The pressure-volume relation of ytterbium up to 9 GPa

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Abstract. The pressure-volume relation of ytterbium has been determined up to 9 GPa using tungsten carbide opposed anvil high pressure x-ray camera. The fcc phase of ytterbium is observed between one atmosphere and 4 GPa and the bcc phase above 3·5 GPa. The bcc phase can be metastably retained down to 1 GPa by gradually decreasing the pressure from a region where only bcc phase alone is observed. The bulk modulus, B_0, at zero pressure and the pressure derivative of the bulk modulus, B_0', are determined by fitting Murnaghan equation to the pressure-volume data. The following values were obtained: $B_0 = 16·3$ GPa and $B_0' = 3·6$ for the fcc phase, and $B_0 = 14·7$ GPa and $B_0' = 1·5$ for the bcc phase. Based on the present data it is suggested that the thermodynamic equilibrium pressure for fcc $\rightleftharpoons$ bcc transformation in ytterbium is below 3·5 GPa. The valence change under pressure has been discussed.

Keywords. Equation of state; high pressure; x-ray diffraction; ytterbium.

1. Introduction

Ytterbium has a face-centred cubic (fcc) structure at room temperature and pressure, and transforms to a body-centred cubic (bcc) structure at 3·9 GPa (Hall *et al* 1963). The equation of state up to 4 GPa was measured by several investigators (Bridgman 1954; Hall and Merrill 1963; Stephens 1964). Though the results obtained by these investigators show an overall agreement, the finer features of the pressure-volume data differ. Further, these measurements were made with piston-cylinder apparatus which had ~ 4 GPa as the upper limit of attainable pressure. As a result, no measurements could be made on the bcc phase and even the measurements of volume change of the transformation are incomplete.

The equation of state of ytterbium up to 9 GPa has been measured using tungsten carbide opposed anvil x-ray apparatus, and the results are reported in this paper. The bulk modulus and its pressure derivative in the fcc phase have been compared with the results available in the literature. Some results on the bcc phase metastably retained much below the transformation pressure are also reported.

2. Experimental details

A tungsten carbide opposed anvil set-up with boron-epoxy gasket and epoxy pressure transmitting medium was used to record the x-ray diffraction patterns at elevated pressures. A small piece of 99·9 % pure ytterbium supplied by Rare Earth Products Limited, USA was thinned down to 0·04 mm by pressing it between two flat surfaces and subsequent polishing on 600 grade emery paper. A piece measuring approximately 0·3 × 0·2 × 0·04 mm was cut from the thinned piece, and placed in the central hole of the boron-epoxy gasket such that the smallest dimension was parallel to the gasket surface. The rest of the space in the hole was filled with epoxy resin, which acted as the pressure

transmitting medium. The epoxy resin was allowed to set; the excess epoxy was removed by polishing on 600 grade emery the gasket and specimen assembly. The gasket with the specimen at the centre was placed on the anvil such that the incident x-ray beam was normal to the 0.3×0.2 face of the specimen. The gasket was compressed to a nominal pressure of $2 \, \text{GPa}$ and brought back to room pressure. The gasket was reloaded in steps of about $0.5 \, \text{GPa}$, and the diffraction patterns recorded using MoK α radiation and a cylindrical film cassette. The hydraulic pressure of the ram, p_r was noted for each experiment.

