at temperatures near their respective melting points. For ytterbium a hexagonal close-packed structure was also observed, which was shown to be stabilized by atmospheric impurities. Evidence for possible high temperature crystalline transformations in gadolinium, terbium, dysprosium, holmium, and lutetium was obtained by means of electrical resistance measurements; erbium gave no such evidence. X-ray data were used to derive empirical equations which describe thermal expansions coefficients of scandium, yttrium and the rare-earth metals. Europium exhibits a rapidly decreasing coefficient of expansion with increasing temperature, which may be a consequence of a gradual promotion of one of the 4f electrons into the conduction band. The hexagonal rare-earth metals were found to have nearly the same axial ratio at their respective transformation temperatures.

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INTRODUCTION

In recent studies of the physical properties of pure rare-earth metals in this laboratory¹⁻⁶ it was found that several of the rare-earth metals exhibit crystalline transformations at temperatures near their melting points. These transformations have been observed in thermal analyses at the following temperatures: lanthanum, 868°C; cerium, 730°C; praseodymium, 798°C; neodymium, 868°C; samarium, 917°C; gadolinium, 1263°C; terbium, 1310°C; and ytterbium, 798°C. Lanthanum undergoes an additional transformation between 250°C and 310°C. Habermann³ has recently observed a transformation in yttrium at 1455°C that Eash⁷ has also found in his study of the yttrium-magnesium system. On the basis of the reports of Barret⁸ and Spedding *et al.*⁹ europium does not exhibit any crystalline transformations.

At room temperature lanthanum, praseodymium, and neodymium have a hexagonal structure (double c-axis) in which crystal planes stack in the "abac..." sequence. Cerium and ytterbium have a face-centered cubic (fcc) structure, samarium a rhombohedral structure, europium a body-centered cubic (bcc) structure, while the remaining stable rare-earth metals, including scandium and yttrium, exhibit a hexagonal close-packed (hcp) structure.

The only high temperature structures previously reported for the rare-earth metals have been fcc lanthanum (stable above 310°C) and the β form of yttrium (above 1495°C), which was inferred to be bcc from phase diagram studies reported by Eash⁷ and Gibson and Carlson¹⁰.

In the present work a detailed study was made of the structures of the high temperature phases of the rare-earth metals. The possibility of existence of other crystalline modifications was also investigated by X-ray methods and by electrical resistivity measurements. Since the crystallographic method offers a means of accurate measurement of the lattice dimensions as a function of temperature, the thermal expansion characteristics of the rare-earth metals were also determined in this study.

EXPERIMENTAL

High temperature X-ray techniques

For the high temperature X-ray studies three different techniques were used. In the first two methods of the type described by Buerger et al.¹¹ was used with appropriate modifications described below.

X-ray method applicable up to 1000°C. Wire specimens of rare-earth metals were fitted with tungsten spacers and mounted in silica capillaries in a vacuum. A platinum wound furnace inside the camera heated the samples to the desired temperature, which was measured with a thermocouple. Calibration with silver indicated an accuracy in temperature measurement of $\pm 7^\circ\text{C}$ in the range 20° to 950°C . The details of this method are given elsewhere¹³.

X-ray method applicable up to 2200°C. Wire specimens of rare-earth metals were mounted in a slotted copper holder which provided space for the entering and diffracted X-ray beams. The ends of the sample were mounted so that current from a 6 volt battery heated the specimen to the desired temperature by its own resistance heating.

The exterior of the copper holder was treated with a plastic spray and then wrapped with "Saran Wrap" which permitted evacuation of the sample chamber to pressures as low as 1×10^{-6} mm, and also provided a very transparent window for the X-rays. The temperature of the specimen was determined by optical pyrometric and electrical resistivity measurements. The details have been described in more detail¹³.

In the third method a high temperature X-ray diffractometer previously described by Chiotti¹² was used to substantiate some observations made on ytterbium by the first method.

