# Structural and Electronic Transitions in Ytterbium Metal to 202 GPa

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Ytterbium (Yb), a member of the rare earth group metals with a filled $f$ shell and a divalent electronic character, has been studied under static high pressures in a diamond anvil cell to 202 GPa. We report a new transformation from a face-centered-cubic structure to a hexagonal phase with 3 atoms/cell (space group $P3_121$ referred to as $hP3$) at $98 \pm 5$ GPa. This $hP3$ phase is similar to that observed in trivalent neodymium and samarium at pressures near 40 GPa. Our high pressure study thus clearly demonstrates that Yb is no longer an "irregular" member of the rare earth metals, and divalent to trivalent electronic transition is completed at megabar pressures. [S0031-9007(99)08553-1]

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Ytterbium (Yb) and europium (Eu) metals are anomalous in their electronic structure among rare earth metals, because of their divalent character as opposed to the trivalent character of most rare earth metals. In fact, because of their divalent electronic structure, Yb and Eu are often compared to divalent alkaline earth metals like calcium, strontium, and barium. The divalent character manifests itself in a higher atomic volume, and Yb has an ambient volume which is 41% larger than the neighboring element lutetium. This has led to extensive theoretical and experimental effort to investigate valence transitions in materials based on these metals by application of external high pressures and/or low temperatures. In particular, early work on Yb metal demonstrated that a gradual valence transition with increasing pressure from $4f^{14}(spd)^2$ to $4f^{13}(spd)^3$ or from $2^+$ to $3^+$ is observed at high pressures to 30 GPa [1–3]. The change in valence of Yb with increasing pressure is now well established; however, its similarity to the trivalent rare earth metals continues to be a matter of considerable debate (a summary of earlier work is given in Ref. [2]). The regular trivalent rare earth metals show hcp → Sm-type → double hcp → fcc → distorted fcc with increasing pressures and decreasing atomic number [4,5]. In a recent study on Yb to 90 GPa [5], it was found that the structural sequence of this metal with pressure is highly irregular and no similarities with other rare earth metals could be discerned. Apart from the expected divalent to trivalent electronic transition in Yb, there are additional predictions of further electronic transition in Yb near 300 GPa [6], which may increase the occupancy of the $f$ shell. The multimegabar pressure capability of the diamond anvil cell devices now allows us to explore this region directly.

The present study is motivated by establishing a clear connection between the high pressure behavior of Yb (a pressure induced trivalent metal) with the other members of the trivalent rare earth series. In particular, we are interested in phase transformation at ultra high pressures near 100 GPa in Yb to identify known phases of other regular trivalent rare earth metals.

Yb was studied in a diamond anvil cell device at room temperature employing copper as an internal pressure standard. Yb foil of 99.9% purity along with copper powder was loaded into a gasket hole of 25 $\mu$m in diameter. The gasket was located on top of a diamond central flat of 65 $\mu$m in diameter with a bevel angle of 7° and culet size of 350 $\mu$m in diameter. Oxidation is a concern in these samples; however, the x-ray diffraction pattern of our sample after sample loading showed a clean face-centered-cubic spectrum and diffraction lines of YbO were absent. The energy dispersive x-ray diffraction spectrum was recorded both on compression as well as during decompression at the X-17C station at NSLS, Brookhaven National Laboratory. Microcollimated x-ray beam of 11 $\mu$m × 6 $\mu$m was employed for energy dispersive x-ray diffraction studies on a Yb sample and a copper marker to 202 GPa.

The following sequence of phase transformation is already well established in Yb to 90 GPa [5]:

$$\mathrm{fcc(I)} \rightarrow \mathrm{bcc} \rightarrow \mathrm{hcp} \rightarrow \mathrm{fcc(II)}\,.$$

The fcc(I) → bcc transition occurs at 4 GPa, the bcc → hcp transition occurs at 26 GPa, and the hcp → fcc(II) transition occurs at 53 GPa. The two fcc phases are labeled as I and II to discriminate the pressure range over which they occur. Otherwise, crystallographically speaking they are the same phase. The fcc(II) phase has been found to be stable to 90 GPa. Our studies in the pressure range below 90 GPa are consistent with earlier published results [1–3,5]. In our experiment when the pressure was increased to 98 GPa, we noticed four new reflections appeared in the x-ray spectra, indicative of a phase transformation. Figure 1 shows the energy dispersive spectrum of Yb at 82 GPa in the fcc phase, at 154 GPa in the new phase, and at the highest pressure of 202 GPa. The pressure was slowly decreased from the highest pressure of 202 GPa, and the fcc phase was recovered during decompression below 98 GPa. The new phase can be indexed very well with a hexagonal unit cell with 3 atoms/cell [7]. The comparison of the

