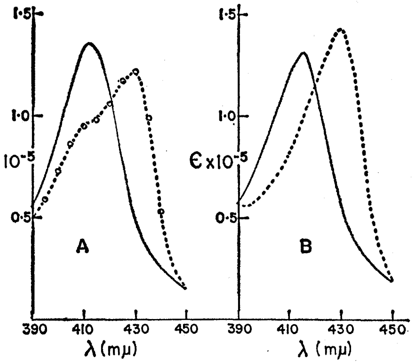

Fig. 1. Spectra after deoxygenation (dotted lines) and spectra after reoxygenation (solid lines). The points are calculated for a mixture of 20 percent methemoglobin and 80 percent deoxyhemoglobin. The initial composition of solution *A* was 0.0085 percent oxyhemoglobin in 0.04*M* phosphate buffer, *p*H 7.4. The initial composition of solution *B* was 0.0085 percent oxyhemoglobin, 1.9 × $10^{-4}M$ DPNH, 5 × $10^{-7}M$ methylene blue, 0.017 mg of methemoglobin reductase per milliliter, in 0.04*M* phosphate buffer, *p*H 7.4. A mixture of the last four components of solution *B* showed no significant absorption in the spectral region shown.

which is quantitatively reduced in the presence of methemoglobin reductase. Rapid deoxygenation in a high vacuum minimizes the formation of methemoglobin, although, even by this method, some methemoglobin is frequently formed.

In summary, therefore, the presence of methemoglobin in a sample of deoxyhemoglobin can be recognized from the spectrum in the Soret region by three features. These are (i) an increase in absorption between 410 and 415 mμ, causing a shoulder, (ii) a decrease in absorption at 430 mμ, and (iii) a shift to wavelengths shorter than 415 mμ in the absorption maximum of the oxyhemoglobin formed on reoxygenation. These spectral features are explained by the fact that the absorption maximum of methemoglobin at 405 mμ is separated by 25 mμ from that of deoxyhemoglobin but only by 10 mμ from that of oxyhemoglobin.

The absorption maxima and extinction coefficients of oxyhemoglobin, deoxyhemoglobin, and methemoglobin found in the course of this work are listed in Table 1. It is clear from these values that the maximum extinction coefficient of deoxyhemoglobin is higher than that of oxyhemoglobin. This relationship is reversed in some of the published spectra (*4, 5*) which is undoubtedly due to contamination with methemoglobin.

Oxyhemoglobin was prepared from normal human blood as described previously (*7*). Methemoglobin was prepared by oxidizing a 4 percent solution of oxyhemoglobin in 0.04*M* phosphate buffer, *p*H 6.8, with 1.2 equivalents of potassium ferricyanide for 1 hour at room temperature. The protein was then freed of ferri- and ferrocyanide by dialysis against three changes of phosphate buffer, *p*H 6.8, 0.2 ionic strength. This was followed by exhaustive dialysis against distilled water. Dialysis against phosphate buffer was effective in removing ferrocyanide which, in contrast to ferricyanide, is strongly bound by hemoglobin. The absence of ferrocyanide in the final solution was proved by a negative Prussian blue test in the filtrate after precipitation of the protein with trichloroacetic acid. The Prussian blue test was strongly positive if the dialysis against phosphate buffer was omitted.

Deoxyhemoglobin was prepared by passage of "prepurified nitrogen," further purified by the sulfate vanadous method (*8*) over the oxyhemoglobin solution in 0.04*M* phosphate buffer, *p*H 7.4, at room temperature for 2 hours. Transfer to cylindrical cuvettes of 1-cm light path was then carried out under nitrogen by an arrangement similar to that described (*9*). All spectra were recorded on a Cary model 14 spectrophotometer. Extinction coefficients are expressed per atom of iron and are based on spectrophotometric determination of hemoglobin concentration as methemoglobin cyanide by using the extinction coefficient of 1.15 × 10^4 at 540 mμ. The concentration of reagents used (see Fig. 1) reduced methemoglobin completely in 10 minutes (*10*).

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10. The methemoglobin reductase was purchased from Calbiochem as "Diaphorase," DPNH was purchased from the Sigma Chemical Co., and the methylene blue was Fisher reagent grade.
11. Work supported by grants from NSF and the National Heart Institute. One of us (R.B.) is a research career investigator of the National Heart Institute.