Determination of phase transformations by electrical resistance measurements

To determine the existence of crystalline transformations by electrical resistance measurements the apparatus described by Chiotti¹⁴ was used. In this method cylindrical samples eight cm long and 0.5 cm in diameter were heated by passing alternating current through them. The electrical resistance of the sample was determined by measuring the voltage across the samples by alternating current potentiometric methods. The temperature of the samples was measured by an optical pyrometer focussed on a small sight hole drilled into the metal, or by a thermocouple imbedded in the metal.

Methods of calculation

The determination of the lattice constants was done by the Cohen's least-squares method¹⁵ on an IBM-650 computer. For cubic lattices, a program was used requiring only the Bragg angles and the Miller

indices as input data. For hexagonal lattices a program was written which indexed the diffraction patterns and then calculated the lattice constants by the least-squares method. For this program a prior knowledge of the approximate lattice constants was required (to within 0.01 Å). The indexing was performed by synthesizing the allowed reflections on the basis of these lattice constants and comparing them to the observed reflections. When a poor guess of the approximate lattice constants was made, the new lattice constants used in the subsequent iteration generally gave rise to the proper indexing of the pattern.

The quality of the diffraction patterns of the rare-earth metals deteriorated with increasing temperature. For temperature ranges where back-reflection lines appeared it was possible to determine the lattice constants with an accuracy of ± 0.005 to ± 0.0005 Å. In such cases the lattice constants and related data were fitted to empirical equations of the type

$$R = A + Bt + Ct^2 + Dt^3 \quad (1)$$

$$\text{or} \quad R = A + Bt \quad (2)$$

where R is a lattice constant or a related property, t the temperature in °C and A, B, C, and D the coefficients of t^n . The linear equation was used in cases where data of inferior accuracy were obtained or for data available for only short temperature ranges.

Source and quality of materials

Most of the metals were prepared by metallothermic reduction of the trifluorides with calcium metal as described by Spedding and

Daane¹. Europium and ytterbium were prepared by vacuum distillation of these metals from a heated mixture of the respective sesquioxides and lanthanum metal, as described by Spedding et al.⁹ and by Daane et al.¹⁶. Scandium, dysprosium, holmium, erbium, and thulium samples were vacuum distilled prior to use, with the exception of the erbium metal used for the electrical resistance measurements.

All of the metals studied were analyzed spectrographically for other rare earths and other common impurities. The neighboring rare earths, calcium, magnesium, and silicon were usually present in hundredths of a per cent. The main metallic impurity was tantalum, which in lutetium amounted to more than one per cent; in yttrium, about 0.4 per cent; in other metals cast in tantalum crucibles, less or equal to 0.1 per cent; and was not detected in the distilled metals. The tantalum was present in dendritic form, and could be recovered as an acid-insoluble residue of pure tantalum.

Chemical analyses revealed the presence of 50 to 250 ppm of carbon and 20 to 450 ppm nitrogen in most of these metals. Yttrium, praseodymium, and neodymium were also analyzed by vacuum fusion, which showed hydrogen to be present in the amounts 130, 10, and 40 ppm, and oxygen in 480, 800, and 1900 ppm, respectively.

RESULTS AND DISCUSSION

Diffraction patterns of the rare-earth metals generally yielded back-reflection lines and, hence supplied accurate data up to 400 to 700°C with the light rare earths and 650 to 1000°C with scandium,

yttrium, and the trivalent heavy rare earths. At approximately 600°C the metals began recrystallizing, giving rise to spotted diffraction lines, which could be easily distinguished from the full lines caused by surface impurities formed at higher temperatures by the reaction of the metals with residual gases. The patterns of the high temperature phases contained only front reflection lines which were also spotted, hence limiting the precision of the lattice constants to hundredths of an Angstrom unit. Although the spotted lines gave a reliable indication that a pattern of a high temperature structure was that of a metal, an additional assurance of this fact was gained by cooling the sample below the transformation point and obtaining the familiar pattern of the lower temperature form.

