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High pressure behaviour of TmTe and EuO

S. Heathman[a], T. Le Bihan[a], S. Darracq[a], C. Abraham[a], D.J.A. De Ridder[a], U. Benedict[a],
K. Mattenberger[b], O. Vogt[b]

[a]*European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany*
[b]*Laboratorium für Festkörperphysik, ETH, Hönggerberg, CH-8093 Zürich, Switzerland*

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Abstract

The high pressure behaviour of TmTe and of EuO have been investigated up to pressures of 49 and 63 GPa respectively, using the energy dispersive X-ray diffraction technique and synchrotron radiation. TmTe shows a phase transformation at 8 GPa to a possible tetragonal structure. Above 35 GPa this structure undergoes a further distortion. EuO shows a normal compressibility curve leading up to an NaCl to CsCl type phase transition beginning at 47 GPa.

Keywords: TmTe; EuO; Diamond anvil cell; High pressure; Structure transformation

1. Introduction

An increase of the lanthanide valence from divalent to trivalent with applied pressure has previously been reported for TmTe [1] and EuO [2]. This phenomenon has already been observed in the case of SmS, SmSe and SmTe [1,3] and is attributed to a 4f to 5d electronic collapse. TmTe and EuO were studied under pressure using the most modern techniques available today at a synchrotron X-ray source to both confirm and extend the previous measurements.

2. Experimental details

2.1. Materials

TmTe was synthesised using the following method: thulium turnings and tellurium were heated in an evacuated and sealed quartz tube up to 700°C resulting in a fine black powder. Afterwards, this powder was pressed into a pellet and sealed under vacuum in a tungsten crucible which was kept at about 50°C below the melting temperature of the chalcogenide, i.e. around 950°C. Within several weeks, single crystals (cubic space group *Fm3m*) were grown by recrystallisation up to 1–5 mm^3.

EuO was prepared by direct reduction of Eu_2O_3 with metallic Eu. Stoichiometric amounts of Eu chips and Eu_2O_3 powder were sealed in a tungsten crucible. The crucible was heated in an electron beam furnace up to 1900°C. EuO single crystals of several millimetres edge length grew within 2 weeks.

The samples employed in our high pressure work were obtained by grinding these crystals to a fine powder. The room temperature–pressure lattice parameters of these materials are reported in Table 1 and are in good agreement with literature values.

2.2. High pressure studies

The compression studies were performed in a diamond anvil cell of the Syassen–Holzapfel type. Samples were loaded into a 200 μm hole drilled into a pre-indented Inconel gasket which was filled with silicone oil used as a pressure transmitting medium. A ruby splinter was also added along with the sample and was used to determine the pressure from the wavelength shift of the ruby fluorescence line using the non-linear pressure scale of Mao et al. [8].

Table 1
Lattice parameters of TmTe and EuO at ambient pressure

Compound	Lattice parameter *a* (pm)	Literature values (pm)
TmTe	634.6	633.7 [4], 633.8 [5], 635 [6]
EuO	514.5	514.4 [7]

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Experimental work was carried out at the EDS facility of the electron storage ring DORIS III of Hasylab, DESY, Hamburg (FRG) using the energy dispersive method. A collimated beam of 50 μm was defined by slits before the pressure cell was used as the X-ray source. The sample diffraction was collected through exit slits behind the pressure cell which led through a helium filled tube to a germanium detector approximately 1 m away also equipped with entrance slits. This set-up enables the best resolution to be obtained and, because of the intensity of the primary beam, good quality spectra could be collected for each pressure point in 15 to 20 min. Diffraction angles θ of 5.258° and 5.501° were used for TmTe and EuO respectively. In addition to the synchrotron measurements, data on TmTe was also collected at the Institute for Transuranium Elements using an energy dispersive set-up [9] which uses a double conical slit assembly to simultaneously collect diffraction data under two different angles ($\theta_1 \approx 5°$ and $\theta_2 \approx 7°$). According to the Bragg equation $2d \sin\theta = hc/E$, the energy E of a given set of lattice planes of spacing d decreases when θ increases. As the useful energy range is limited by the maximum voltage that can be applied to the X-ray tube, a given lattice will generate more diffraction lines in this range for $\theta = 7°$ than for $\theta = 5°$. On the contrary, the larger angle can shift some of the lines corresponding to large d values into the energy range where they are superseded by the intense characteristic fluorescence lines generated by the elements present in the sample. The spectra obtained at either angle thus give complementary information, which is of particular importance in the case of TmTe where the Tm and Te fluorescence lines fall within the energy range of particular interest for observing diffraction data. The exact values of the Bragg angles were determined using a UC standard in the exact configuration as was used for the chalcogenide samples. The lattice spacings were calculated as a function of the applied pressure for each sample using these calibrations and the energy dispersive diffraction data. For each pressure step, the lattice parameters and the relative volume V/V_0 were calculated. The $V(P)$ data were fitted to the Birch and Murnaghan equations of state [10–12] to obtain the bulk modulus B_0 and its pressure derivative B_0' (the subscript zero indicates ambient pressure).

