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Abstract

High-pressure x-ray diffraction studies have been performed on US up to 40 GPa using synchrotron radiation and a diamond anvil cell. The measured value of the bulk modulus $B_0 = 92$ GPa is in reasonable agreement with calculations. The high-pressure behaviour indicates a phase transformation to US III at about 15 GPa. The transformation is a smooth deformation process, which starts with a tetragonal structure $a_{tetr} = a_{cub}/\sqrt{2}$, $c_{tetr} = 2a_{cub}$ and continues with an orthorhombic structure with a = 375(3) pm, b = 345(3) pm, c = 1069(24) pm at 35 GPa; it is of second order nature within experimental errors and it should involve some contributions from uranium f electrons.

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1. Introduction

The uranium chalcogenides with rock-salt structure to which US belongs are materials with a metallic character and a high electronic specific heat and susceptibility. They are characterized by hybridized 5f and 6d electrons in addition to conduction electrons close to the Fermi energy(1). The structure as determined by Shable(2) at room temperature is the rock-salt structure, space group Fm3m. It continues up to the melting temperature. US orders ferromagnetically below 180 K. Associated with this ordering is an anomaly in the molar heat capacity, C_p(3) and a transformation from cubic to rhombohedral symmetry(4). Electronic specific heat measurements have revealed a very large density of states at the Fermi energy (9.9 electrons - ev^{-1} $atom^{-1}$) which indicates a location of the 5f electrons at this energy. Photoemission spectra supports an atom-like rather than an extended state of the 5f electrons. However, the energy position of the 5f band is favourable for a delocalization of the 5f electrons by increasing the pressure or the temperature(5). Accordingly the 5f electrons of US form levels intermediate in character between the extended 3d states of the transition metals and the localized 4f states of the rare earths. Neutron diffraction measurements on a single crystal of US have shown that the direction of easy magnetization is along the [111] axis(6) in the ferromagnetic state.

In the present work we have studied US powder at room temperature for pressures up to 40 GPa with the aim of comparing the high pressure behaviour with the behaviour at low temperature mentioned before. We have measured the compressibility in order to see if there exist new allotropic structures at decreased lattice parameters

corresponding to a transition across the transition zone of the Hill plot.

2. Experimental

The x-ray experiments were performed using synchrotron radiation from the electron storage ring DORIS at HASYLAB-DESY (Hamburger Synchrotronstrahlungslabor am Deutschen Elektronen-Synchrotron) in Hamburg. The electron energy was 3.7 GeV to 5 GeV in various periods of the experiments. The time averaged electron current was different at the various electron energies used, for example 20 to 40 mA in 20 bunches at 4 GeV. The white beam energy dispersive diffractometer (7) or the triple axis spectrometer working in the energy-dispersive mode were used.

The high-pressure equipment consists of a diamond anvil high pressure cell of the Holzapfel-Syassen type used at room temperature. The maximum pressure in the present work was 40 GPa.

The US powder was prepared at the European Institute for Transuranium Elements in Karlsruhe. The finely powdered material was filled in the diamond cell and a sample 200 μm in diameter and 80 μm thick was enclosed in an Inconel gasket. A 4:1 methanol-ethanol mixture and a ruby were added to the powder to allow for hydrostatic pressure conditions and a proper calibration of pressure, respectively. Diffraction from the gasket was avoided by reducing the incident beam cross section to 0.1 x 0.1 mm^2 using tantalum slits. A good geometrical resolution was obtained by using a large distance (40 cm) between sample and detector, and a slit (0.2 mm) in front of the detector to define the scattered beam. A pure germanium solid state detector with an energy resolution of 150 eV (FWHM) at 5.9 keV was used.

The energy analysis of the diffracted x-rays was carried out by means of a multichannel pulse-height analyser covering the range from 10 keV to 70 keV. The exposure time was usually between 500 and 1000 sec. depending on the beam conditions. The energies of the diffraction maxima were determined either by the peak search programme of the multichannel analyser system or by subsequent computer calculations.