High temperature allotropy

Below 292°C lanthanum was found to exhibit a mixture of hcp (double c-axis) and fcc structures, the amounts of which varied sporadically for different samples. The presence of surface impurities seemed to stabilize the fcc structure below 293°C. The patterns of both structures were diffuse, indicating lattice defects. Above 293°C only the fcc phase was present, yielding sharp lines in the diffraction pattern. The transformation of the hcp (double c-axis) form to the fcc form was accompanied by a decrease of 0.5 per cent in volume. Above 868°C the latter form transformed into a bcc form for which the pertinent crystallographic data appear in Tables I and II. The atomic volumes of the three solid phases of lanthanum are shown in Fig. 1.

Cerium, praseodymium, and neodymium retained their room temperature structures up to the reported transformation temperatures of 730, 798, and 868°C, respectively, and above these temperatures they all exhibited a bcc structure. In one sample, surface impurities lowered the transformation temperature of neodymium to at least 850°C. The details concerning the high temperature structure of these metals are given in Tables I and II.

Europium was investigated crystallographically from room temperature up to 450°C and it was found to be bcc in this temperature range. Above this temperature extensive vaporization of the metal prevented further attempts to obtain diffraction patterns, even though the samples were kept in an atmosphere of argon. A similar difficulty was encountered in the case of samarium. Thermal analyses indicate europium to have no crystallographic transformations in the solid state.

Ytterbium, being about as volatile as europium, presented similar problems. It was found, however, that by sealing an ytterbium specimen in a silica capillary filled with air (about 2 mm³ of air, which is only about 4 per cent of the amount necessary to completely convert the sample to YbO and YbN) and heating it, a tight transparent coating was formed which prevented the metal from evaporating, and contributed an easily identified fcc pattern to the composite pattern. Thus it was possible to obtain X-ray patterns of the metal to above 800°C. These patterns indicated that the metal retained its fcc structure up to at least 732°C. Above this temperature ytterbium exhibited a bcc structure the details of which are given in Tables I and II. The presence of the

atmospheric impurities lowered the transformation temperature to as low as 720°C.

When one sample of ytterbium in the bcc form was cooled to below 700°C, instead of the expected fcc form, a hcp form appeared which persisted to about 260°C, where it transformed into the original fcc form. The hcp and the bcc structures reappeared when the sample was heated above 260°C and 720°C, respectively. The crystallographic data for the hcp structure are given in Table III. The atomic volumes of the three phases may be seen in Fig. 2.

In order to determine which of the two ytterbium structures appearing above 260°C was stable, a massive sample measuring 2.5 x 1.25 x 0.5 cm was studied using a high temperature diffractometer. The sample was heated under a vacuum and was thermally cycled at least two times above the fcc-bcc transformation temperature to duplicate the thermal history of the sample which exhibited the hcp structure. The massive sample failed to exhibit the hcp structure; the extensive vaporization of this sample which took place at high temperatures apparently minimized the formation of a surface film. Since, on the other hand, the wire specimen was in intimate contact with intentionally deposited surface impurities which could easily diffuse into the sample, it was concluded that the hcp structure was not a stable form of pure ytterbium, but was merely stabilized by these impurities.

Calcium exhibits an allotropic behavior similar to that of ytterbium. According to Smith et al.¹⁷, 99.96 per cent pure calcium

exists only in fcc and bcc forms, the transformation temperature being 464°C. However, calcium samples of inferior purity show the presence of a hcp phase and an additional complex phase, the hcp phase being stabilized by small amounts of hydrogen, as reported by Smith and Bernstein¹⁸. The lattice dimensions of hcp calcium and ytterbium are strikingly similar, the lattice constants of calcium being $a = 3.97 \text{ \AA}$ and $c = 6.49 \text{ \AA}$ with $c/a = 1.63$.

Gadolinium was investigated by the second high temperature X-ray technique described above and was found to retain its room temperature structure (hcp) up to at least 1200°C. Above 1262°C some evidence was obtained for the existence of a bcc structure. Of the first four possible reflections two were observed as plainly visible spots and two as rather faint spots. The approximate lattice constant obtained was $4.06 \text{ \AA}$, yielding a value of the atomic volume two per cent smaller than the extrapolated atomic volume of the hcp phase.

Lutetium was also found to be hcp to at least 1400°C. Vaporization of the sample in the camera above this temperature interfered with further X-ray investigation.

