pressed.[11] It is

$$F_{N,1/4}(k)=\binom{2N}{k}\Big/4^N. \qquad (7)$$

Unfortunately, $F$ is not simple for $\gamma\neq\frac{1}{4}$, but one may check that Eq. (7) is very close to a normal distribution for $F>10^{-12}$. For other values of $\gamma$, one may therefore write with some confidence

$$F_{N,\gamma}(k)=\int_{-\infty}^{(N-k)/\sigma}\exp(-y^2/2)dy/(2\pi)^{\frac{1}{2}}, \qquad (8)$$

where

$$\sigma=(2\gamma N)^{\frac{1}{2}}. \qquad (9)$$

For small $F$, the expansion

$$F_{N,\gamma}(k)=\frac{\sigma}{(N-k)(2\pi)^{\frac{1}{2}}}\left[1-\left(\frac{\sigma}{N-k}\right)^2+\cdots\right]\times\exp\left[-\frac{(N-k)^2}{2\sigma^2}\right] \qquad (10)$$

is convenient.

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[11] E. N. Gilbert, Bell Telephone Laboratories (private communication).

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# Thermal Expansion of Rare Earth Metals*

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Thermal expansion measurements at temperatures ranging up to 900°C for polycrystalline samples of La, Ce, Pr, Nd, Gd, Tb, Dy, Er, and Yb metals are reported. La, Ce, Pr, and Nd exhibit plastic flow properties at temperatures well below their melting points. High-temperature phase transformations are reported for Pr, Nd, and Yb. The coefficient of expansion for Yb is found to be three times as large as the coefficients for the other metals reported. Negative coefficients are observed near the Curie points of Gd, Tb, and Dy.

## I. INTRODUCTION

In recent years rare earth metals have become available in good purity and in sufficient quantity to make possible fairly reliable measurements of their intrinsic properties. The present dilatometric study of several of these metals was undertaken in an attempt to detect possible unknown phase transitions in these elements and to clarify certain transitions previously indicated by studies of other physical properties.

Of particular interest were regions of the high-temperature thermal arrests found by Spedding and Daane[1] in their thermal analyses of lanthanum, cerium, praseodymium, neodymium, samarium, and ytterbium. Herrmann, Daane, and Spedding[2] showed that large changes in the electrical resistivities of several of these metals occurred at corresponding temperatures; they were unable to determine the crystal structures of the high-temperature forms, however, since x-ray diffraction patterns became extremely diffuse above these transitions.

In the cases of gadolinium, terbium, and dysprosium, magnetic transitions are known to occur not far below room temperature. An extension of dilatometric measurements into this region was thus also of interest and was included in the present study.

## II. SAMPLES TESTED

Dilatometric measurements were made on polycrystalline samples of lanthanum, cerium, praseodymium, neodymium, gadolinium, terbium, dysprosium, erbium, and ytterbium. The salts from which these metals were produced were separated and purified by an ion-exchange process described by Spedding and others.[3,4] The metals, with the exception of ytterbium, were prepared by a reduction of the rare-earth fluorides with calcium metal.[5,6] Excess calcium was removed by distillation in a subsequent vacuum casting. In the case of ytterbium, however, a reduction of the oxide with lanthanum metal was necessary.[7] The ytterbium metal, with its high vapor pressure, was then distilled off from the remaining lanthanum and lanthanum oxide.

The actual samples used were cast to the approximate size required, finished by turning to shape, and annealed by a preliminary heating in the apparatus. In all cases

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* Contribution No. 483. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

† Now at International Business Machines, Poughkeepsie, New York.

[1] F. H. Spedding and A. H. Daane, J. Metals **6**, 504 (1954).

[2] Herrmann, Daane, and Spedding, J. Metals (to be published).

[3] F. H. Spedding and others, J. Am. Chem. Soc. **73**, 4840 (1951).

[4] F. H. Spedding and others, Ind. Eng. Chem. **44**, 553 (1952).

[5] F. H. Spedding and A. H. Daane, J. Am. Chem. Soc. **74**, 2783 (1952).

[6] A. H. Daane and F. H. Spedding, J. Electrochem. Soc. **100**, 442 (1953).

[7] Daane, Dennison, and Spedding, J. Am. Chem. Soc. **75**, 2272 (1953).