The scattering angle has to be determined as a fixed parameter in the energy-dispersive method. In the present work the scattering angle was determined from the recorded spectra at zero pressure and the known structure of US. Conceivable small shifts in the sample position after pressurizing the cell are assumed to have a negligible effect on the scattering angle because of the large sample-to-detector distance. The estimated uncertainty of the scattering angle is less than 0.01°. The uncertainty of the pressure determined from the frequencies of the two ruby lines is estimated to 0.2 GPa for $P < 10$ GPa. For $P > 10$ GPa the non-hydrostatic conditions in the sample together with pressure gradients might result in a larger uncertainty.

3. Results

The US sample has the rock-salt structure (space group Fm3m) at room temperature and zero pressure as mentioned above. The lattice constant a = 548.8 pm determined experimentally by a Debye-Scherrer pattern is in good agreement with the value a = 548.53 pm found in the literature(8).
Fig. 1a shows an energy-dispersive diffraction spectrum of US at zero pressure in the diamond cell. The scattering angle $2\theta = 9.97^{\circ}$ has been determined from the observed peak positions and the known lattice constant. Other scattering angles have also been used in order to get more diffraction peaks in the recorded spectra, in particular for the 5 GeV runs. Uranium fluorescence peaks are also seen but no other diffraction peaks from e.g. uranium oxide.

A Rietveld fit to the zero pressure spectrum has shown a reasonable agreement between observed and calculated intensities.

The observed diffraction spectra can be indexed according to the cubic structure up to about the pressure 15 GPa. When the pressure is further increased a new structure develops. The peaks are shifted (in either direction) from the cubic positions, some peaks are broadened or split into double peaks and some new peaks develop. Fig. 1b shows a diffraction spectrum at 35 GPa. The 111 peak of the low-pressure cubic phase has now become a broader peak. whereas the former 200 peak is still a sharp peak. The former 220 can now be resolved in a double peak. The other high-pressure peaks are not resolved but appear as broad peaks. New peaks, some sharp some broad, can also be seen. Their intensity increases with increasing pressure, particularly from 30 GPa on.

Fig. 2 shows the interplanar spacings as functions of pressure up to 35 GPa. The diagram has been drawn for increasing pressure.

4. Discussion

The unit cell volume V can be calculated from the experimental diffraction spectra. The V(P) data for $P < 15$ GPa (fig. 3) calculated as cubic, NaCl type, have been fitted to Murnaghan's equation of state

$$P = (B_0/B_0')\left[(V_0/V)^{B_0'} - 1\right] \qquad (1)$$

where V_0 is the unit cell volume at ambient pressure, B_0 is the isothermal bulk modulus and B_0' its pressure derivative also at ambient pressure. A non linear least squares fitting gave the following results

$B_0 = 92 \pm 9$ GPa

$B_0' = 9.1 \pm 1.6$

where the quoted errors are the standard errors of the fit.

The B_0 value of the present work is in reasonable agreement with the theoretical value $B_0 = 74$ GPa given by Holden, Buyers, Svensson, Jackman, Murry, Vogt & DuPlessis(9). These authors have made a force constants analysis of the lattice vibrations of uranium compounds (UX) using a rigid ion model. It also follows from the force constants analysis of Holden et al.(9) that US exhibits a negative Poisson's ratio originating in the negative C_{12} elastic constant. A similar effect is found for the intermediate valence compound $Sm_{0.75}Y_{0.25}S$ and for TmSe. Thus under pressure, a 5f electron may be promoted into the 6d band resulting in a loss of screening and a contraction of the atomic volume.

However, the effects are likely to be less dramatic for the uranium compounds than for $Sm_{0.75}Y_{0.25}S$ for which the bulk modulus is smaller than that of the uranium compounds.