The remaining rare-earth metals including scandium and yttrium and excluding samarium were investigated up to about 1000°C. They were all found to retain their hcp room temperature structure up to at least the following maximum temperatures: Sc, 1009°C; Y, 957°C; Tb, 950°C; Dy, 970°C; Ho, 966°C; Er, 917°C; and Tm, 1004°C.

The changes in volume occurring during the crystalline transformations described above are small in comparison to the volume

change for the transformation in cerium from the normal fcc form to the collapsed fcc form, which has been attributed to an electronic transition between tri- and tetravalent cerium. Therefore, it appears that in the phase transformation described here the metals retain their original valence.

Detection of phase transformations by means of electrical resistance

Electrical resistance measurements were performed on gadolinium, terbium, dysprosium, holmium, erbium, and lutetium from 900°C to their melting points. To prevent the samples from evaporating at high temperatures they were kept under an atmosphere of helium. This provision was not sufficient for the more volatile dysprosium, holmium, and erbium metals, and these metals had to be enveloped in a 0.063-mm tantalum foil; in these samples, the sight hole drilled into the metal to simulate black-body conditions was lined with a 0.013-mm tantalum foil. The tantalum envelope conducted approximately 10 per cent of the total current through the sample, so that discontinuities in the electrical resistance of the rare earth metals were not masked out by tantalum.

The plots of electrical resistivity as a function of temperature for gadolinium, terbium, and lutetium are shown in Fig. 3, 4, and 5, respectively. Gadolinium and terbium exhibit similar discontinuities at $1262 \pm 14^\circ\text{C}$ and at $1316 \pm 10^\circ\text{C}$, respectively, both agreeing quite well with the previously reported transformation temperatures of 1263°C^2 and 1310°C^3 , respectively. The rather large ranges of

temperature in which the transformations occurred were apparently caused by temperature gradients in the sample arising from the samples' ends being fastened to water-cooled copper electrodes.

An evidence of a second possible transformation was observed in terbium, appearing as a hysteresis loop between 1115°C on heating and 995°C on cooling. The anomaly on heating occurred instantly, whereas on cooling, the apparent isothermal break was completed in about 20 minutes. Subsequent thermal cycling showed that all the anomalies were reproducible, with the exception that the discontinuity observed at 995°C took place at 1016°C and lasted about 15 minutes. It is apparent that the phase existing above 1115°C in terbium has a tendency to supercool.

In lutetium a hysteresis loop in the electrical resistivity was observed between 1407°C on heating and 1260°C on cooling. Neither of the anomalies seemed to be time dependent.

The absolute values of the electrical resistivity of dysprosium, holmium, and erbium could not be obtained conveniently because these samples were enveloped in tantalum. For dysprosium a discontinuous increase in resistivity occurred at $1392 \pm 8^{\circ}\text{C}$, being reproducible for several heating and cooling cycles. In holmium a slight discontinuous increase in resistivity occurred at $1442 \pm 8^{\circ}\text{C}$. The resistivity-temperature curve of erbium did not exhibit any anomalies indicative of crystalline transformations.

Thermal expansion of the rare-earth metals

The lattice constants of the rare-earth metals were determined at approximately 50°C intervals, except in the case of ytterbium where about thirty patterns were taken in the temperature range of 20 to 600°C, and in the case of the high temperature structures, where usually several patterns were taken in small temperature intervals. As mentioned above, the more accurate data were related to temperature by means of empirical equations. The coefficients A, B, C, and D [Eqs. (1) and (2)] are given in Table IV, where the following symbols were used: M, the metal studied; R, the physical property; S, the crystal structure; T, the maximum temperature in °C at which the equation applies; σ , the standard deviation of the experimental points from the calculated curves (in the same units as the given property); "a" and "c", the lattice constants (in Angstrom units); c/a, the axial ratio; v, the atomic volume (in cm³/mole); d, the density (in g/cm³). The lowest temperature at which these equations apply is 20°C, except in the case of gadolinium, where the lowest temperature is 88°C. The lattice constants "c" of gadolinium between 20 and 50°C exhibited an anomalous increase of about 0.002 Å over that at 88°C, this phenomenon probably being due to the onset of ferromagnetism at 16°C.