The pressure on the specimen, p_s was determined by calibrating the hydraulic pressure of the ram, p_r in terms of the pressure experienced by the specimen. For this purpose, separate runs were made with sodium chloride samples mixed with epoxy resin (in the ratio $1:4$). The diffraction patterns from NaCl were recorded at various ram pressures. The specimen pressure was calculated from the observed unit cell volume and the theoretically calculated equation of state of NaCl (Decker 1971). The typical $p_r - p_s$ plots are shown in figure 1. These calibration curves were used to determine the specimen pressure at any ram pressure. The calibration curve was found to depend markedly on the gasket thickness and the ratio of boron and epoxy in the gasket. For the high degree of reproducibility of the $p_r - p_s$ relation, the gasket thickness was maintained within $0.01 \, \text{mm}$. The compression of the gasket and specimen assembly prior to gathering the data further improves the reproducibility of the $p_r - p_s$ relation. A precise control of boron-epoxy ratio while making the gaskets is difficult. It becomes necessary to calibrate each batch of gaskets separately. The freshly prepared
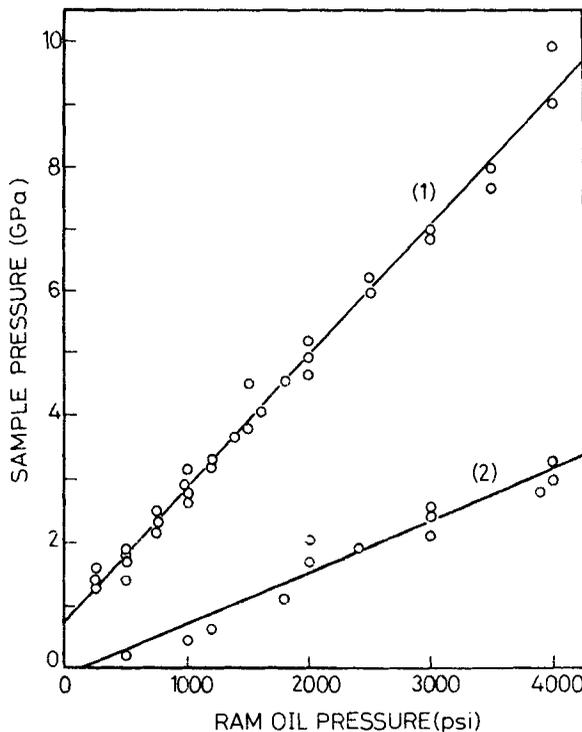

Figure 1. Plot of specimen pressure against hydraulic ram pressure. (1) 3 mm anvil (2) 5 mm anvil.

gaskets often showed larger scatter in the $p_r - p_s$ plot than the gaskets which were stored for sometime after preparation. The gaskets were therefore stored at room temperature for nearly a month before use. The other relevant experimental details are given elsewhere (Singh and Kennedy 1976).

The error in the specimen pressure for a given error in the ram pressure can be reduced to some extent by using anvils with larger faces. For this reason the anvils with 5 mm face diameter were used up to 4 GPa and 3 mm face diameter up to 9 GPa.

The volume changes during the reverse transformation (bcc → fcc) were studied by the following procedure. The pressure was increased in steps until the x-ray diffraction patterns indicated the presence of bcc phase alone. The pressure was then decreased in steps and x-ray patterns recorded after each decrement. The specimen was found to remain in fully bcc phase until the pressure was reduced to $\approx$ 1 GPa. The diffraction patterns from the coexisting fcc and bcc phases were recorded. The pressure on the specimen was calculated by using the observed cell volume of the fcc phase and the experimentally determined equation of state.

The quality of x-ray diffraction patterns was reasonably good. Normally, five lines from the fcc phase and four lines from the bcc phase could be recorded. When the two phases coexisted, the quality of the diffraction pattern was poorer. This was reflected in a large scatter in the pressure-volume data.

3. Results and discussion

The pressure-volume data are shown in figure 2. The bulk modulus at one atmosphere, B_0 and its pressure derivative, B_0' were determined by fitting to the pressure-volume data Murnaghan equation of the form,

$$V/V_0 = \left(1 + \frac{B_0' p}{B_0}\right)^{-1/B_0'},$$

where V_0 and V denote the volumes of the unit cell respectively at one atmosphere and
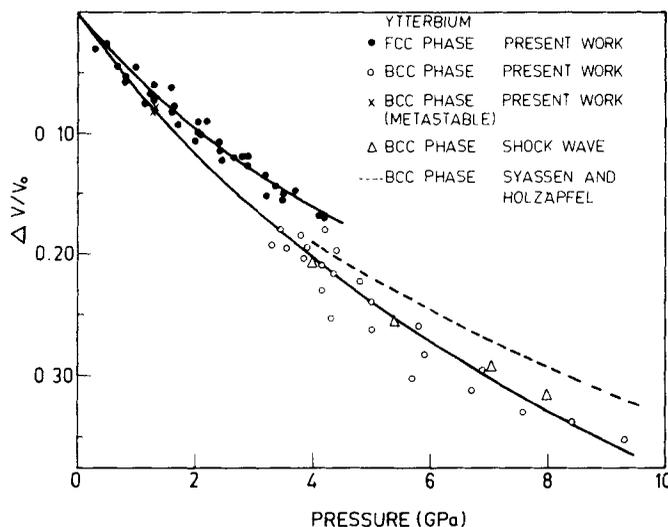

Figure 2. Pressure-volume data.

at a pressure p. The pressure-volume data up to 3·5 GPa were used to obtain the values of B_0 and B_0' of the fcc phase. The values of B_0 and B_0' of the bcc phase were obtained using data in the pressure range 4–9 GPa. Assuming the error to be in the measurement of (V/V_0) alone, the standard deviation in (V/V_0) was calculated and found to be 0·008. These errors are nearly twice as large as those in some of the best experimental devices which employ liquid pressure transmitting medium and *in situ* pressure measurement using ruby fluorescence technique or NaCl pressure marker.