TABLE I. Analysis of samples.

| Metal | Analysis |
|---|---|
| Lanthanum | C, 0.02%; N, 0.004%; Ca, 0.04%; Al, Be, Ce, Dy, Er, Cu, Fe, Gd, Ho, Lu, Nd, Pr, Se, Sm, Ta, Tb, Tm, Y, and Yb, not detected. |
| Cerium | C, 0.02%; N, 0.04%; La, 0.05%; Pr, 0.05%; Nd, 0.4%; Fe, 0.04%; Si, 0.03%; Ca, 0.04%; Ta and Be, not detected |
| Praseodymium | C, 0.03%; N, 0.05%; Ta, 0.03%; Si, 0.03%; Fe, 0.006%; Nd, 0.02%; Ce, 0.1%; La, 0.01%. |
| Neodymium | C, 0.02%; N, 0.06%; Pr, 0.08%; Sm, 0.06%; Ca, 0.01%; Si, 0.025%; Ta, 0.05%; Fe, 0.006%; La and Ce, not detected. |
| Gadolinium | Ta, 0.3%; Ca, 0.04%; Si, 0.01%; Fe, 0.01%; Mg, 0.01%. |
| Terbium | Dy, 0.05%; Gd, 0.05%; Ca, 0.04%; Eu, Fe, Ho, Si, and Ta, not detected. |
| Dysprosium | Ca, 0.2%; C, 0.01%; N, 0.003%; Tb, 0.1%; Ho, 0.05%; Er, 0.02%; Ta, 0.5%; Fe, 0.005%; Si, 0.02%; Gd, not detected. |
| Erbium | C, 0.01%; N, 0.01%; Ca, 0.07%; Dy, 0.005%; Fe, 0.03%; Ho, 0.01%; Si, 0.04%; Tm, 0.002%; Yb, 0.01%. |
| Ytterbium | C, 0.06%; N, 0.01%; Ca, 0.5%; Cu, trace; Er, 0.01%; Fe, 0.05%; Lu, 0.005%; Si, 0.05%; Ta, 0.03%; Tm, 0.01%. |

the final samples were in the form of rods about 5 cm in length and some 0.6 cm in diameter.

A spectrographic analysis and an analysis for carbon and nitrogen content were made on each of the samples used. The results of these analyses are listed in Table I.

The samples were not analyzed for oxygen because reliable analytical methods have not been perfected.

## III. EXPERIMENTAL METHOD

The dilatometer used in the present work consisted essentially of a "fused quartz tube and dial-indicator" dilatometer[8] in which increased sensitivity was obtained by replacing the dial-indicator with an optical interferometer. A diagram of the principal parts of the dilatometer is shown in Fig. 1.

The sample holder consisted of a fused-quartz tube with a sealed, conical bottom on which the sample rested. Resting in turn upon the sample was a fused-quartz rod which supported the lower optical flat. The upper optical flat was supported by three adjusting screws making it possible to obtain interference fringes when the flats were illuminated with monochromatic light. The mercury green line, $\lambda = 5461$ A, was employed for illumination. Since the expansion of fused quartz is well known[9] and is quite small compared to that of metals, it was possible to calculate the absolute expansion of the sample from the number of interference fringes passing the field of view.

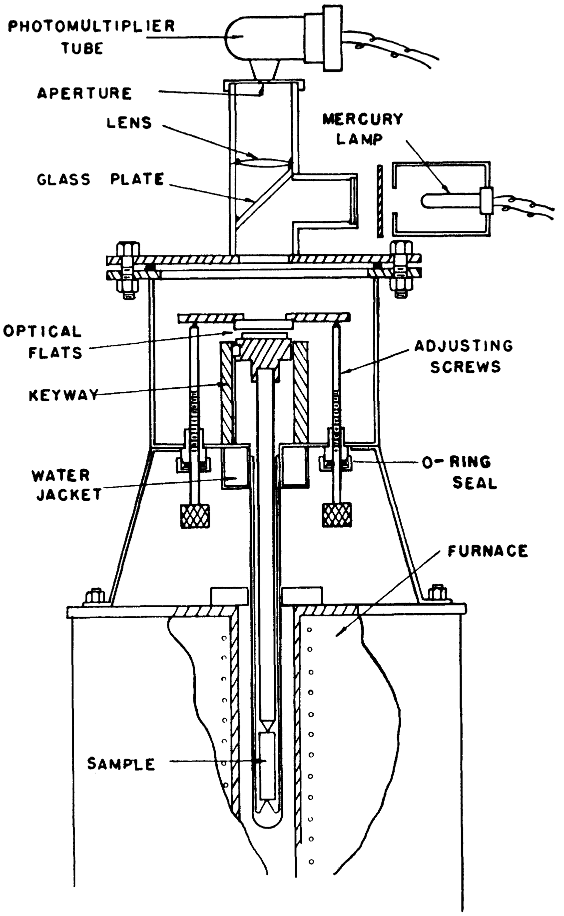

FIG. 1. Schematic diagram of the apparatus.