Hill(10) has compared the behaviour of different uranium compounds as function of U-U distance in the so-called Hill plot. According to this plot, uranium compounds are separated into two groups with respect to the magnetic behaviour and the localization of the 5f electrons. The separation of uranium atoms in US at zero pressure in the cubic phase is equal to 3.881 Å. At the maximum pressure where the rock-salt phase still exists we find the corresponding distance 3.76 Å. This decrease in distance has not yet reached the transition zone of the Hill plot. Therefore a decrease of the U-U distance below this zone needs a higher pressure or a change of the structure.

The changes in the structure of US for $P > 15$ GPa are rather small even at the maximum pressure of 40 GPa used in this experiment. Moreover the structure distortions seem to be a smooth process starting from the cubic phase, passing through phases of lower symmetry and not ending at a defined new structure up at 40 GPa. This distortion process is evident from the behaviour of d_{hkl}'s as a function of pressure shown in Fig. 2. Already at 8-9 GPa, the fit to the cubic structure starts showing larger deviations Δd. Starting from about 15 GPa the d values of the f.c.c. 111 and 200 lines have a different pressure dependence, with the d_{111} practically showing no decrease and the d_{200} having almost the same slope in the whole interval from $p = 0$. Splitting of lines starts mainly with the reflection 220. The appearance of new lines is evident at pressures > 30 GPa, but their intensity remains quite small. So during the phase transition there is no volume discontinuity within the experimental errors, and the transition can be considered to be of second order nature. Therefore the distortion has to go to a subgroup of Fm3m and a general description of this "extended homomorphism" has been recently reported by Haisa(11). The same assumption of a phase transformation of second order nature has, e.g., been made, by Grosshans et al.(12) for the phase transition of praseodymium metal under pressure. A reasonable fit on the data at 35 GPa has been obtained with a tetragonal cell, space group P4/mmm having $a_{tetr} = a_{cub}/\sqrt{2} = 364\ (2)$pm, $c_{tetr} = 2a_{cub} = 1122\ (17)$pm, obtained by least-squares refinement from measured d_{hkl} values $\left[(\Sigma w(d_{obs}-d_{calc})^2/(\text{number of reflections} - 2) = 5.5\text{x}10^{-4})\right]$. A further distortion was assumed and the least squares refinement was then carried out on an orthorhombic cell giving a = 375(3), b = 345(3), c = 1069(24)pm $\left[(\Sigma w(d_{obs} - d_{calc})^2/(\text{number of reflections} - 3) = 3.2\text{x}10^{-4})\right]$. The final data for both refinements are reported in Table 1. The fit of the orthorhombic cell seems better and moreover it explains the shape of the most intense lines e.g. the original cubic lines 111 and 200. In fact the broadening of the 111 reflection comes from the new 102 and 012 that have slightly different d values, while the sharp 200 becomes the 110 which is single.

The indices of the reflections are obtained from those of the cubic structure by the transformation matrix $\left\{\begin{matrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 2 \end{matrix}\right\}$ on hkl. These are reported as main reflections in Table 1 and in fig. 2. Starting atomic parameters for uranium atoms are (0,0,0), (1/2, 1/2, 1/4); (0,0, 1/2); (1/2, 1/2, 3/4) which are the atomic positions of the cubic Fm3m structure placed in the new cell, which could be considered as belonging to space group Pmmm, the space group with the highest symmetry. The description of the new structure should require the knowledge with some degree of accuracy of the integrated intensities. At the present state of the art intensity data are unfortunately affected by serious effects which are difficult to be corrected, such

as broadening of lines by non ideal hydrostatic conditions, preferred orientation due to pressure and the limited amount of crystallites on the sample which gives rise to fluctuations in intensity according to sample position.

Table 1 shows that the observed interplanar spacing and those calculated from the orthorhombic indexing fit at 35 GPa. It is seen that the diffraction lines are grouped around the original lines of the low-pressure fcc structure. The resolution in the energy-dispersive method is limited, mainly by the detector, and therefore the broad peaks are not resolved in the spectrum.