17 February 1964

Allotropy in Some Rare-Earth Metals at High Pressures

Abstract. *Allotropes of lanthanum, cerium, praseodymium, and neodymium have been observed at elevated pressures with an x-ray diffraction camera which incorporates a diamond-anvil, high-pressure cell. In each case a high-pressure modification was observed which has a face-centered cubic structure. At room temperature the unit cell dimensions* (a_0) *for the high-pressure face-centered cubic structures and approximate pressures at which they were determined are as follows: La, 5.17 Å (23 kb); Ce, 4.82 Å (15 kb); Pr, 4.88 Å (40 kb); and Nd, 4.80 Å (50 kb). The unit cell dimensions for the high-pressure forms of La, Pr, and Nd apparently have never been reported.*

In recent years a notable increase in activity in high-pressure research has taken place which is due in part to the successful development of new experimental techniques for conducting studies at high and ultrahigh pressures (*1*). With the advent of increased accessibility of high-pressure data, a renewed interest in electronic transitions such as the one observed in Ce metal (*2*) at elevated pressures has developed both from an experimental as well as theoretical viewpoint (*3*). Cerium metal transforms from a face-centered cubic structure to a "collapsed" face-centered cubic structure at 7.5 kb (1 kb ≈ 10^3 atm) (*2*). It is generally accepted that this transition involves the promotion of a 4*f* electron to the 5*d* band. Although a number of other metals such as Cs and Rb are suspected of having electronic transitions at elevated pressures (*3*), to date, it appears that only the electronic transition in Ce has been verified by x-ray diffraction studies (*2*).

The determination of the crystallographic nature of the phase transformations observed in La and Pr at elevated pressures by compression and electrical resistance measurements (*4–6*) would be highly desirable, because the electronic configurations of the free atoms of La, Pr, and Ce are very similar. To this end we have obtained x-ray data on high-pressure allotropes of La, Ce, Pr, and Nd with a high-pressure x-ray camera developed in this laboratory (*7*). The data reveal a high-pressure modification for each metal which has a face-centered cubic, close-packed structure (Cu type). The results also show that, except for the case of Ce, no electronic transitions occur in these metals in the pressure range at which they were studied. In this report, each metal is discussed separately in connection with previously reported data obtained at high pressures.

Evidence for a phase transition in lanthanum was first reported by Bridgman who showed from compression (*4, 5*) and electrical resistance (*4, 6*) measurements on hexagonal lanthanum that a transition occurs at approximately 23 kb. He reported a 0.26 percent volume decrease associated with this transition. The hexagonal structure of lanthanum has the stacking sequence ABAC, ABAC, and so forth, with a stacking fault occurring in every fourth layer, thus requiring a doubling of the *c* axis. In this stacking arrangement, the second, third, and fourth layers correspond to cubic closest-packing of atoms. This hexagonal structure (*A*3′) is found only in a few rare-earth metals, namely La, Ce, Pr, and Nd, and all but cerium exhibit the structure at 1 atm and 25°C (*8*). Hexagonal lanthanum (α-La) transforms to a face-centered cubic structure at about 310°C (β-La) (*9*). Because the reverse transition is sluggish, a determination of the unit-cell dimension (a_0) of this temperature-induced phase was permitted at a pressure of 1 atm and room temperature. The value reported for these conditions is 5.304 ± 0.006 Å (*10*). The volume decrease associated with the transition was reported as 0.3 percent (*9*), and is presumably the value for the transition at elevated temperatures. The volume decreases for the transitions induced by temperature and high pressure are very similar, as observed, and it is on this basis that Barson *et al.* (*9*) propose that the transitions are identical.

Our x-ray diffraction patterns of lanthanum under pressure reveal that the hexagonal structure (α-La) is transformed to a face-centered cubic (fcc) structure at moderately high pressures, presumably at about 23 kb, which is the value reported by Bridgman (*4*). Estimated pressures are given in our studies because experience with this anvil-type pressure cell has shown that calculated pressures are generally lower than the actual pressure on the specimen (*7, 11*). When transition pressures obtained from electrical resistance and compression data are available, as in the case of La, Ce, and Pr, we rely on the reported transition pressure for the metal and obtain x-ray diffraction patterns at calculated pressures slightly higher than these reported values. Our calculated pressures for each point are estimated to be reliable to within 20 percent (*7*). At room temperature the unit-cell dimension of the high-pressure fcc phase of La was determined as 5.17 Å at approximately 23 kb. From Bridgman's compression data on α-La (*4*), the specific volume at the reported transition pressure was determined, and from his data and the measured unit-cell dimension of the fcc phase at 23 kb, a volume decrease of 0.17 percent is calculated for the transition, which is in reasonable agreement with the reported value, 0.26 percent. The reverse transition $\mathrm{La_{fcc}} \rightarrow \mathrm{La_{hex}}$ is sluggish and the fcc phase does not revert to the hexagonal structure upon removal of pressure. The determination of the unit-cell dimension of the fcc phase at 1 atm gave a value of 5.29 Å, which agrees well with the value 5.304 Å obtained for the temperature-induced fcc phase. No discontinuities were observed in the x-ray diffraction patterns which would indicate an fcc-to-fcc type transition similar to that found in Ce, and in view of this result it appears that Barson's proposal is verified. As a consequence of the identity of the temperature- and high-pressure-induced fcc phases, it is of interest to note that the slope (dT/dP) of the equilibrium phase boundary between α- and β-La in the *P-T* diagram of La must be negative.