3.1 *Fcc phase*

The values of B_0 and B_0' of the fcc phase as obtained from the present data along with those obtained by the other investigators are listed in table 1. The values of B_0 reported by the various investigators range from 13 GPa to 17 GPa. The present value agrees well with those reported by Hall and Merrill (1963), Stephens (1964), and Gust and Royce (1973). The value reported by Bridgman (1954) appears to be too low. The values of B_0 obtained from the measurement of ultrasonic sound velocity (Smith *et al* 1957; Rosen 1971) are significantly lower than the present value, but agree well with Bridgman's (1954) value. The present value of B_0' is significantly larger than the values reported by Bridgman (1954) and Stephens (1964). However, B_0' for most solids is closer to 4, as indicated by the validity of Birch equation of state, the present value of B_0' appears realistic.

The measurements by Hall and Merrill (1963) indicated a break in slope of the pressure-volume curve at 1·8 GPa. This was, however, not supported by other experiments made with similar apparatus (Stephens 1964). The reported change in slope (Hall and Merrill 1963) is too small to be detected in the present experiments.

It is interesting to compare the bulk modulus of ytterbium with those of the other rare earths. This can be done with the help of a $\log B_0 - \log v_0$ plot (Anderson and Nafe 1965), where v_0 is atomic volume. Such a plot for compounds having similar bonding characteristics results in a straight line, indicating that the bulk modulus increases exponentially as the atomic volume decreases. The $\log B_0 - \log v_0$ plot for rare earth elements is shown in figure 3. The solid line is a least-squares fit to the data for rare earths. It is seen that the ytterbium point falls much below this line.

A similarity between the high pressure behaviour of ytterbium and alkaline earth elements specially strontium has long been noted (Jayaraman *et al* 1963). Strontium, like ytterbium, has a fcc structure at one atmosphere and transforms to bcc phase at ~ 4 GPa. These similarities prompted a comparison of the bulk modulus of ytterbium with the bulk moduli of alkaline earth elements. The data for calcium, strontium and

Table 1. Compression parameters of ytterbium (fcc phase) in the pressure range (0–4 GPa)

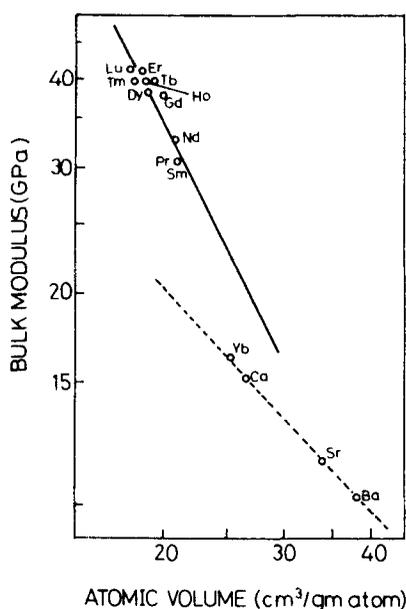| B_0(GPa)	B_0'	Method	Reference
13·3	1·22	Piston-cylinder	Bridgman (1954)
17·2	—	-do-	Hall and Merrill (1963)
15·3	1·57	-do-	Stephens (1964)
13·8	—	Ultrasonic	Smith *et al* (1957)
13·5	—	-do-	Rosen (1971)
15·0	—	-do-	Gust and Royce (1973)
16·3	3·6 ± 0·9	X-ray	Present results

Figure 3. A $\log B_0 - \log v_0$ plot. The B_0-value for ytterbium is from the present experiments and for others from Gschneidner (1964).

barium are also plotted in figure 3. It is seen that the points fall on a straight line suggesting a strong similarity between ytterbium and alkaline earth elements so far as the dependence of bulk modulus on atomic volume is concerned.