The unit cell volume of US is shown in fig. 4. The full curve at low pressure represents the Murnaghan equation of state, fitted to the V(P) data of the fcc phase for P < 15 GPa. The curve of the Murnaghan equation is continued as a dashed line in the figure. The calculated volume V(P) for P > 15 GPa using the orthorhombic structure discussed above, is shown by the open symbole. The full curve is continued from the low-pressure region to the high-pressure region with a change of slope at the transition point. However, there is no abrupt change of volume at the phase transition, and we conclude that the transition is of second order nature.

US has about two f electrons and a delocalization of these can be induced by applying pressure so that they will participate in bounding and low symmetry crystal structures are observed. This is seen in the case of Ce and Pr with originally localized $4f^n$ electrons and according to Johansson, Skriver & Krogh Andersen(13) uranium should be compared with light lanthanides.

In the distorted orthorhombic structure the U-U distances in the (001) plane become 366 and 356 pm to be compared with 388 pm at P = 0. Nothing can be said about the distances along the [001] direction apart that they are certainly longer. According to the calculations of Hill this means that we are near to the transition region and still higher pressures are necessary before we pass that region changing the properties of the compound.

Conclusions

The rock-salt structure of US is conserved up to 15 GPa but at this pressure there is a change to an orthorhombic structure US III. The structure can be described as a slightly distorted fcc structure, and the transformation is of second order nature as seen from the absence of any discontinuous volume change in the V(P) curve. However, we assume some influence of the f electrons in order to explain the behaviour at increasing pressure. The bulk modulus B_0 = 92 GPa for the low pressure US is in approximate agreement with theoretical calculations for the fcc uranium chalcogenides. With the present pressure range we are approaching the transition region in the Hill plot but still higher pressures are necessary to pass this region.

Acknowledgement

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Table 1. Diffraction spectrum of US powder, P = 35 GPa

Tetragonal indexing : a = 364(2), c = 1122(17) pm

Orthorhombic indexing: a = 375(3), b = 345(3), c = 1069(24)pm

d_{obs}	intensity	$(d_{calc})_{Tetr}$	hkl	$(d_{calc})_{Orth}$	hkl	Equivalent hkl (cubic)
3.083	m	3.054	102	3.069	102	111
				2.898	012	
2.546	s	2.575	110	2.538	110	200
2.332	w	2.340	112	2.293	112	
2.064	w	2.121	113	2.067	113	
1.876	s	1.897	114	1.840	114	
		1.870	006			
		1.821	200	1.874	200	220
1.733	w	1.732	202	1.724	020	
1.572	m	1.564	212	1.574	212	311
		1.527	204	1.535	204	222
1.265	m	1.287	220	1.269	220	400
		1.279	221			

Figure captions

Fig. 1. X-ray energy-dispersive diffraction spectra of US powder.

a) Rock-salt structure at zero pressure.

b) Orthorhombic structure at 35 GPa.

Fig. 2. Interplanar spacing as functions of pressure. (hkl) indices according to the fcc structure are given to the left, those according to the orthorhombic structure (distorted fcc) to the right.

Fig. 3. Unit cell volume as a function of pressure for the rock-salt structure. The full curve is the fit to the Murnaghan equation with B_0 = 92 GPa and B_0' = 9.1. The shown points are from different experiments.

Fig. 4. Unit cell volume normalized to 4 units of US as function of pressure for both the rock-salt (filled circles) and the orthorhombic structure (open squares). The full curve represents the Murnaghan equation of state fitted to the fcc points for P < 15 GPa and is extrapolated by the dashed curve to the region P > 15 GPa. The full curve is continued through the points for P > 15 GPa.