By the use of these equations the coefficients of expansion were obtained. A comparison of these results with the dilatometric data obtained by Barson et al.⁵ and by Born¹⁹ showed the best agreement at the mid-range temperature (approximately 400°C). The average deviation of the two sets of data was less than + 5 per cent at this

temperature, the maximum deviation being 13 per cent. At the two extreme temperatures the average deviations were about 20 per cent, although the values obtained in the present work were in most cases somewhat higher than the dilatometric data. When using the equations in Table III to derive the approximate coefficients of expansion, the reader should be aware of these deviations.

In Table V are given the values of the thermal expansion coefficients of the rare-earth metals at 400°C. For europium, to point out its rather unusual behavior, the data are given at 50°C and 300°C. Data for samarium were not obtained.

The large values of the thermal expansion coefficients of europium and ytterbium can be attributed to the fact that these metals are divalent, whereas the rest of the rare-earth metals are considered trivalent. An unusual effect in europium is that this property decreases in magnitude at a rapid rate with increasing temperature. A possible explanation of this anomalous behavior is that one of the 4f electrons is being gradually promoted to the conduction band, the extent of this promotion being governed by the Boltzmann distribution law. The increase of the number of electrons in the conduction band tends to enhance bonding and, hence, to shrink the lattice, thereby diminishing the expansion of the lattice caused by thermal vibrations. The promotion of the 4f electron into the conduction band is not unlikely, since the 4f band and the conduction band in europium metal must be close in energy, judging from the fact that the element exhibits di- and tri valence in its compounds, where trivalence is preferred.

Relationship between axial ratios and phase transformations

The axial ratios as a function of temperature for the hcp heavy rare-earth metals are shown in Fig. 6 where the heavy lines represent the experimental data fitted to empirical equations and the light lines represent the linear extrapolation of the axial ratios up to the melting points of these metals. Two short vertical lines on each curve signify points from which the extrapolations were made, and the points marked as "x" are the observed transformation temperatures. In the case of terbium, the second transformation is marked by "o".

An observation of interest is that the axial ratios tend to converge to a nearly constant value at the transformation temperatures. In the case of yttrium, gadolinium, terbium, holmium, and lutetium, the transformations were observed when the values of the axial ratios lay between 1.600 and 1.602. The value not falling in this range at the transformation temperature was 1.610 for dysprosium; however, this discrepancy might have been due to the excessively long temperature range over which the extrapolation was carried out. The second transformation in terbium is not considered a discrepancy, since the metal probably is not hcp above the first transformation.

Erbium, which did not give evidence of any crystalline transformation, failed to attain this limiting value of the axial ratio, thus giving support to the observation that a limiting axial ratio is required for a solid phase transformation to take place in these metals.

Data on the existence of crystalline transformations in scandium and thulium are lacking. However, if the axial ratio criterion holds,

one can expect to find transformations in these metals in the temperature ranges of 1009 to 1140°C and 1370 to 1480°C, respectively. (Since this manuscript was prepared, Beaudry²⁰ has observed a transformation in scandium at 1335°C).

Lanthanum, cerium, praseodymium, and neodymium also exhibit a limiting value of the axial ratio, the individual values of $1/2(c/a)$ being 1.619, 1.618, 1.619, and 1.621, respectively, as shown in Fig. 7. The value of the axial ratio of cerium is that reported by Mc Hargue et al.²¹.

The impurity stabilized hcp structure of ytterbium has a slightly greater than ideal axial ratio at lower temperatures. With increasing temperature this axial ratio approaches the ideal value.