Table 1. Summary of results on the high-pressure modifications of La, Ce, Pr, and Nd.

Metal	Structure type	Unit-cell dimension (Å)	Pressure (kb)
La	fcc	5.17	23
Ce	fcc	4.82	15
Pr	fcc	4.88	40
Nd	fcc	4.80	50

The unit-cell dimension of the fcc La phase was also determined at an estimated pressure of 40 kb. The observed a_0 of 5.02 Å at this pressure indicates an overall compression ($-\Delta V/V$) of 14.5 percent between 1 atm and 40 kb. The compression of fcc La from 1 atm to 23 kb was determined as 6.7 percent by using a value of 5.17 Å for the a_0 at 23 kb. From these data it appears that the compressibility increases with increase in pressure, an observation similar to that reported by Bridgman for the compressibility of Ce metal prior to its electronic transition at 7.5 kb (*4*). We think that our pressure measurements are not in sufficient error to account for the observed compressibility relationship. On this basis it is entirely plausible that at some pressure above 40 kb another phase transformation perhaps analogous to that found in Ce may occur in La metal.

Our studies on elemental cerium corroborate previously reported results on the high-pressure form of Ce obtained by compression measurements (*7*) and by an x-ray diffraction technique (*2*). Cerium metal which normally exists in an fcc structure (γ-Ce) at one atmosphere pressure and 25°C (*12*) transforms to a "collapsed" fcc structure (α-Ce) at approximately 7.5 kb and 30°C (*2*). The large volume decrease (13 percent) associated with this transition (*8*) is attributed to the shift of a 4*f* electron to the valence or conduction band, presumably the 5*d* (*2*). The unit cell dimension of α-Ce was reported as 4.84 ± 0.03 Å at about 15 kb and 25°C (*2*). At approximately the same temperature and pressure 4.82 Å was obtained in our study.

Evidence of allotropy in Pr at elevated pressures was reported by Bridgman (*13*), who observed breaks in his curves for shear stress versus pressure. From the shape of these curves Bridgman noted that the transition in Pr is from a comparatively hard metal at low pressures to one of great softness at high pressures. Later, resistance measurements by Bridgman (*5*) yielded evidence of a phase transition in Pr in the 50 kb range.

Our x-ray studies at elevated pressures reveal that Pr exhibits the same type of allotropy that was observed in La. The transition from the hexagonal (*A*3′, La type) to fcc form is estimated to occur at about 40 kb. At this pressure and room temperature the unit-cell dimension of the fcc phase of Pr was determined as 4.88 Å.

Compression studies up to 40 kb (*4*) and electrical resistance measurements up to 100 kb (*5*) have been made on Nd. No evidence of allotropy was found in these studies. Our x-ray data reveal that Nd transforms from the hexagonal structure (*A3′*, La type) to an fcc structure at a pressure which is estimated to be in the 50 kb range. At this pressure and room temperature a unit-cell dimension of 4.80 Å was determined for the fcc phase.

Table 1 summarizes the results on the high-pressure fcc modifications of these rare-earth metals. The unit-cell dimensions (a_0) for these modifications are listed along with the corresponding approximate pressures at which the values were determined.

The similarities observed among the metals La, Ce, Pr, and Nd are of interest not only from the usual electronic aspect, but also from the viewpoint of allotropy as we have demonstrated in this report. It would be of interest to study the cubic close-packed structures of La, Pr, and Nd at higher pressures in an effort to detemine if Ce is the only metal in this group which undergoes an electronic transition. From the results of this work it appears that pressures considerably higher than those attainable with the present pressure cell would be required to carry out this study.