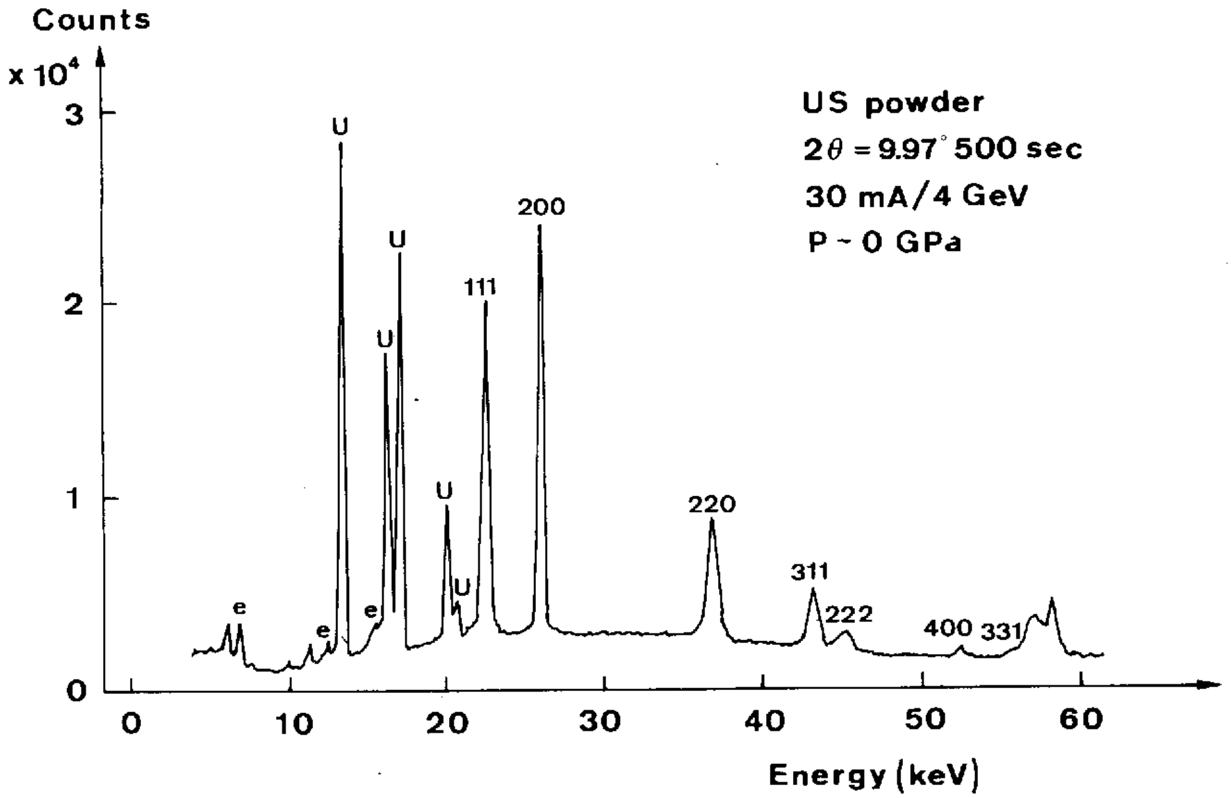
Counts
x 10⁴
3
2
1
0
US powder
2θ = 9.97° 500 sec
30 mA/4 GeV
P ~ 0 GPa
U
U
U
U
U
e
e
e
111
200
220
311
222
400
331
0
10
20
30
40
50
60
Energy (keV)