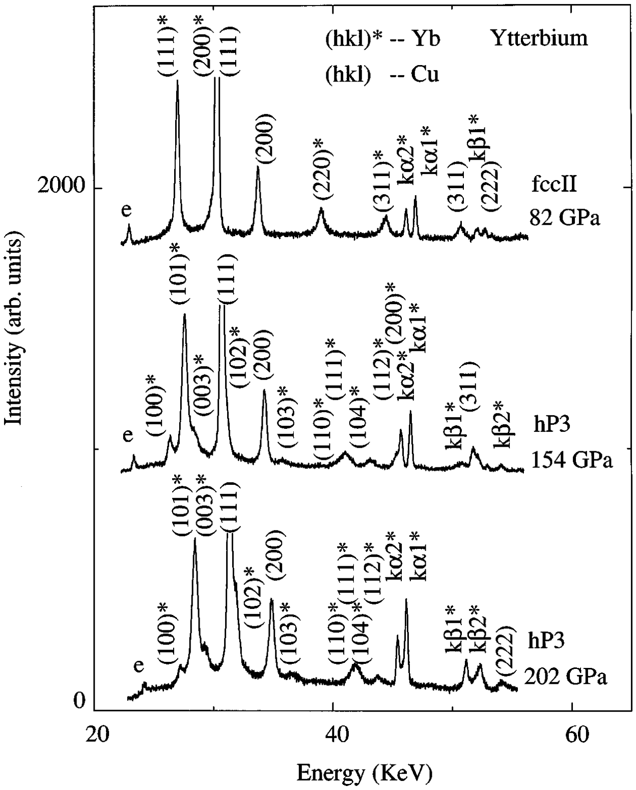

FIG. 1. Energy dispersive x-ray diffraction spectrum of the ytterbium sample mixed with a copper pressure standard at various pressures: at 82 GPa in the fcc(II) phase before transformation, at 154 GPa in the $hP3$ phase, and at the highest pressure of 202 GPa before decompression. The product of energy and interplanar spacing $Ed = 56.951$ keV Å; peak marked $e$ is an escape peak; Yb sample fluorescence peaks $k\alpha$ and $k\beta$ are also indicated.

TABLE I. The comparison of the observed and calculated interplanar spacings $d_{hkl}$ and the observed and calculated intensities for the x-ray diffraction data for ytterbium at 154 GPa. The calculated $d_{hkl}$ are based on $a = 2.588$ Å and $c = 6.092$ Å for the $hP3$ phase. The calculated intensities are based on the $u$ parameter equal to 0.47.

| $hkl$ | $d_{\text{obs}}$ (Å) | $d_{\text{calc}}$ (Å) | $I_{\text{obs}}$ | $I_{\text{calc}}$ |
|---|---|---|---|---|
| 100 | 2.241 | 2.241 | 11 | 11 |
| 101 | 2.103 | 2.103 | 100 | 100 |
| 003 | 2.033 | 2.031 | 26 | 26 |
| 103 | 1.499 | 1.505 | 2 | 5 |
| 110 | 1.295 | 1.294 | 5 | 4 |
| 111 | 1.266 | 1.266 | 8 | 9 |
| 104 | 1.258 | 1.260 | 10 | 12 |
| 112 | 1.189 | 1.191 | 7 | 7 |

observed and calculated interplanar spacings and intensities is given in Table I. The calculated intensities are based on space group $P3_121$ referred to as $hP3$ structure (Table I). It should be noted that the $hP3$ structure can be thought of as being derived from the fcc structure, where atoms are displaced in the (111) plane of the fcc lattice. In the case of the axial ratio $c/a$ of 2.45 ($\sqrt{6}$) and the $u$ parameter of $\frac{1}{3}$, the $hP3$ structure reduces to the fcc phase. The measured lattice parameters for the $hP3$ phase at 202 GPa are $a = 2.522$ Å, $c = 5.908$ Å, and $c/a = 2.343$. The axial ratio of $hP3$ is plotted in Fig. 2 to illustrate the deviation of this structure from the fcc phase. There is a definite trend of the axial ratio deviating more from the fcc phase as pressure increases. In fact, $c/a$ of the $hP3$ phase can be fitted by the following linear equation:

$$c/a = 2.399 - (2.9 \times 10^{-4})P,$$
$$(202 \geq P \geq 98\ \text{GPa}).$$

The structural parameter $u$ can be determined from the measured intensities and is found to be between 0.42 and 0.50 over the entire pressure range between 98 and 202 GPa. It is to be noted that the average value of $u = 0.46$ is far removed from the $\frac{1}{3}$ value for an fcc phase and hence represents substantial distortion in the (111) planes of the fcc phase. Also, the observed values for $c/a$ and $u$ parameters for Yb are very similar to $c/a = 2.35$, and $u = 0.45$ observed for the $hP3$ phase of Sm [7].