In order to record the number of fringes conveniently, a photomultiplier tube was employed in a manner similar to that of Work,[10] Peck and Obetz,[11] and others. As the fringes crossed the field of view, the photomultiplier tube "saw" through a small aperture a sinusoidal variation of light. The output of the tube was fed to one pen of a two-pen strip chart recorder and appeared as a sinusoidal curve whose peaks indicated the number of interference fringes passing by. The second pen of the recorder was reserved for temperature indication, continuously recording the emf of a calibrated chromel-alumel thermocouple placed near the sample in the furnace tube. The resulting strip chart thus gave a continuous record which was readily interpreted as the change in length of the sample with temperature.

Since the rare-earth samples measured are extremely reactive at elevated temperatures, and a few are rather volatile as well, certain precautions were necessary to protect both the samples and the apparatus.

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[8] See, for example, the review of dilatometry by P. Hidnert and W. Souder, National Bureau of Standards Circular 486 (U. S. Government Printing Office, Washington, D. C., 1950).

[9] J. B. Saunders, J. Research National Bureau of Standards 28, 51 (1942).

[10] R. N. Work, J. Research National Bureau of Standards 47, 80 (1951).

[11] E. R. Peck and S. W. Obetz, J. Opt. Soc. Am. 43, 505 (1953).

The samples were separated from the quartz sample holder by a thin sheet of tantalum foil wrapped around the samples and by very thin disks of tantalum foil at each end of the samples. Provision was also made to perform all high-temperature work with an atmosphere of purified helium gas within the sample holder.

In making a run the furnace voltage was automatically advanced 1 v at the beginning of each hour, which brought about a change of nearly 25° by the end of the hour. At this time the temperatures of the sample, the container, and the thermocouple were changing very slowly and were close to thermal equilibrium. Data were read from the charts at the end of each hour when these optimum conditions obtained.

Judging from trial runs with a pure copper sample and from the reproducibility of successive runs with any given metal, it is believed that the results reported below are accurate to about two or three percent in the values of the expansion coefficients given and to about 1% in the total change in length of each metal over the range covered.

## IV. RESULTS‡

Figure 2 shows the expansion of lanthanum and cerium metals as a function of temperature. The most distinctive feature in the curves for lanthanum was the transition at 310°C with considerable hysteresis. The transformation corresponds to the hexagonal to face-centered cubic transformation, the hexagonal form being stable at lower temperatures. In the warming direction the change was quite sharp and was centered at about 310°C. In the cooling direction the transition was sluggish and apparently incomplete, occurring largely between 200°C and 240°C. This is in rather good agreement with the results of Trombe and Foex[12] who reported a hysteresis loop between 150°C and 350°C, but the volume change of 0.19% found by those authors is considerably less than the 0.3% change indicated by the present work. It might be noted that Bridgman[13] detected an abrupt volume decrease of 0.26% under high pressures, a value close enough to that found here to suggest that the transformations are the same in both cases.

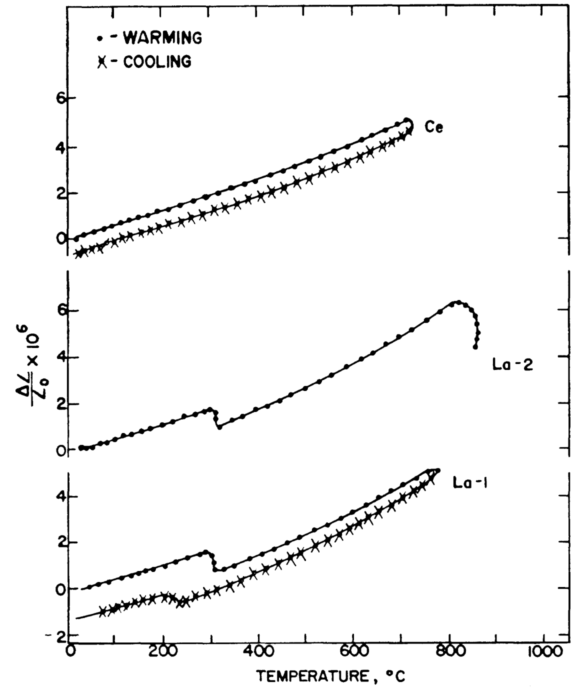

FIG. 2. Relative changes in length of La and Ce *vs* temperature.