Fig.1a

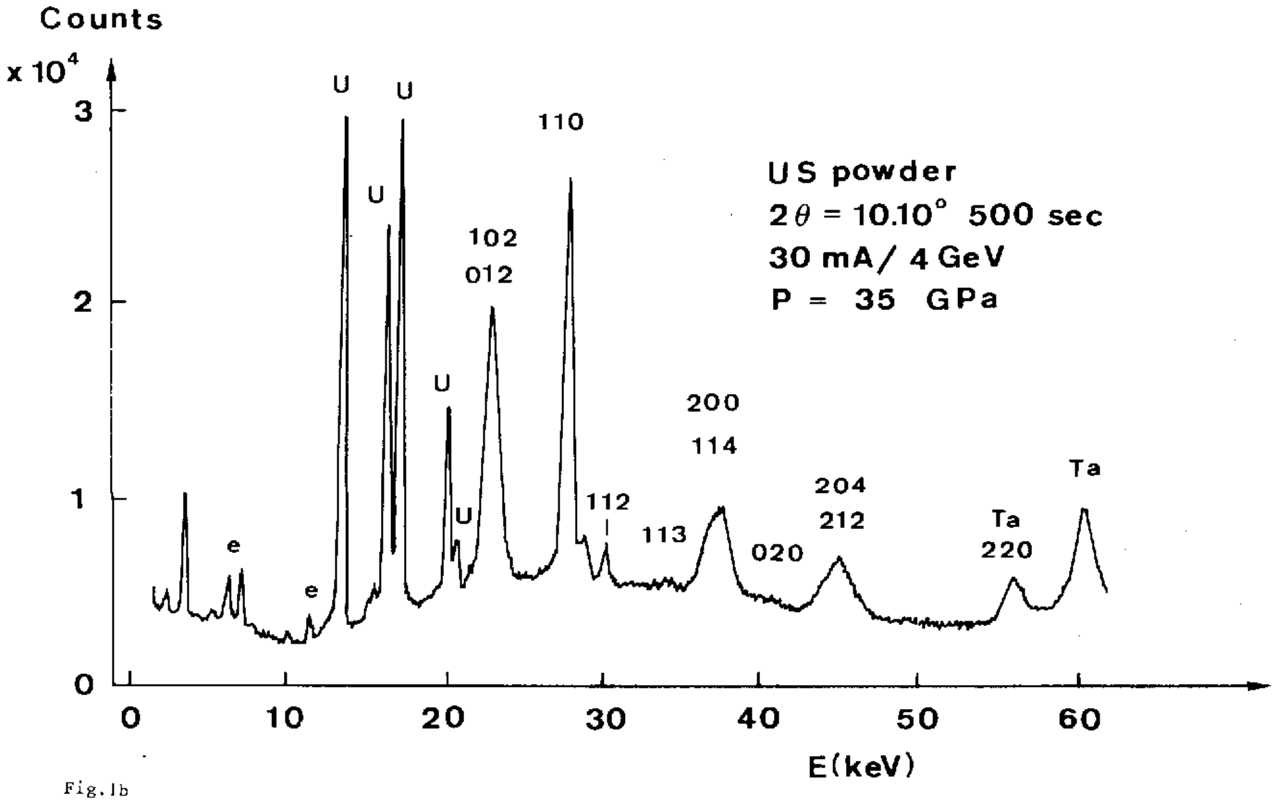
Counts
x 10⁴
3
2
1
0
US powder
2θ = 10.10° 500 sec
30 mA/ 4 GeV
P = 35 GPa
U
U
U
U
U
e
e
102
012
110
112
113
200
114
020
204
212
Ta
220
Ta
0
10
20
30
40
50
60
E(keV)