3. Results and discussion

3.1. TmTe

The relative volume–pressure behaviour of three separate loadings of TmTe were studied up to 49 GPa in 39 steps of increasing pressure. The NaCl type phase found at ambient pressure was conserved up to 8 GPa where a phase transition started to occur which was completed at 12 GPa (Fig. 1). The high pressure phase has previously been indexed in an anti-NiAs type hexagonal structure [4]. Our high pressure spectra cannot be indexed using this structure, because, in particular, as can be seen in Fig. 1 the NaCl phase (200) reflection clearly splits into two separate peaks which do not correspond to the above structure. Owing to the difficulty in identifying all the high pressure peaks because of masking by fluorescence lines, spectra were also recorded in Karlsruhe using the double conical slit method. Angles of $\theta = 4.891°$ and 6.841° were used to give a clear view of all the peaks present in the high pressure phase.

The best indexation of the high pressure structure occurs using a tetragonal unit cell with lattice parameters $c_{\mathrm{tetragonal}}$ of about $\frac{1}{2}c_{\mathrm{cubic}}$ and $a_{\mathrm{tetragonal}}$ of about $a_{\mathrm{cubic}}/\sqrt{2}$. The tetragonal system has seven possible crystal systems comprising 68 space groups.

From the powder diagram only a limited number of

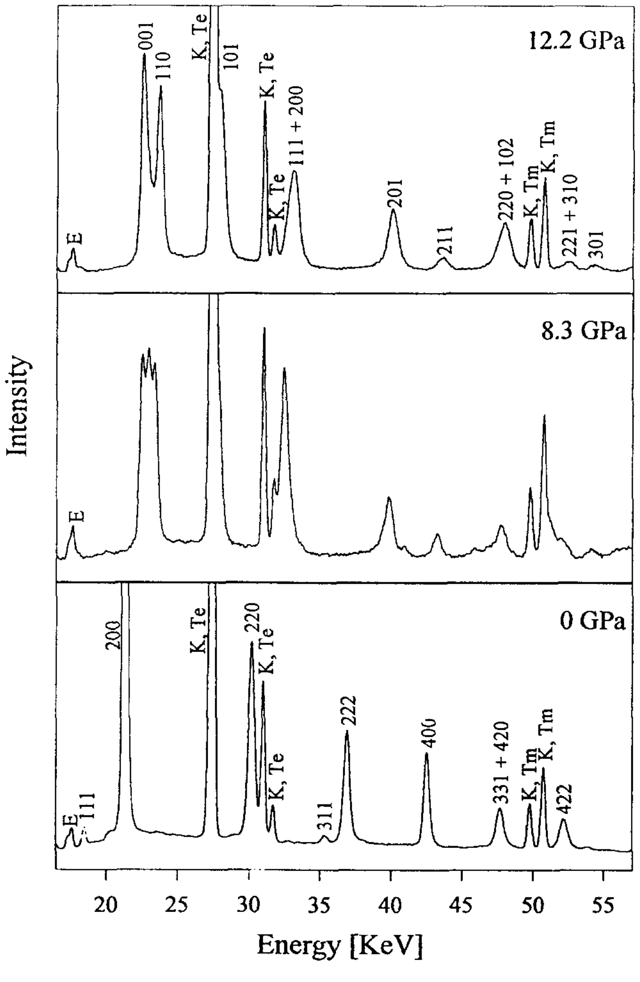

Fig. 1. Diffraction spectra of TmTe showing NaCl to tetragonal phase transition.

reflections are available from which a space group determination is not unambiguous. A crystal belonging to the tetragonal system can only have two possible Bravais lattices: primitive (*P*) or body-centred (*I*). Since there are a number of reflections for which the sum of the Miller indices is odd, the lattice has to be primitive and 19 possible space groups can be excluded.