In Fig. 3 we show the measured equation of state data of Yb to 202 GPa at room temperature. Yb shows a maximum compression of 73.7% at 202 GPa (measured $V/V_0 = 0.263$). We have also included in Fig. 3 low pressure data to 70 GPa from Refs. [2,3] and [5]. The measured equation of state data can be fitted to the

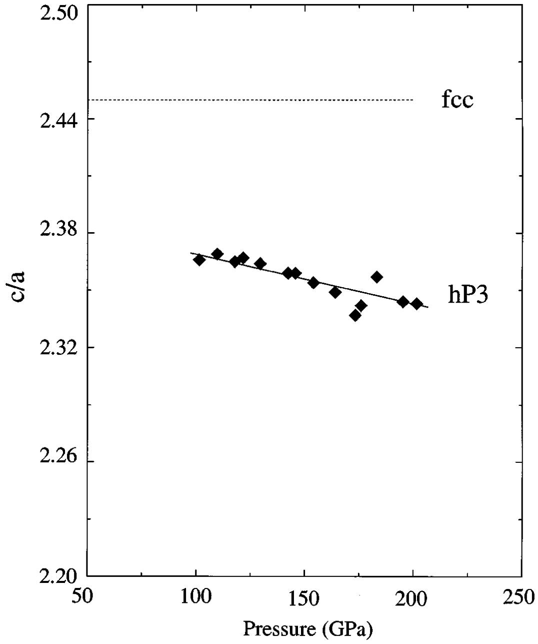

FIG. 2. The measured value of the axial ratio for the $hP3$ phase of Yb in the pressure range of 100–200 GPa. The dashed line is the ideal fcc value of $\sqrt{6}$, and the solid line is the fit described in the text.

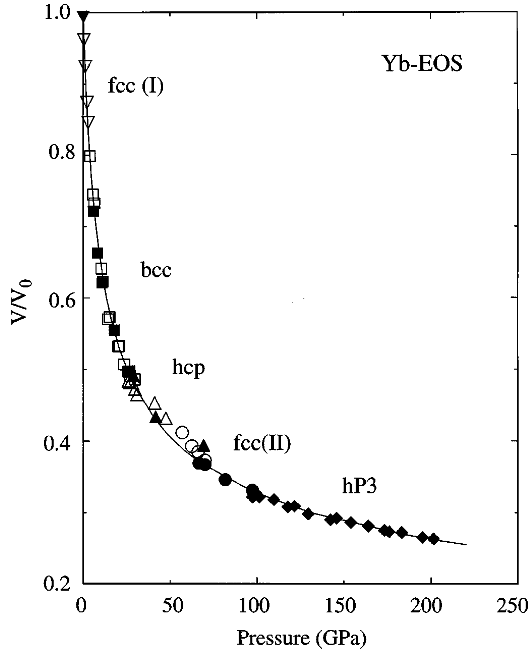

FIG. 3. The measured equation of state of ytterbium to 202 GPa at room temperature. Five stable phases are indicated by various symbols. The open symbols represent data to 70 GPa from Refs. [2,3] and [5], respectively. The solid symbols represent data from the present series of experiments to 202 GPa. The solid curve is the global fit to the modified universal equation of state described in the text.

modified universal equation of state [8,9],

$$\ln H = \ln B_0 + \eta(1 - x) + \beta(1 - x)^2,$$

$$H = Px^2/[3(1 - x)] \quad \text{and} \quad x^3 = V/V_0 .$$

The copper shock equation of state [10] can be fitted to $B_0 = 143.7$ GPa, $\eta = 4.356$, and $\beta = 13.77$. We do a global fit to all the observed phases of Yb and ignore the small volume discontinuities of 1%–3% at the phase boundaries. The fitted parameters for Yb are $B_0 = 14.6$ GPa, $\eta = 0.307$, and $\beta = 11.92$ for the entire pressure range to 202 GPa. $\eta = (\frac{3}{2})(B_0' - 1)$, where $B_0'$ is the pressure derivative of the bulk modulus. The low value of $B_0' = 1.205$ for Yb is indicative of the unusual compressibility associated with the gradual divalent to trivalent electronic transition at high pressures. In addition, in the trivalent phase, transfer of electrons from an extended $s$ band to a more compact $d$ band under pressure usually results in a low value of pressure derivative of bulk modulus $B_0'$ [11].