Fig.1b

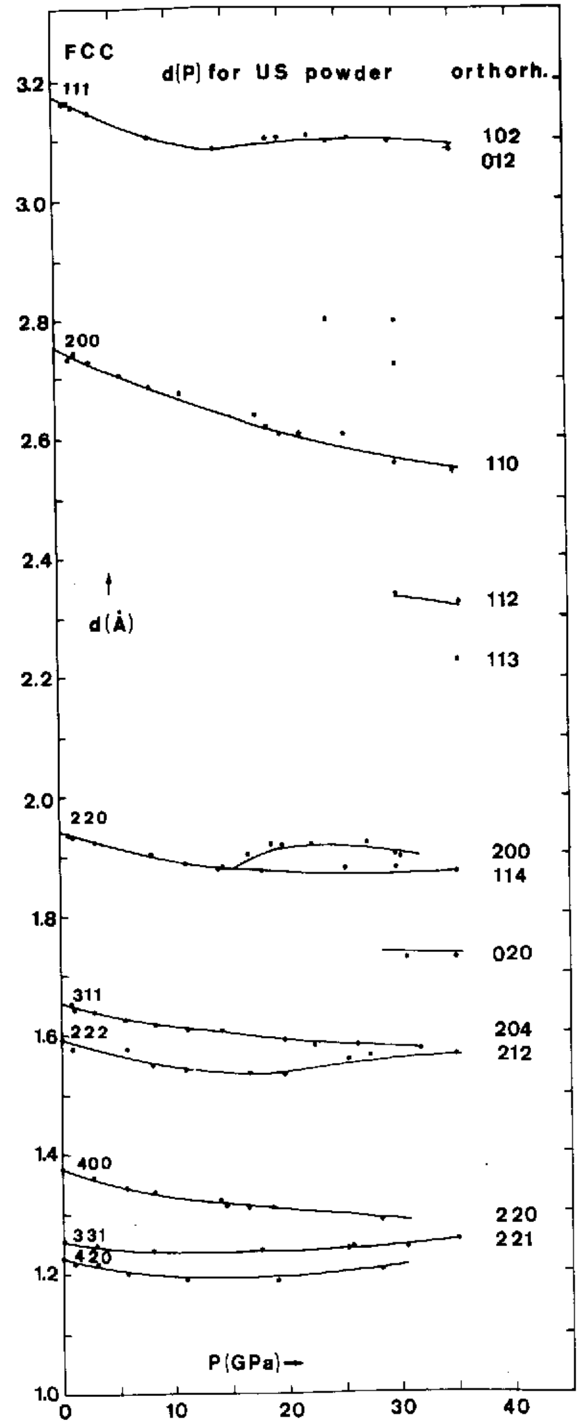
FCC
d(P) for US powder
orthorh.
111
102
012
200
110
112
113
220
200
114
020
311
222
204
212
400
331
420
220
221
d(Å)
P(GPa)
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0
10
20
30
40

Fig. 2

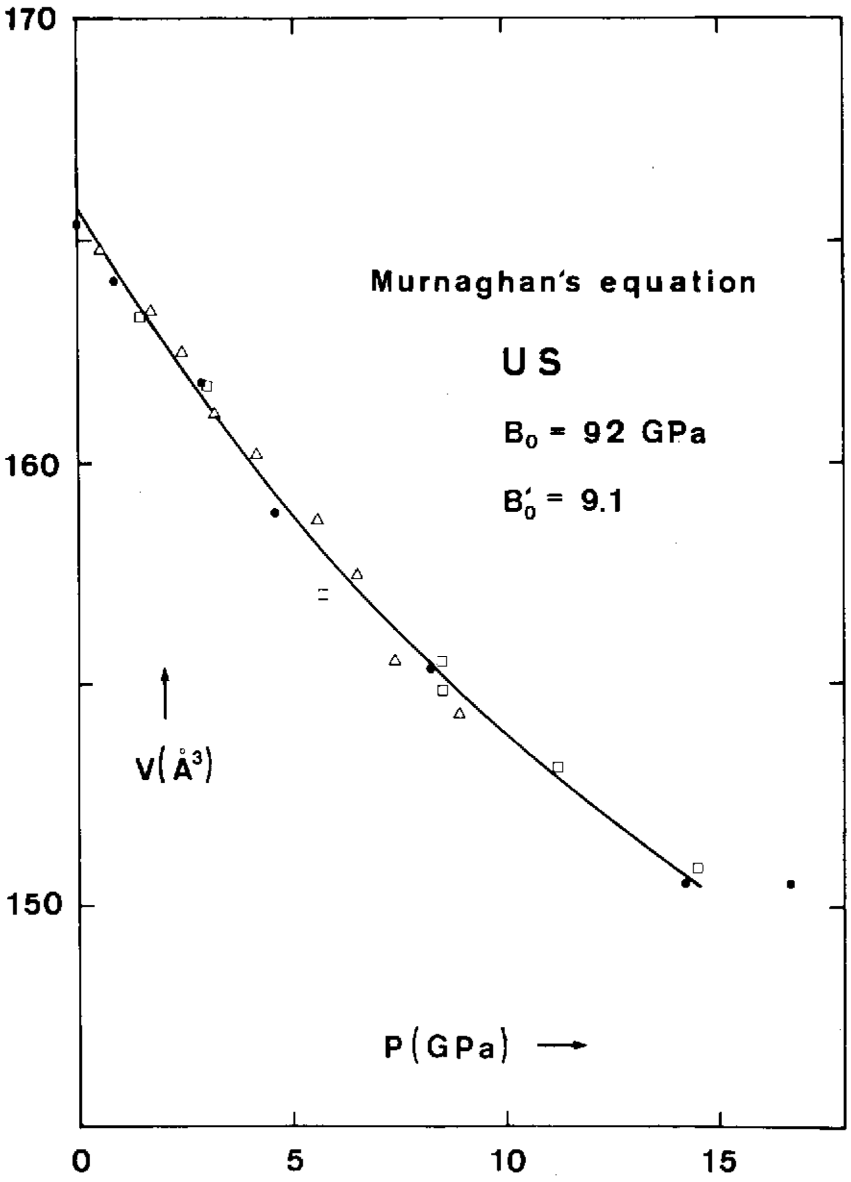
Murnaghan's equation
US
B_0 = 92 GPa
B'_0 = 9.1
V(Å^3)
P(GPa)
170
160
150
0
5
10
15