The crystal just before the phase transition has four (TmTe) entities in the unit cell (i.e. $Z = 4$) and the atoms are in a special position with multiplicity equal to 4. The volume of the unit cell after the phase transition is reduced to about 25% of the volume at ambient pressure which means that $Z = 1$. From this it follows that the atoms have to be in a special position with multiplicity equal to 1. Only seven tetragonal space groups have special positions with multiplicity equal to 1: $P4$ (No. 75), $P\bar{4}$ (No. 81), $P4/m$ (No. 83), $P422$ (No. 89), $P4mm$ (No. 99), $P\bar{4}2m$ (No. 111), $P\bar{4}m2$ (No. 115) and $P4/mmm$ (No. 123). These seven possible space groups can be divided into two types: a first type consisting of $P4$ and $P4mm$ which have two special positions $0,0,z$ and $\frac{1}{2},\frac{1}{2},z$; the second type consisting of the five other space groups with four special positions 0,0,0; 0,0,1/2; 1/2,1/2,0 and 1/2,1/2,1/2. It should be noted that in the case of a single-crystal measurement an unequivocal space-group determination can only be through the least-squares refinement of the structure in the two and five candidate space groups respectively, and distinguishing between them through significance tests [13]. In the present case, with a limited data set of a powder diffractogram, no distinction can be made and the discussion will therefore be limited to both space group types.

If in the latter space group type one atom is placed at 0,0,0, the second atom has to be placed in one of the other three possible special positions. The special position $0,0,\frac{1}{2}$ can be excluded by the fact that the interatomic distance would only be 1.505 Å whereas the sum of the covalent radii is 2.92 Å (the minimum Tm–Te interatomic distance at ambient pressure is 3.173 Å). If the second atom is put at $\frac{1}{2},\frac{1}{2},0$ the calculated powder diffractogram shows two reflections which are questionable; moreover, the interatomic distance of 2.895 Å is less than the sum of the covalent radii. If the second atom is put at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ the interatomic distance is 3.263 Å, but in this case the calculated powder diffractogram shows a bad intensity profile for the reflections (201) and (001). These observations seem to give sufficient proof that the high pressure structure of TmTe does not crystallise in one of these five space groups.

In contrast to these five space groups which have only special positions in which all coordinates are fixed, the first space group type (i.e. $P4$ and $P4mm$) has one variable parameter z. The minimum interatomic distance occurs when both atoms have the same value for z. In this case the distance of 2.895 Å is less than the sum of the covalent radii and, moreover, the agreement between the observed and the calculated powder diffractogram is poor. If the interatomic Tm–Te distance is assumed to be equal to the sum of the van der Waals radii, the difference in z should be 0.13. A difference in $z \cong 0.24$ would correspond to the interatomic distance in the high pressure $Fm\bar{3}m$ structure just before the phase transition (2.981 Å at 6.4 GPa). The agreement between observed and calculated powder diagram is good if one atom is put at 0,0,0 and the second at $\frac{1}{2},\frac{1}{2},0.2$ which corresponds to an interatomic Tm–Te distance of 2.957 Å.

It might be argued that both $P4$ and $P4mm$ have only a low frequency of occurrence among the 230 different space groups for all compounds in general [14] or for lanthanides and actinides in particular [15]. However, these statistical data are mainly referring to crystal structure determinations at ambient pressures (and temperatures) so that it may well be possible that these space groups have a higher frequency of occurrence at higher pressures.

Upon the pressure-induced phase transition a volume collapse of just a few percent occurs. If it is assumed that during the phase transition there is only a decrease in crystallographic symmetry (i.e. a phase transition of the second order), there should exist a chain of maximal (non-)isomorphic subgroup starting with $Fm\bar{3}m$ (space group of TmTe at ambient pressure) and leading to space group $P4$ or $P4mm$. It is indeed possible to find such a chain:

$$\begin{tikzcd}
Fm\bar{3}m \arrow[r] & I4/mmm \arrow[r] & P4/mmm \arrow[r] \arrow[d] & P4/m \arrow[r] & P4 \\
 & & P4mm & &
\end{tikzcd}$$

The mechanism would thus consist of four (→$P4$) or three (→$P4mm$) consecutive second order phase transitions.