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Ferric Tourmaline from Mexico

Abstract. *Dark brown crystals, up to 10 mm long, occur in rhyolite at Mexquitic, San Luis Potosí, Mexico. They are short prismatic, showing* $\{11\bar{2}0\}$, $\{30\bar{3}0\}$, $\{10\bar{1}1\}$, $\{02\bar{2}1\}$, *with* c/a *0.4521, measured with a goniometer, and distinct* $\{11\bar{2}0\}$ *cleavage. With an unusual combination of cell dimensions, high density, high refractive indices, and extreme birefringence, this tourmaline falls outside the known elbaite-schorl and schorl-dravite series. A chemical analysis, recalculated on the basis of cell volume and density, gives close to the theoretical 150 atoms per cell, whether the iron is ferrous or ferric, but the physical properties indicate a ferric tourmaline.*

In the spring of 1962 specimens of brilliant dark-brown crystals on a rhyolite matrix were being sold by dealers in the western states as enstatite from San Luis Potosí, Mexico. The precise locality where this mineral was found (*1*), according to R. V. Gaines, is Mexquitic near San Luis Potosí City. The perfection of crystal form and the remarkable nature of the paragenesis (a magnesium-rich pyroxene is incompatible with the geochemistry of rhyolite, in which the ferromagnesian minerals normally have a high ratio of iron to magnesium) raised doubts concerning the validity of the identification of this mineral as enstatite. Its optical properties showed that it was not a pyroxene; its morphology and an x-ray powder photograph identified it as tourmaline. Because the optical properties and the density lay well outside the range of known tourmalines, the present investigation was undertaken.

Typical specimens show individual crystals up to 10 mm in length and 5 mm in thickness attached to the rhyolite and embedded in a clayey material. This material has a mean refractive index about 1.50 to 1.51, birefringence about 0.01, and an x-ray powder photograph shows a single halo at $d = 4.0$ to 4.5 Å; it is tentatively identified as allophane. Small crystals of sanidine are present in this clayey material.

The tourmaline crystals have short prismatic habit. The following forms have been identified and measured on the two-circle goniometer: $\{11\bar{2}0\}$, $\{30\bar{3}0\}$, $\{10\bar{1}1\}$, $\{02\bar{2}1\}$, leading to the axial ratio $(c/a)_{\text{gon}} = 0.4521$. The crystals are dark brown, almost black, with a bronze schiller; the streak is yellow-brown. The mineral has distinct prismatic cleavage in contrast to the very poor cleavage usually reported for tourmaline. It is optically negative; (indices of refraction) $\omega = 1.735$ (yellow-brown), $\epsilon = 1.655$ (very pale yellow), both ±0.003. The birefringence, 0.080, is extreme for a tourmaline; the maximum birefringence for tourmaline recorded by Deer, Howie, and Zussman (*2*, p. 306, anal. 1) is 0.035. The cell dimensions were obtained from single-crystal and diffractometer data. The diffractometer data were refined by least squares (*3*); $a = 15.873$, $c = 7.187$ Å, standard deviation 0.002 Å, giving $(c/a)_{\text{x-rays}} = 0.4528$. This combination of cell dimensions is also unusual: on a graph of c plotted against a (Fig. 1) this tourmaline falls outside the solid-solution series elbaite-schorl and schorl-dravite.

Density (D) determinations showed many of the crystals to contain small quartz inclusions. The pure mineral has $D = 3.31 \pm 0.01$ g/cm³, a value which is outside the range for known tourmalines, 3.03 − 3.25 (*2*, p. 300).

The chemical analysis in percentage by weight, made by H. B. Wiik (*4*), is as follows: SiO_2, 33.19; TiO_2, 0.46; Al_2O_3, 30.87; FeO, 18.6; MnO, 0.20; MgO, 0.17; CaO, 0.36; Na_2O, 3.40; K_2O, 0.08; H_2O^+, 0.42; H_2O^-, 0.02; B_2O_3, 11.5; F, 1.77; total, 101.04, less O for F, 0.72, 100.32. Wiik remarks that although the iron is reported as

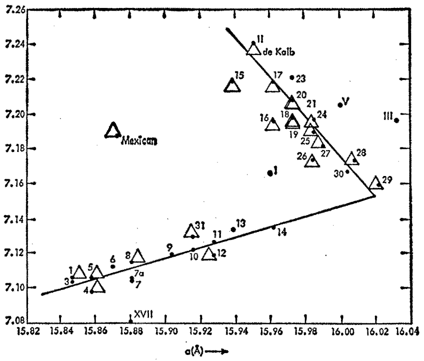

Fig. 1. Cell dimensions of tourmalines. The literature data and reference numbers are from Epprecht (*10*). The composition, when known, is shown by the position of the point inside the triangle: elbaite (lower left), schorl (lower right), dravite (upper corner).