The first lanthanum run, indicated lanthanum-1 on Fig. 2, showed signs of creep or softening at high temperatures, a permanent deformation remaining upon cooling. In a second determination, indicated as lanthanum-2 in Fig. 2, the measurements were extended to higher temperatures. The metal became so plastic at these higher temperatures that it would not support even the slight weight of the quartz rod and lower optical flat which rested upon it. Cerium metal exhibited a similar plastic flow, a permanent deformation being indicated in the expansion curve shown, and a more extreme effect being observed in subsequent runs not shown here. For both of these metals, this effect occurred some 50° or 75° below the reported melting point and made it impossible to take useful data through the region of the anticipated high-temperature transition.

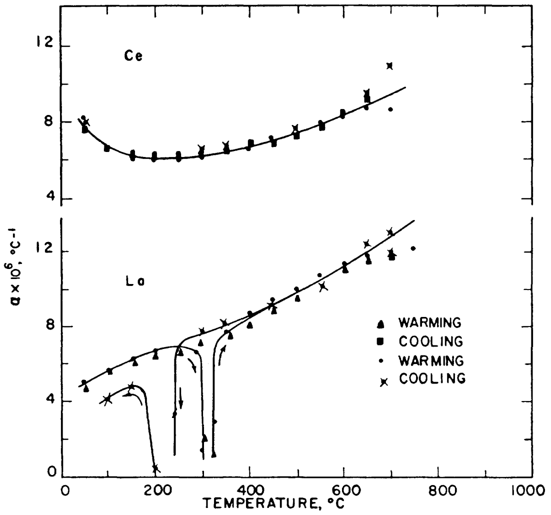

FIG. 3. Thermal expansion coefficients of La and Ce *vs* temperature.

Figure 3 shows the results of a graphical determination of coefficients of expansion for lanthanum and cerium. The negative coefficient in lanthanum is associated with the hexagonal-cubic transformation.

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‡ Errata: The ordinates in Figs. 2, 4, 6, and 10 should be abeled $\Delta L/L_0 \times 10^3$ instead of $\Delta L/L_0 \times 10^6$.

[12] F. Trombe and M. Foex, Compt. rend. **217**, 501 (1943).

[13] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 65 (1948).

The minimum in the coefficient of expansion of cerium is anomalous behavior for a metal and may be attributed to the same hexagonal to cubic transformation as in lanthanum.

The expansion data for praseodymium and neodymium are displayed graphically in Fig. 4. Again some high-temperature deformation occurred, and a permanent shortening of the sample was observed. In these two metals, however, it was possible to extend the measurements to include the high-temperature anomaly anticipated. The creep was so great and the volume change so small at the transition, that the effect was practically completely masked in the warming direction. Upon cooling, however, the creep added to the thermal contraction and a slight anomalous contraction was observed in both praseodymium and neodymium. These contractions are indicated by arrows in Fig. 4.

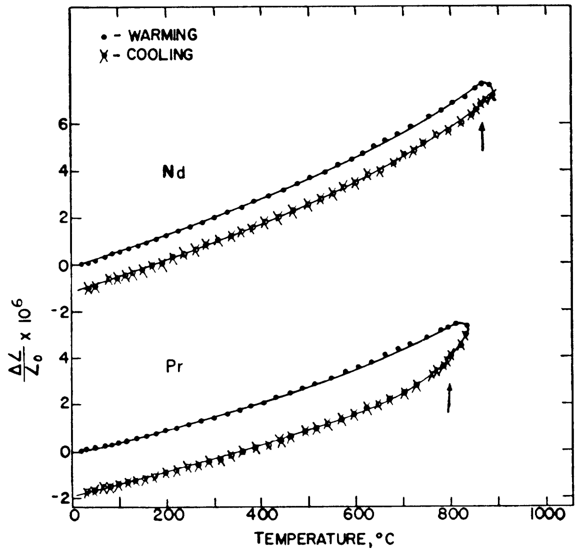

FIG. 4. Relative changes in length of Pr and Nd *vs* temperature.

The volume change at these transitions was found to be only about 0.1% in each case, an unexpectedly small amount in view of the 5 or 6% change in electrical resistivity found in each of these metals by Herrmann, Daane, and Spedding[2] and the "isothermal and sizeable" arrests in the thermal analyses reported by Spedding and Daane.[1] The temperature of the volume change as here determined was 790°–793°C for praseodymium, a value in excellent agreement with the 790°–795°C reported in the electrical resistivity measurements and 798°C as determined in the cooling curves. For neodymium the present work indicated a transition temperature of 865°–869°C which is once more in good agreement with 861°–863°C as found in the electrical measurements and 868°C as determined thermally.