The theoretical lines as calculated by ENDIX [16] for this structure are shown superimposed on the diffraction spectra at 12 GPa in (Fig. 2) and fit extremely well over the whole energy range. The tetragonal lattice parameters at 12 GPa are $a = 408$ pm and $c = 297$ pm. Some ambiguity exists with regard to the intensities obtained, particularly for the two lower order reflections. Owing to the small sample volume and possible preferred orientation the intensities obtained in high pressure spectra can only be regarded as approximate. The calculated volume of this high pressure structure at the phase transition is marginally lower than that of the NaCl phase just before, and indicates that it is of a second order nature.

At a pressure of 35 GPa the (101) reflection develops a shoulder which increases in intensity up to the

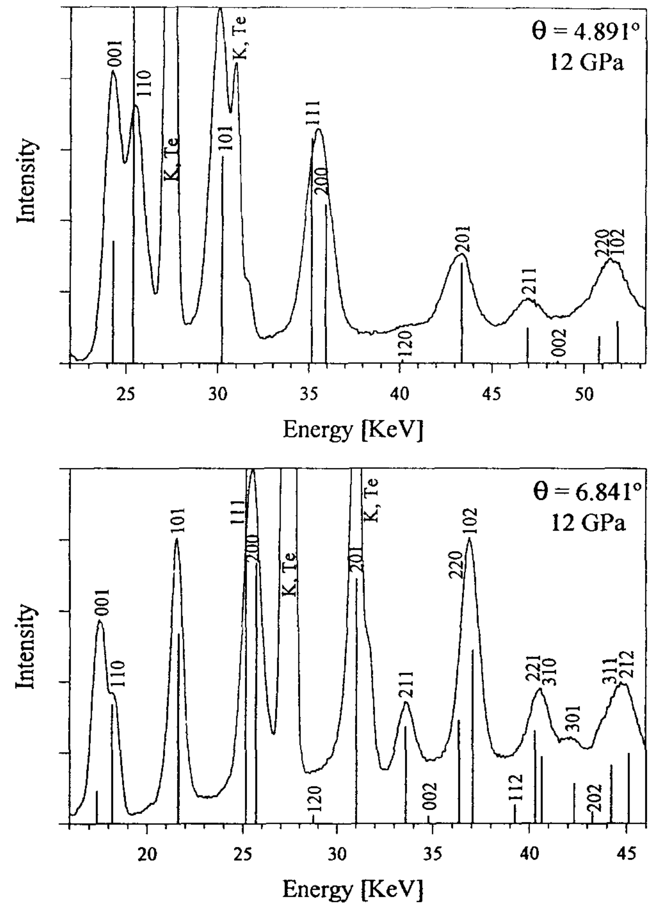

Fig. 2. TmTe at 12 GPa and $\theta = 4.891°$ and 6.841° with superimposed theoretical patterns.

maximum pressure of 49 GPa as shown in (Fig. 3). This distortion of the high pressure phase has yet to be explained due to the poor intensities of the higher order reflections present at this pressure. The compressibility curve before the phase transition is anomalous due to a 4f to 5d electronic collapse. The effect is less obvious than for SmS, SmSe and SmTe

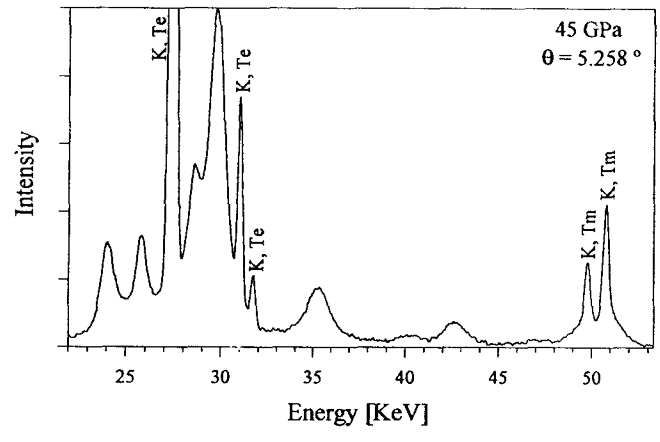

Fig. 3. Distorted high pressure structure of TmTe at 45 GPa.