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Table I. X-ray diffraction data for bcc La, Ce, Pr, Nd, and Yb

hkl	$\sin^2 \theta$					
	La	Ce	Pr		Nd	Yb
			K_α	K_β		
110	0.0661	0.0710	0.0705	0.0576	0.0703	0.0604
200	0.1325	0.1414	0.1403	0.1147	0.1406	0.1212
211	0.1976	0.2119	0.2098	0.1715	0.2104	0.1806
220	0.2637	0.2810	0.2794	0.2286	0.2802	0.2407
310	0.3282	0.3528	0.3482	-----	0.3490	0.3013
222	0.3945	0.4249	-----	-----	0.4194	0.3620
321	0.4604	0.4941	0.4888	-----	0.4888	0.4214
400		0.5642	-----	-----		-----
411, 330			-----	-----		0.5432
420			0.6963	0.5680		0.6012

Table II. Lattice constants and related data for bcc La, Ce, Pr, Nd, and Yb

Metal	Number of experimental points	Average tempera- ture °C	Lattice constant Å	Atomic volume cm ³ /mole	Density gm/cm ³	Change in volume on transforma- tion to bcc, per cent
La	3	887	4.26	23.2	5.98	+1.3±0.4
Ce	8	757	4.12	21.0	6.67	+0.1±0.7
Pr	6	821	4.13	21.2	6.64	+0.5±0.7
Nd	4	883	4.13	21.2	6.80	+0.1±0.6
Yb	5	774	4.44	26.5	6.54	-0.1±0.4 ^a

^a The change of volume from the fcc or the hcp structure to the bcc structure is the same.

Table III. X-ray diffraction data for HCP ytterbium

hkl	$\sin^2 \theta$ obs.	$\sin^2 \theta$ calc.	$\sin^2 \theta$ obs. - $\sin^2 \theta$ calc.
001	-----	0.0145	-----
100	0.0513	0.0517	-0.0004
002	0.0582	0.0579	+0.0003
101	0.0662	0.0662	-0.0000
102	0.1105	0.1096	+0.0009
003	-----	0.1302	-----
110	-----	0.1552	-----
103	0.1818	0.1820	-0.0002
200	-----	0.2069	-----
112	-----	0.2130	-----
201	0.2216	0.2213	+0.0003
004	0.2304	0.2316	-0.0012
202	0.2658	0.2648	+0.0010
104	0.2836	0.2833	+0.0003
203	0.3386	0.3371	+0.0015
005	-----	0.3618	-----
210	0.3628	0.3620	-0.0008
211	0.3771	0.3765	+0.0006
114	0.3848	0.3867	-0.0019
105	0.4147	0.4135	+0.0012
212	0.4199	0.4199	-0.0000
204	0.4363	0.4384	-0.0021
300	-----	0.4654	-----
213	0.4918	0.4923	-0.0005
006	0.5206	0.5210	-0.0004
302	-----	0.5242	-----
205	0.5710	0.5687	+0.0023
106	0.5710	0.5727	-0.0017
214	0.5925	0.5936	-0.0011
220	-----	0.6216	-----
310	0.6740	0.6723	+0.0017
116	-----	0.6761	-----
222	-----	0.6785	-----
311	0.6891	0.6868	+0.0023
304	-----	0.6970	-----
007	-----	0.7091	-----
215	0.7254	0.7238	+0.0016
215	0.7249	0.7238	+0.0011
206	0.7287	0.7274	+0.0013
206	0.7282	0.7274	+0.0008
312	-----	0.7302	-----

Table III. (Continued)

hkl	$\sin^2 \theta$ obs.	$\sin^2 \theta$ calc.	$\sin^2 \theta$ obs. - $\sin^2 \theta$ calc.
107	0.7629	0.7608	+0.0021
107	0.7628	0.7608	+0.0020
313	0.8038	0.8026	+0.0012
313	0.8046	0.8026	+0.0022
400	-----	0.8275	-----
401	-----	0.8419	-----
224	-----	0.8521	-----
216	0.8844	0.8830	+0.0014
216	0.8844	0.8830	+0.0014
402	-----	0.8854	-----
314	0.9047	0.9039	+0.0008
314	0.9048	0.9039	+0.0009
207	0.9169	0.9160	+0.0009
207	0.9164	0.9160	+0.0004
008	-----	0.9262	-----
403	-----	0.9577	-----
108	0.9786	0.9779	+0.0007
108	0.9777	0.9779	-0.0002

$$a = 3.911 \pm 0.003 \text{ \AA}$$

$$c/a = 1.637$$

$$c = 6.403 \pm 0.003 \text{ \AA}$$

$$\text{Atomic volume} = 25.54 \text{ cm}^3/\text{mole}$$

$$t = 268^\circ\text{C}$$

$$\text{Density} = 6.775 \text{ g/cm}^3$$

Change of volume on transformation from fcc to hcp = +0.7 per cent

Table IV. Coefficients of empirical equations relating the rare-earth metal properties determined by X-ray studies to temperature