The coefficients of thermal expansion of praseodymium and neodymium are shown in Fig. 5.

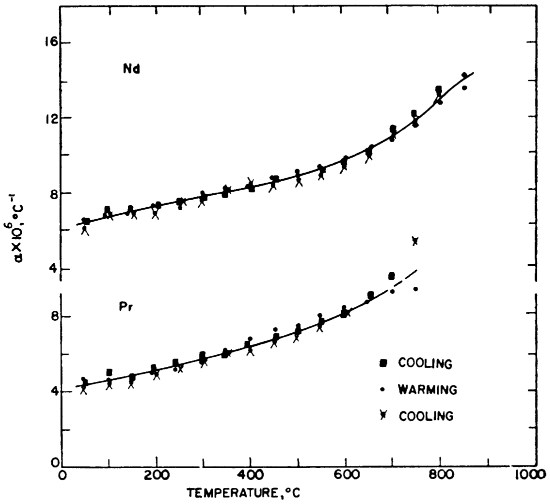

FIG. 5. Thermal expansion coefficients of Pr and Nd *vs* temperature.

Gadolinium is known to be ferromagnetic, its Curie point being just below room temperature at about 16°C.[14–16] Hence it was of interest to try to extend the range of the dilatometric study to lower temperatures to include this region. This was done by plugging the bottom of the tube furnace, cooling it with liquid nitrogen, and permitting furnace, sample holder, and sample to warm slowly by heat conduction and by heating with the furnace as needed. Temperature control was rather poor by this method in the very-low-temperature range, but a trial run with a sample of pure copper gave results in good agreement with values reported in the literature. It is felt that the results above −100°C are of comparable accuracy to the high-temperature measurements reported here and that the results down to −160°C are still at least semi-quantitatively correct. Terbium and dysprosium metals, with their magnetic transitions in the low-temperature region, were also run in this manner, and the results for these two metals as well as for gadolinium are shown in Fig. 6.

It is seen that the shapes of these curves are all similar in the region of the magnetic transformations, a sudden break in the expansion curve appearing at about the transformation temperature and a region below this temperature exhibiting a negative expansion coefficient; that is, the metals expand upon cooling for some distance below the transition.

From x-ray studies on gadolinium and dysprosium, Banister *et al.*[17] have shown that this expansion on cooling through the Curie point is associated with an abnormal increase in the $c_0$ parameter of the hexagonal

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[14] Urbain, Weiss, and Trombe, Compt. rend. **200**, 2132 (1935).

[15] W. Klemm and H. Z. Bommer, Z. anorg. u. allgem. Chem. **231**, 138 (1937).

[16] Elliott, Legvold, and Spedding, Phys. Rev. **91**, 28 (1953).

[17] Banister, Legvold, and Spedding, Phys. Rev. **94**, 1140 (1954).

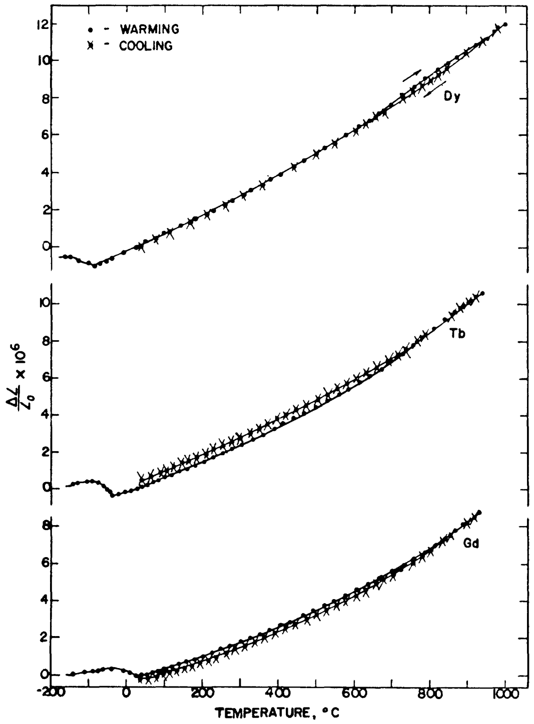

FIG. 6. Relative changes in length of Gd, Tb, and Dy *vs* temperature.

close-packed lattice while the $a_0$ parameter contracts normally.

In the case of gadolinium the sharp break in the expansion curve occurred at about 28°C, somewhat higher than the Curie point as determined magnetically. The coefficient of expansion shown in Fig. 7 was found to be negative from 28°C down to about $-40$°C. The data are in fairly good agreement in this region with those of Trombe and Foex,[18] who found a plateau, or region of zero expansion coefficient, for some distance below the Curie point. However, the slight transformation with hysteresis, found by those authors at 100° and 200°C, was not confirmed by the present investigation.