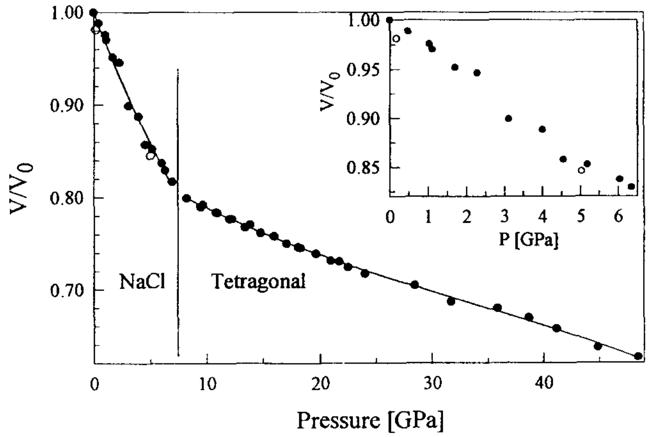

Fig. 4. Relative volume of TmTe as a function of pressure.

[3,4] although still noticeable, as can be seen in (Fig. 4).

All the transformations observed were found to be reversible upon releasing the pressure.

The bulk modulus B_0 and its pressure derivative B_0' were determined for the low pressure phase by fitting the pressure–volume data to the Birch and Murnaghan equations of state and gave values of Birch $B_0 = 30.0$ GPa, $B_0' = 1.7$ and Murnaghan $B_0 = 31.6$ GPa, $B_0' = 0.6$.

3.2. EuO

EuO was ground to a fine white powder and studied up to 63 GPa in 22 steps of increasing pressure. In contrast to previous measurements [2] no Eu^{2+} to Eu^{3+} valence transition was observed in the 28 to 40 GPa region. Instead, a smooth compression curve was obtained up until 47 GPa where a phase transformation to a CsCl type structure began. This transformation was accompanied by an 8% change in volume and was not quite complete at 63 GPa, the highest pressure attained. Data were fitted to the Birch and Murnaghan equations of state and gave values of Birch $B_0 = 114$ GPa $B_0' = 2.8$ and Murnaghan $B_0 = 118$ GPa $B_0' = 2.2$ for the bulk modulus and its pressure derivative respectively. These results are in good agreement with the ones found by Jayaraman [2]. Fig. 5 shows the almost complete high pressure CsCl phase at 63 GPa and the compressibility curve for EuO.

4. Summary

A new tetragonal high pressure structure has been proposed for TmTe above 8 GPa using the space groups *P*4 or *P*4*mm* with atoms at 0,0,0 and 1/2,1/2,0.2 which fits well to the experimental results obtained. Above 35 GPa a further distortion of this

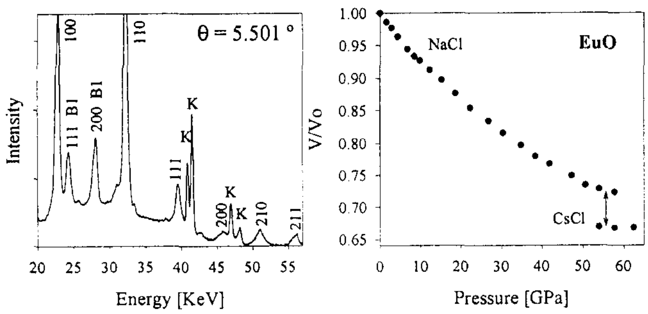

Fig. 5. (a) Diffraction spectrum of EuO CsCl-phase at 63 GPa, fluorescence lines are marked with K. (b) Relative volume of EuO as a function of pressure.

structure occurs progressively which has yet to be identified.

Measurements on EuO have shown no indication of a previously reported valence transition but confirm the NaCl to CsCl type phase transition above 47 GPa. A difference in stoichiometry between our EuO sample and those used in previous experiments may be a possible cause for this disagreement due to slight Eu_2O_3 impurities, although this has yet to be confirmed.

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