3.2 *Bcc phase*

The values of B_0 and B'_0 of the high pressure phase (resulting from a transformation) cannot be obtained by fitting to the pressure-volume data an equation of state in standard form, because often a discontinuous volume change is associated with the transformation. This difficulty is simply overcome by shifting the origin of co-ordinates to (p_t, V_t), where p_t and V_t are respectively the observed pressure of transformation and the volume at p_t; any equation of state in standard form can then be used. The equation fitted in this manner indicates that $V \neq V_0$ at $p = 0$. This physically means that the room pressure density of the starting material is different from the density of the high pressure phase at room pressure. The volume measurements on the metastable bcc phase at ~ 1 GPa indicate that the situation in the case of bcc ytterbium is different. The volume difference between the fcc and bcc phases decreases rapidly with decrease in pressure and seems to vanish at $p = 0$. The pressure-volume curve thus passes through the origin of co-ordinates. A Murnaghan equation was therefore fitted to pressure-volume data in the pressure range 4–9 GPa. The value of B_0 and B'_0 were respectively 14·7 GPa and 1·5.

Syassen and Holzapfel (1979) determined the pressure-volume relation for the bcc phase of ytterbium up to nearly 30 GPa using a diamond anvil camera. The values of B_0 and B'_0, however, were not reported. On fitting Murnaghan equation to the data the following values were obtained: $B_0 = 14·7$ and $B'_0 = 2·49$. The value of B_0 agrees very well with the present value, but the B'_0 value is significantly larger than the present value. This is also reflected in the fact that the overall volume compression obtained by Syassen and Holzapfel (1979) is smaller than that obtained in the present experiments.

Table 2. Compression parameters of ytterbium (bcc phase) in the pressure range (4–9GPa)

B_0(GPa)	B'_0	$(\Delta V/V_0)_t^*$ at 4GPa	Reference
—	—	−0·032	Hall et al (1963)
12·0	2·71	—	Gust and Royce (1973)
14·7	2·49	—	Syassen and Holzapfel (1979)
14·7	1·50	−0·043	Present results

* $(\Delta V/V_0)_t$ is the volume change associated with the fcc-bcc transformation.

Table 3. The fcc → bcc transformation pressure (start pressure) in ytterbium

Transformation pressure (GPa)	References
4·0	Bridgman (1954)
4·0	Hall et al (1963)
4·0	Souers and Jura (1963)
3·8	Stager and Drickamer (1963)
4·0	Hall and Merrill (1963)
4·0	Jayaraman (1964)

The present pressure volume data for the bcc phase, however, lie closer to those obtained in shockwave experiments (Gust and Royce 1973). The compression parameters derived from the data of various investigators are listed in table 2. The volume change associated with the transformation is −0·043, and is marginally higher than the value obtained by Hall et al (1963).

The volume compression of ytterbium is much larger than that of the other rare earths. It is only above 15 GPa that the volume compression of ytterbium becomes comparable to that of the other rare earths (Syassen and Holzapfel 1979). Further, the present data indicate that the bulk modulus of the fcc phase is larger than that of the bcc phase at the same pressure. For example, at 4 GPa the bulk moduli are 30·7 GPa and 20.7 GPa respectively for the fcc and bcc phases. The anomalous compression of bcc ytterbium and its relation to a possible electronic transition will be discussed in §3.4.

3.3 Pressure of transformation

The fcc → bcc transformation pressure has been reported by many investigators (table 3). The pressures reported were the pressures at which the transformation was found to start in experiments wherein either the pressure was continuously increased or the pressure was increased in small steps with a reasonable waiting period (a few min) between the steps. It is seen in table 3 that the start pressure of the transformation was close to 4 GPa in most experiments. Souers and Jura (1963) noted the fcc ⇌ bcc transformation was characterized by a large hysteresis and felt that the equilibrium pressure was close to the start pressure for the fcc → bcc transformation. The present data indicate that bcc phase could ofteñ be observed around 3·5 GPa in the experiments

wherein pressure was increased in steps and held constant during the x-ray exposure. In the experiments with decreasing pressure, the bcc phase was metastably retained down to pressures as low as 1 GPa.

A transformation can proceed only if the applied pressure is more than the equilibrium pressure. Since the fcc → bcc transformation was found to occur even at 3·5 GPa, the equilibrium pressure is expected to be much below 3·5 GPa. In fact, the study by resistometric method of the kinetics of the fcc → bcc transformation under isobaric-isothermal conditions indicated that the kinetics of the transformation became slower at lower pressures, and the fcc → bcc transformation was found to occur even at 3·3 GPa (Singh *et al* 1982, 1983; Singh 1983; Divakar *et al* 1984). It is certain that the transformation will occur at pressures below 3·3 GPa if sufficient time is allowed. These data and also the present results indicate that the equilibrium pressure for fcc ⇌ bcc transformation in ytterbium is much below 3·3 GPa and not close to 4 GPa as many earlier investigators believed.