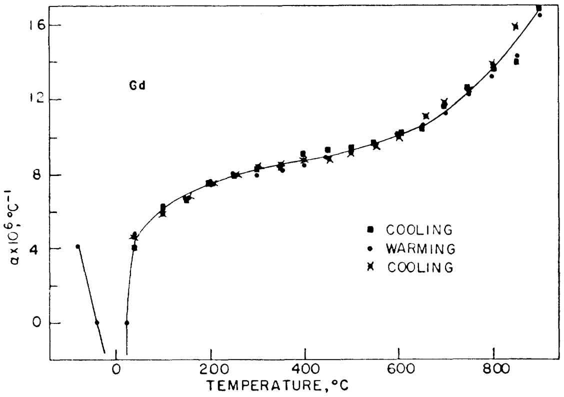

FIG. 7. Thermal expansion coefficient of Gd *vs* temperature.

For terbium metal, magnetic measurements by Thoburn *et al.*[19] indicated a ferromagnetic Curie point of about $-40$°C. The dilatometric work presented here seems, by analogy with gadolinium, to be in good agreement with this Curie point determination. The expansion with decreasing temperature was even more pronounced in terbium than in gadolinium. In the high-temperature range, terbium showed a slight anomaly between about 700° and 850°C. This effect is emphasized in the graph of the coefficient of expansion, Fig. 8. It was more pronounced in the warming runs than in cooling and was reproducible in successive runs. No crystalline transformation has previously been reported for terbium in this range; however, very few experiments have been performed on this metal.

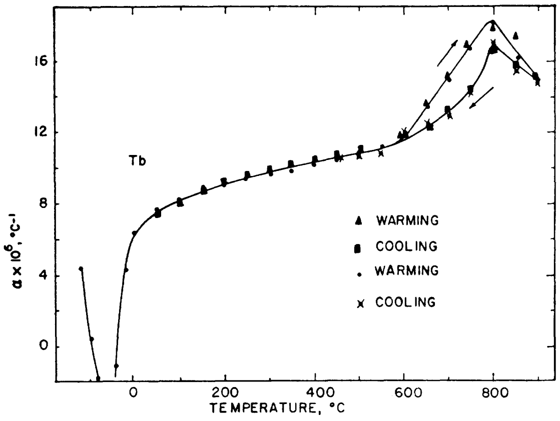

FIG. 8. Thermal expansion coefficient of Tb *vs* temperature.

The expansion of dysprosium metal, shown in Fig. 6, followed the pattern of gadolinium and terbium in the low temperature region, even though the magnetic transition in dysprosium is not a ferromagnetic Curie point but rather an antiferromagnetic Néel point.[20,21] The break in the expansion curve as found here at $-96$°C is in excellent agreement with the temperature of the transition as determined magnetically at $-97$°C. The coefficient of expansion in this region, shown in Fig. 9, was found to be negative from $-96$°C down to about $-150$°C, a region approximating that for which Trombe and Foex[22] found a zero expansion coefficient. In the high-temperature region of dysprosium, a slight hysteresis loop was observed between about 650°C and 900°C. The change in volume was only about 0.1 percent, and the effect was larger in the warming runs than in cooling. Again no transformation has been reported previously in this range.

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[18] F. Trombe and M. Foex, Compt. rend. **235**, 42 (1952).

[19] Thoburn, Rhodes, Legvold, and Spedding, Ames Laboratory, Iowa State College, 1956 (unpublished research).

[20] Elliott, Legvold, and Spedding, Phys. Rev. **94**, 1143 (1954).

[21] F. Trombe, Compt. rend. **221**, 19 (1945).

[22] F. Trombe and M. Foex, Compt. rend. **235**, 163 (1952).

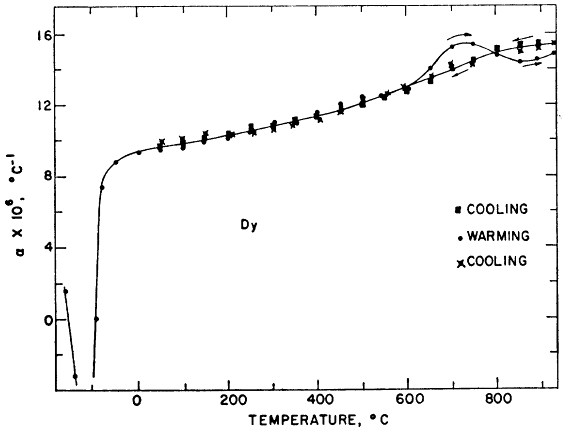

FIG. 9. Thermal expansion coefficient of Dy *vs* temperature.

