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High pressure X-ray diffraction of cerium compounds in an improved diamond anvil cell

J. M. Leger

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Résumé. — On a obtenu des diagrammes de poudre par diffraction X sur des échantillons soumis à de hautes pressions produites dans une cellule à enclumes de diamant. L'alignement des deux diamants est obtenu grâce à la libre rotation des deux axes portant le piston et le cylindre. On discute les premiers résultats obtenus jusqu'à 25 GPa sur CeB_6 et CeTe . Le volume relatif de CeB_6 diminue régulièrement avec la pression et on ne trouve pas de différence par rapport aux résultats rapportés sur LaB_6 . Le volume de CeTe varie de façon anormale avec la pression et présente une transition de phase $\text{NaCl} \rightarrow \text{CsCl}$.

Abstract. — Powder X-ray diffraction patterns were recorded for samples submitted to high pressures in an improved diamond anvil cell where the alignment of the two diamonds is achieved by the free rotation of both axes bearing the piston and cylinder. First results on CeB_6 and CeTe up to 25 GPa are discussed. The relative volume of CeB_6 decreases smoothly with pressure and no difference with previously reported results on LaB_6 is noticed. The volume of CeTe shows an anomalous pressure dependence and a $\text{NaCl} \rightarrow \text{CsCl}$ phase transformation.

A diamond anvil cell has been designed for powder X-ray diffraction under high pressures. This cell is based on the lever-arm system of the NBS type [1] and includes the long piston cylinder assembly of the cell by Mao and Bell [2] but has also additional new features.

Force is produced by compressing a spring by terms of a screw and the applied load is magnified by a factor of two on being transmitted to the diamonds via the lever arm system. The essential feature is that the piston which bears the lower diamond and the cylinder retaining the upper diamond are both linked to the lever arms by two axes which are able to rotate freely and smoothly. A constant and perfect alignment of the piston and cylinder axes is so provided whatever are the heights of the diamonds or the thickness of the gasket. The two rotation axes also avoid the need of sliding of the piston relatively to the thrust block and no seizing has ever been observed. Many causes of cracking the diamonds are thus eliminated and no need of lapping the piston to the cylinder has been encountered. In the same way the spring and the screw are also linked to the lever arms through two rotation axes which provide a very smooth variation of the applied load without any displacement of the application point of the force on the lever arms due to sliding. The classical hemi-

sphere-plane geometry is used to secure centering and parallel alignment of the diamond faces (≈ 0.7 mm). The diamond seats are made of tungsten carbide; all the alignment screws are independent of the fixation ones. Routine work to 25 GPa is now performed but no attempt for higher pressures has yet been made.

The incident X-ray beam is produced by a molybdenum fine focus tube operated at 45 kV and 9 mA; Zr filtered radiation is used. A collimator made from two crossed slits 0.15 mm wide is located near the lower diamond. The 2θ diffraction angle allowed is 40° . A centring device is used to move the whole diamond anvil cell so that only the sample is subjected to the X-ray beam; no diffraction line due to the gasket is observed in the X-ray pattern. The film technique has been used. The upper diamond table to film distance is mechanically kept constant (≈ 23 mm) and corrections for variations of the gasket thickness are applied. The recording film is flat and shrinkage is measured by use of a marker of known length in contact with the film. The patterns were analysed with a low magnifying microscope (6 X or 18 X). With this device, good diffraction patterns are obtained within 24 hours.

The studied compound is mixed with the pressure marker and the pressure transmitting medium and then

placed into a 0.2 mm hole drilled in a X 750 Inconel fully hardened gasket. The pressure marker is NaCl or CsCl. Silicon grease is used as the pressure transmitting medium for the following reasons :

— it is chemically inert with samples which are extremely moisture sensitive;

— it is soft at normal pressure, solidifies very rapidly (0.3-0.4 GPa) but gives then only two strong diffraction lines (~ 6.70 and 3.56 Å) which progressively vanish ; above 2.5 GPa only the large d line remains which itself disappears completely around 6 GPa.

Early solidification does not introduce perturbatory effects in the pressure range of interest here in opposition to usual liquids which freeze in the 4-15 GPa range. In effect, using a solid pressure transmitting medium generates anisotropic stresses in the sample which lead to a larger apparent volume [3]. However at higher pressure these remain constant and their influence become weak and so the state equation of a solid has been here determined by following the procedure outlined by Kinsland [4].

The low pressure data (2-2.5 GPa with silicon grease) are discarded. A Birch or Murnaghan state equation is then fitted to the data with the initial volume as a third unknown parameter, the two other ones being the bulk modulus and its first pressure derivative at normal pressure. This procedure is only necessary when the bulk modulus of the sample is markedly higher than the bulk moduli of the pressure marker and pressure transmitting medium. Otherwise no difference between the calculated and true values of the initial volume is observed.

Results.

1. CeB₆. — The lanthanide hexaborides crystallize in the cubic structure with the Pm3m space group. The cell parameter of CeB₆ is 4.146 ± 0.005 Å in normal conditions. Under pressure the following diffraction lines were observed : (100), (110), (111), (200), (211), (300), (310) and sometimes the (210), (220), (311) and (321) of lower intensities. The standard deviation for the cell parameter varies from 0.007 to 0.013 Å and depends essentially on the time exposure. The pressure marker was NaCl in this case and the observed diffraction lines were as follows : (200), (220), (400) and (420). The observed deviation for the lattice constant of NaCl corresponds to a 0.3-0.4 GPa deviation for pressures around 10 GPa, which is probably of the order of the pressure anisotropy.

The bulk modulus of CeB₆ appears high and the above procedure has been used. A least square fit

Fig. 1. — Relative volumes of CeB₆ and CeTe as a function of pressure at room temperature. $\blacktriangle$ CeB₆, present work, $\bullet$ CeTe, present work, ———— LaB₆ (the dashed lines show values calculated using the B_0 and B'_0 from Ref. [5] and Ref. [6]).

to the data using the Murnaghan state equation yields then $B_0 = 166$ GPa and $B'_0 = 3.15$.

The uncertainties on this values are estimated to be about 5 GPa and 0.5 respectively. The volume compression of CeB₆ follows closely the results reported for LaB₆ [5, 6] but the values of the initial bulk modulus and first pressure derivative given above are more accurate because of the larger pressure range investigated and the better data fitting procedure used here.

2. CeTe. — The initial bulk modulus of CeTe is only 52.8 ± 4 GPa and the above procedure is no longer necessary; it increases very rapidly ($B'_0 = 13.6 \pm 2$). At 8 GPa a first order NaCl-CsCl crystallographic transition occurs. The structure of the high pressure phase has been ascertain by a run without any pressure marker. The volume change of CeTe with pressure has been interpreted [7] by a Kondo reentrant behaviour preferably to a back valence change by 0.3 at the transition.)

The X-ray technique used here (low power X-ray tube associated with a planar photographic detection) and the diamond anvil cell with its alignment device allow to obtain good quality X-ray diffraction patterns in the laboratory within reasonable time (24 h). Routine work to 25 GPa is presently performed and considerable extent of the maximum working pressure should be obtained due to the improvements brought in the design of the diamond anvil cell.

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