The fcc → bcc transformation in ytterbium under isobaric conditions exhibits incubation period which decreases exponentially with increase in pressure (Divakar *et al* 1984). The start pressure of the transformation is close to the pressure at which the incubation time becomes small as compared with the loading time. Because of the exponential nature of the pressure-dependence of the incubation time, large changes in the incubation time can be brought about by relatively small changes in pressure. Thus, the experimentally observed start pressure is not very sensitive to the rate of loading. This, together with the fact that the rates of loading employed by various investigators do not vary widely, explains why highly reproducible values for the start pressure (table 3) were obtained by the various investigators, even though the transformation can occur over a wide range of pressures under isobaric conditions.

3.4 *Electronic transition*

The electrical resistivity of ytterbium increases with increase in pressure reaching a maximum near 4 GPa (Bridgman 1954; Stager and Drickamer 1963), followed by a large decrease. Lawson (1956) suggested that this decrease in resistance was due to a transfer of a 4*f* electron to the conduction band. Hall and Merrill (1963) established that the decrease in resistance was associated with the fcc → bcc transformation. Hall *et al* (1963) observed that the experimentally determined radius (1·75 A) of ytterbium in the bcc phase at 4 GPa was close to that of trivalent ytterbium at one atmosphere. On this basis it was concluded that the fcc → bcc transformation was accompanied by a change in valency of ytterbium from 2 + to 3 +.

The fcc → bcc transformation in ytterbium was compared with a similar structural transformation in strontium (Jayaraman *et al* 1963; McWhan and Jayaraman 1963; Jayaraman 1964). There are no 4*f*-electrons in strontium, and as such the 4*f*-electrons are not involved in the transformation of its structure, and therefore in ytterbium also 4*f*-electrons are not involved in the structural transformation.

McWhan and Jayaraman (1963) suggested that the decrease in ionic radius observed by Hall *et al* (1963) in fact could be accounted for by incorporating a correction for the change in co-ordination number, when the structure changes from fcc to bcc. The radius in the bcc phase at 4 GPa is 1·75 A and becomes 1·80 A after applying a correction for the change in coordination number (Gschneidner 1961). It was argued that the difference between this value (1·80 A) and the observed value (1·82 A) in the fcc

phase at 4 GPa was not significant. Therefore, it was concluded that the metallic radii were same in both fcc and bcc phases, and that there was no electronic transition involved in the fcc → bcc transformation in ytterbium.

It is to be noted that the volume per atom with a radius of 1·8 A in the fcc phase is less than that with a radius of 1·82 A by 3·2 %. This is exactly equal to the change in volume observed at the structural transformation (Hall et al 1963). Thus, even though the radius in the bcc phase is corrected for the change in the co-ordination number, still there is 3·2 % decrease in volume. This is to be expected for the following reason. The correction for the change in co-ordination number has been derived by Gschneidner (1961) by considering a few temperature-induced structural transformations in elemental solids. The transformations considered show a change in co-ordination number but practically no change in volume. Since most structural transformations under pressure result in a decrease in volume, the atomic radius in the high pressure phase even after the correction for co-ordination number change will be smaller than the radius in the low pressure phase at the same pressure. Thus, the changes under pressure in the atomic radius cannot be used as an indicator of the valence change.

It has been suggested by Coqblin and Blandin (1968) and Coqblin (1971) that since trivalent ytterbium has 13 f-electrons, the unpaired spin should order magnetically. Katzman and Mydosh (1972) measured the temperature dependence of electrical resistivity down to 1·3 K and at pressures between 5–16 GPa. These experiments did not indicate the presence of superconductivity or magnetic effects and it was concluded that bcc ytterbium is not in trivalent state. The theoretical calculations of Johansson and Rosengren (1975) and Rosengren and Johansson (1976) suggest a valence transition near 14 GPa. The LIII-absorption edge studies made by Syassen et al (1981) with diamond-anvil cell and x-rays from synchroton source suggest that the valency of ytterbium changes from 2 + to 3 + continuously over the pressure range 3–33 GPa.

It is certain that the fcc → bcc transformation in ytterbium does not involve a change in valency. The evidences for change in valency even at higher pressures are not clear cut. The s, p, d band structure model (Souers and Jura 1963; McWhan et al 1969) which attempts to explain the behaviour of ytterbium in terms of the shift of 5d band with respect to 6s, 5p bands is an alternative model. However, the role of 4f electron in ytterbium cannot be ignored altogether because the existence of 4f level close to the Fermi level is suggested by optical (Broden et al 1970) and x-ray photoemission (Hagstrom et al 1970) experiments.

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