The expansion of erbium, shown in Fig. 10, was smooth and reproducible, with no evidence of any transformations appearing in the interval covered. Also shown in Fig. 10 are the results for the divalent metal ytterbium. The high vapor pressure of this metal and the very puzzling loop at high temperatures make the data above 700°C somewhat doubtful, but below this temperature the results on two separate samples were in good agreement. There was evidence in both cooling runs of a phase transition at 730°C with a small decrease in volume on cooling.

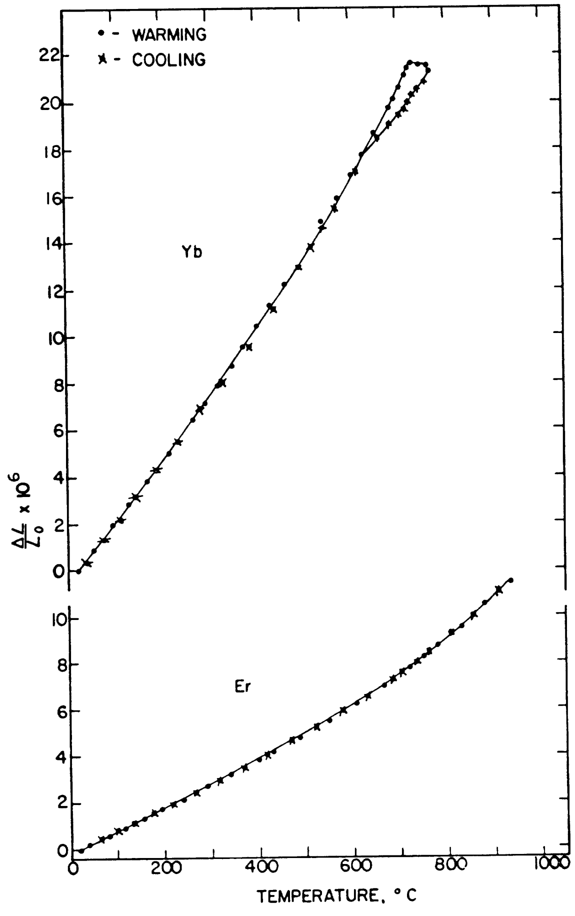

FIG. 10. Relative changes in length of Er and Yb *vs* temperature.

The coefficients of expansion for erbium and ytterbium are shown in Fig. 11 where it can be seen that the coefficient for ytterbium is about three times as large as are those for the other rare earth metals reported here. This is as might be expected, inasmuch as ytterbium is a divalent metal and the others are trivalent metals.

## V. DISCUSSION

The great amount of plastic deformation which appeared in several of the lower melting rare earths under a very slight load is unusual at temperatures relatively far from the melting point. The strong temperature dependence of this effect and the fact that it seemed to have a roughly time-independent rate of deformation suggest that the phenomenon is similar to ordinary quasi-viscous creep on an exaggerated scale.

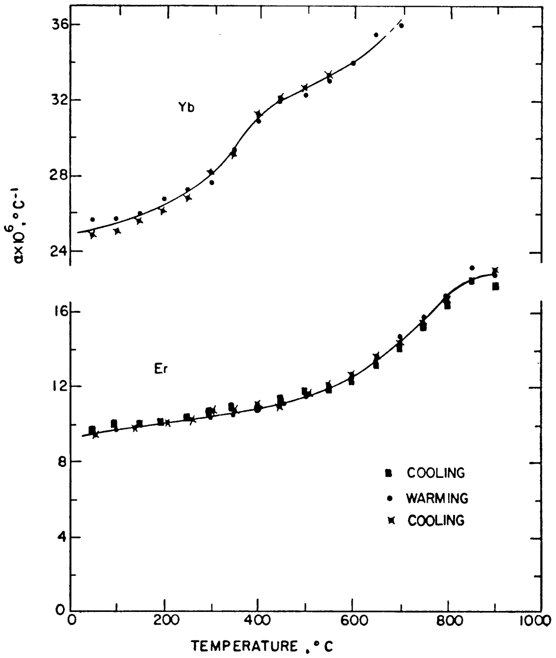

FIG. 11. Thermal expansion coefficients of Er and Yb.

A second type of anomaly noted in the rare-earth metals studied was, of course, the negative coefficient of expansion near the magnetic transitions. A discussion of the volume changes at the Curie point is given by Bozorth[23] in terms of Bethe's interaction curve. This curve indicates that if the ferromagnetic exchange energy is plotted as a function of $R/r$, the ratio of the atomic radius $R$ to the radius $r$ of the incomplete

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[23] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), p. 444.