Fig. 3

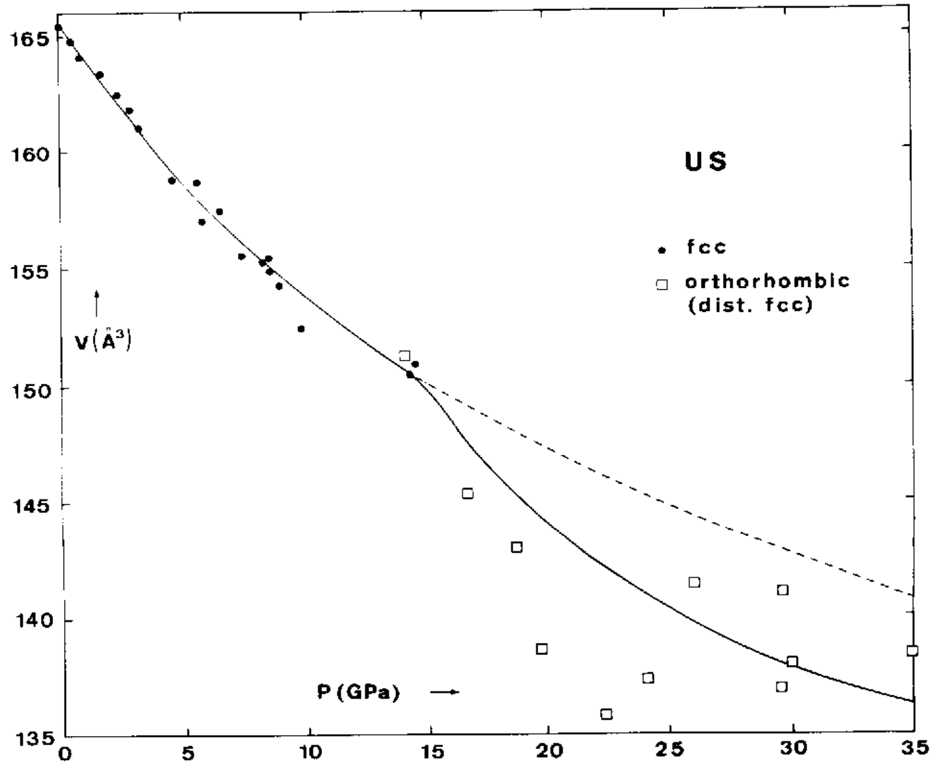
US
• fcc
□ orthorhombic (dist. fcc)
V(Å³)
P (GPa)
165
160
155
150
145
140
135
0
5
10
15
20
25
30
35

Fig. 4