M	R	S	T	σ	Equation coefficients			
					A	B $\times 10^5$	C $\times 10^8$	D $\times 10^{11}$
La	a	hcp	293	0.002	3.770	1.7	--	--
La	c	hcp	293	0.02	12.13	33.0	--	--
La	v	hcp	293	0.03	22.50	70.	--	--
La	d	hcp	293	0.008	6.174	-19.1	--	--
La	a	fcc	598	0.002	5.303	3.4	1.0	0.0
La	v	fcc	598	0.02	22.46	44.	13.	0.
La	d	fcc	598	0.005	6.186	-12.0	-3.8	0.8
Ce	a	fcc	619	0.0005	5.1604	3.28	-0.59	1.37
Ce	v	fcc	619	0.006	20.695	38.3	-3.2	13.4
Ce	d	fcc	619	0.001	6.771	-12.6	1.5	-4.5
Pr	a	hcp	449	0.0008	3.6702	1.66	--	--
Pr	c	hcp	449	0.004	11.828	13.3	--	--
Pr	v	hcp	449	0.008	20.778	42.4	--	--
Pr	d	hcp	449	0.003	6.782	-13.7	--	--
Nd	a	hcp	696	0.0008	3.6582	3.18	-3.96	4.92
Nd	c	hcp	696	0.004	11.802	16.6	-14.1	17.8
Nd	v	hcp	696	0.01	20.60	65	-70.	88.
Nd	d	hcp	696	0.003	7.004	-21.9	23.2	-28.7
Eu	a	bcc	352	0.001	4.578	17.4	-28.2	31.0
Eu	v	bcc	352	0.02	28.91	309.	-439.	457.
Eu	d	bcc	352	0.004	5.259	-56.6	84.5	-86.8
Gd	a	hcp	644	0.0009	3.631	4.26	-5.49	5.05
Gd	c	hcp	644	0.001	5.777	4.8	5.4	-3.5
Gd	c/a	hcp	644	0.0004	1.590	-0.27	3.02	-2.36
Gd	v	hcp	644	0.01	19.88	49.	3.	3.
Gd	d	hcp	644	0.005	7.895	-25.0	17.0	-17.5
Tb	a	hcp	852	0.0009	3.5990	3.37	-0.72	1.03
Tb	c	hcp	852	0.001	5.696	6.9	3.8	0.6
Tb	c/a	hcp	852	0.0006	1.5827	0.43	1.38	-0.31
Tb	v	hcp	852	0.009	19.245	59.2	5.5	13.7
Tb	d	hcp	852	0.004	8.272	-25.4	-1.8	-5.3
Dy	a	hcp	685	0.0004	3.5923	2.73	-3.53	3.69
Dy	c	hcp	685	0.0009	5.6545	8.74	1.43	3.34
Dy	c/a	hcp	685	0.0004	1.5741	1.24	1.93	-0.68
Dy	v	hcp	685	0.005	19.032	58.7	-33.0	51.1

Table IV. (Continued)