TABLE II. Grüneisen constant.

| Metal | $\gamma_{\mathrm{Gr}}$ | $\gamma_{\mathrm{Sl}}$ |
|---|---|---|
| Lanthanum | 0.29 | 1.6 |
| Cerium | 0.25 | [−11.0] |
| Praseodymium | 0.27 | 0.8 |
| Neodymium | 0.42 | 1.0 |
| Gadolinium | 0.63 | 1.5 |
| Dysprosium | 0.74 | 1.2 |
| Erbium | 0.90 | 1.2 |

shell involved in the ferromagnetism, then, qualitatively at least, there will be a maximum in the interaction curve. For metals lying to the left of the maximum, a decrease of $R/r$, such as would be caused by compression, would decrease the exchange integral and hence lower the Curie point. A thermodynamic argument indicates that for such metals the thermal expansion coefficient would be greater above the Curie point than below it. Conversely, metals lying to the right of the maximum in Bethe's curve would have a greater coefficient in the ferromagnetic state than in the paramagnetic state.

Bozorth indicates that the ratio $R/r$ for gadolinium, where $r$ is the radius of the $4f$ shell, is about 3.1. This would place the metal far out to the right of the maximum in Bethe's curve and predict a greater expansion coefficient below the Curie point than above it. This is clearly not the case in the experimental data presented in the present paper. If one is to believe the arguments based on the rise of Bethe's curve, then gadolinium must lie to the left of the maximum; that is, the experimental value of $R/r$ turns out to be much less than the calculated value. Perhaps, since the $4f$ shell is buried rather deeply within the structure of the rare-earth atoms, the exchange is indirect and, therefore, in this calculation one should use for $r$ the radius of the $5d$ shell or some other outer shell.

Since many other properties of several of the rare earth metals have been measured previously, the calculation of the Grüneisen constant[24] for these metals was thought to be of interest. The Grüneisen constant is given by the relationship $\gamma = 3\alpha V/C_v k$, where $\alpha$ is the linear coefficient of expansion, $V$ is the volume, $C_v$ the specific heat, and $k$ the volume compressibility. Specific heats were obtained from the results of Parkinson, Simon, and Spedding[25] by a rather bold extrapolation to room temperature, and from the data of Skochdopole, Griffel, and Spedding.[26,27] Compressibilities and densities were taken from Bridgman's work.[28] The resulting Grüneisen constants for several of the rare earth metals are indicated as $\gamma_{\mathrm{Gr}}$ in Table II. They are considerably below the usual values of 1.5 to 2.5 for most metals.

As a further check, Bridgman's compressibility data were fitted to curves of the type $\Delta V/V_0 = -a_1 P + a_2 P^2$. This was done only approximately by using two widely separated points and finding the values of $a_1$ and $a_2$. Slater[29] has shown that the Grüneisen constant can be taken as $\gamma = (a_2/a_1^2) - \frac{2}{3}$ and that this second method of calculation is independent of the first. The resulting values are shown as $\gamma_{\mathrm{Sl}}$ in Table II. With the exception of cerium, whose compressibility is anomalous due to an oncoming transition, the values of $\gamma$ so determined are still slightly lower than the usual, but are in poor agreement with the values found by the first method of calculation. It is inconceivable that the experimental values are in error by so large an amount. The assumptions made in the calculation of the expressions for $\gamma_{\mathrm{Gr}}$ and $\gamma_{\mathrm{Sl}}$ are that the modes of vibration of the lattice all vary as the inverse $\gamma$ power of the volume and that the Poisson ratio is independent of volume changes. It may be that one or both of these assumptions is inappropriate for the rare earth metals.

## VI. ACKNOWLEDGMENTS

The authors are indebted to Dr. J. Powell for preparing the pure rare earth salts needed and to Mr. R. Valetta for producing the metal samples used. Mr. A. Read designed parts of the electronic recording apparatus, and Mr. D. Strandburg gave much valuable assistance in the treatment of data.

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[24] E. Grüneisen, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), Vol. 10, Part 1.

[25] Parkinson, Simon, and Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

[26] Skochdopole, Griffel, and Spedding, J. Chem. Phys. **23**, 2258 (1955).

[27] Griffel, Skochdopole, and Spedding, Phys. Rev. **93**, 657 (1954).

[28] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **83**, 1 (1954).

[29] J. C. Slater, Phys. Rev. **57**, 744 (1940).