The issue of valence change at high pressures and its effect on the compressibility warrants further discussion. It is a general trend in divalent $4f$ materials that the application of pressures will cause a configurational crossover from an initial $4f^n$ configuration to a $4f^{n-1}$ configuration at high pressures [12,13]. It is clear from the experimental data presented in Fig. 3 that the $4f^{14} \rightarrow 4f^{13}$ transition in Yb proceeds in a rather continuous manner, and there are no large volume discontinuities of magnitude greater than 3%. The continuous valence transition from $2^+$ to $3^+$ is also documented in the monochalcogenides of Yb [14]. To illustrate the unusually high compressibility of Yb, we compare its compression with the recently published data on the neighboring trivalent element lutetium [15]. The measured compression for Yb at 202 GPa is $V/V_0 = 0.26$, and the extrapolated value for lutetium at the same pressure is $V/V_0 = 0.37$. Therefore, it is clear that Yb is much more compressible than the neighboring rare earth metals. It is likely that Yb ions undergo rapid interconfiguration fluctuation ($4f^{14} \rightarrow 4f^{13}$) in the pressure range below 100 GPa, and the unusually high compressibility is related to these fluctuations [12,13].

There has been a considerable debate about the high pressure behavior of Yb from the standpoint of irregularity in crystal structures observed under high pressures. This was, in part, due to the fact that the rare earth crystal structure sequence hcp → Sm-type → double hcp → fcc → distorted fcc was never observed in Yb under high pressure [5]. Therefore, it was argued that Yb behavior is “irregular” compared to other members of the rare earth series. Our results clearly demonstrate that at megabar pressures (>98 GPa), Yb is stable in the $hP3$ structure typical of light rare earth metals like samarium (Sm) and neodymium (Nd). It is observed in the light rare earth metals like Sm and Nd that the “distorted” fcc structure transforms to the $hP3$ phase above 40 GPa [7]. It is useful to note that the $hP3$ phase has four short bonds characteristic of so many $f$-bonded materials so we cannot rule out the possibility of significant $spd$ and $f$ hybridization at megabar pressures. Theoretical first principle calculations on the $hP3$ phase of Yb at megabar pressures are needed to ascertain $f$ band width and the occupancies of various bands.

We offer the following conclusions:

(1) Ytterbium metal shows the following sequence of phase transformation with increasing pressure:

$$\text{fcc(I)} \rightarrow \text{bcc} \rightarrow \text{hcp} \rightarrow \text{fcc(II)} \rightarrow hP3 ,$$

with the fcc(II) → $hP3$ transition at 98 GPa. The $hP3$ phase of Yb has a wide range of stability between 98 and 202 GPa.

(2) Our results show that the gradual divalent to trivalent electronic transition in Yb is completed at megabar pressure. Yb thus becomes a member of the regular trivalent rare earth series and is isostructural with trivalent samarium and neodymium under high pressures.

(3) Yb shows an unusually high compression of 74% at 202 GPa ($V/V_0 = 0.26$), and we attribute this to interconfiguration valence fluctuations ($4f^{14} \rightarrow 4f^{13}$) and $s \rightarrow d$ electronic rearrangements in the compressed state.

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[1] K. Syassen, G. Wortmann, J. Feldhaus, K. H. Frank, and G. Kaindl, Phys. Rev. B **26**, 4745 (1982).
[2] K. Takemura and K. Syassen, J. Phys. F **15**, 543 (1985), and references therein.
[3] W. A. Grosshans and W. B. Holzapfel, J. Magn. Magn. Mater. **47 & 48**, 295 (1985).
[4] A. Jayaraman, Phys. Rev. **135**, A1056 (1964).
[5] Y. C. Zhao, F. Porsch, and W. B. Holzapfel, Phys. Rev. B **49**, 815 (1994).
[6] J. F. Herbst and J. W. Wilkins, Phys. Rev. B **29**, 5992 (1984).
[7] Y. C. Zhao, F. Porsch, and W. B. Holzapfel, Phys. Rev. B **50**, 6603 (1994).
[8] P. Vinet, J. Ferrante, J. H. Rose, and J. R. Smith, J. Geophys. Res. **92**, 9319 (1987).
[9] S. K. Sikka, Phys. Rev. B **38**, 8463 (1988).
[10] R. G. McQueen, S. P. Marsh, J. W. Taylor, J. M. Fritz, and W. J. Carter, in *High Velocity Impact Phenomena,* edited by R. Kinslow (Academic, New York, 1970), Chap. VII.
[11] Y. K. Vohra, S. K. Sikka, and W. B. Holzapfel, J. Phys. F **13**, L107 (1983).
[12] L. L. Hirst, J. Phys. Chem. Solids **35**, 1285 (1974).
[13] J. M. Robinson, Phys. Rep. **51**, 1 (1979).
[14] A. Werner, H. D. Hochheimer, A. Jayaraman, and J. M. Leger, Solid State Commun. **38**, 325 (1981).
[15] G. N. Chesnut and Y. K. Vohra, Phys. Rev. B **57**, 10 221 (1998).