M	R	S	T	σ	Equation coefficients			
					A	B $\times 10^5$	C $\times 10^8$	D $\times 10^{11}$
Dy	d	hcp	685	0.002	8.536	-26.3	15.0	-22.1
Ho	a	hcp	708	0.0007	3.5761	2.64	-2.55	2.42
Ho	c	hcp	708	0.0008	5.6174	11.13	-3.78	4.71
Ho	c/a	hcp	708	0.0004	1.5708	1.95	0.05	0.25
Ho	v	hcp	708	0.008	18.742	61.6	-32.4	37.0
Ho	d	hcp	708	0.003	8.803	-30.4	18.7	-18.9
Er	a	hcp	917	0.0003	3.5590	2.95	-2.99	4.37
Er	c	hcp	917	0.001	5.592	11.9	-4.1	4.9
Er	c/a	hcp	917	0.0002	1.5711	2.06	0.13	-0.56
Er	v	hcp	917	0.006	18.473	70.2	-45.8	63.5
Er	d	hcp	917	0.003	9.051	-33.8	20.9	-28.3
Tm	a	hcp	853	0.0006	3.5372	3.19	-1.41	1.19
Tm	c	hcp	853	0.0007	5.5619	12.51	-3.89	3.27
Tm	c/a	hcp	853	0.0003	1.5723	2.15	-.55	0.43
Tm	v	hcp	853	0.007	18.151	73.7	-26.7	23.1
Tm	d	hcp	853	0.004	9.332	-37.4	14.0	-11.2
Yb	a	fcc	598	0.001	5.481	14.1	7.0	-6.2
Yb	v	fcc	598	0.02	24.80	191.	103.	-85.
Yb	d	fcc	598	0.004	6.977	-54.1	-23.0	23.4
Lu	a	hcp	956	0.0007	3.5050	.77	4.83	-2.17
Lu	c	hcp	956	0.0006	5.5486	11.50	-4.55	3.16
Lu	c/a	hcp	956	0.0002	1.5831	2.90	-3.44	1.86
Lu	v	hcp	956	0.008	17.779	45.0	34.1	-11.1
Lu	d	hcp	956	0.005	9.842	-24.7	-18.4	6.9
Sc	a	hcp	1009	0.0008	3.3080	2.46	0.78	0.01
Sc	c	hcp	1009	0.0009	5.2653	8.06	-0.52	0.79
Sc	c/a	hcp	1009	0.0003	1.5917	1.23	-0.51	0.22
Sc	v	hcp	1009	0.009	15.028	45.5	5.7	2.7
Sc	d	hcp	1009	0.002	-2.992	-9.1	-0.9	-0.4
Y	a	hcp	897	0.0007	3.6451	2.76	-1.92	2.16
Y	c	hcp	897	0.0009	5.7305	12.40	-3.13	2.92
Y	c/a	hcp	897	0.0002	1.5722	2.21	-0.09	-0.09
Y	v	hcp	897	0.01	19.86	73.	-32.	34.
Y	d	hcp	897	0.002	4.478	-16.8	8.1	-7.9

Table V. Thermal expansion coefficients of the rare-earth metals at 400°C

Metal	Structure	Thermal expansion coefficient, (°C) ⁻¹		
		a-axis	c-axis	average linear
La	fcc	---	----	7.9
Ce	fcc	---	----	6.7
Pr	hcp (2-c)	4.5	11.3	6.8
Nd	hcp (2-c)	6.5	11.7	8.3
Eu	bcc	---	----	32.2 ^a
Eu	bcc	---	----	19.2 ^b
Gd	hcp	6.3	13.0	8.9
Tb	hcp	9.1	17.9	12.1
Dy	hcp	4.7	20.3	9.9
Ho	hcp	4.9	18.4	9.5
Er	hcp	7.5	19.5	11.5
Tm	hcp	7.5	19.7	11.6
Yb	fcc	---	----	30.6
Lu	hcp	10.2	16.9	12.5
Sc	hcp	9.3	15.2	11.4
Y	hcp	6.2	19.7	10.8

^aValue for 50°C^bValue for 300°C

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

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FIGURE CAPTIONS

1. Atomic volume vs temperature plot for lanthanum, showing the three crystallographic forms.
2. Atomic volume vs temperature plot for ytterbium, showing hcp phase stabilized by impurities.
3. Electrical resistivity vs temperature plot for gadolinium.
4. Electrical resistivity vs temperature plot for terbium.
5. Electrical resistivity vs temperature plot for lutetium.
6. c/a axial ratios of normal hcp rare-earth metals vs temperature.
7. c/a axial ratios of the light rare earths vs temperature.