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Anomalous behavior of CeTe under high pressures

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The compression curve of CeTe up to 25 GPa was measured by x-ray diffraction in a diamond anvil cell. Below 8 GPa, CeTe maintains the NaCl-type structure with a bulk modulus and its first pressure derivative equal to 52.8 GPa and 13.6, respectively. These values are anomalous and indicate the presence of an extra electronic contribution to the free energy. At 8 ± 1 GPa, the NaCl-type structure transforms into a CsCl type and the increase of the cerium-tellurium distance is larger than expected from the increase of the coordination number. At higher pressures, up to 25 GPa in the CsCl phase, the bulk modulus does not increase with pressure, and so an additive contribution to the lattice one is again present. The volume variations of CeTe with pressure are discussed assuming a valence change of the cerium ion or a strong enhancement of the Kondo interaction under pressure.

I. INTRODUCTION

Rare-earth monochalcogenides including monoxides which are known in this last case only from lanthanum to europium in addition to ytterbium, crystallize in a face-centered-cubic (fcc) structure of the NaCl type.[1,2] When the rare-earth element is trivalent, the volumes of the corresponding monochalcogenides show the usual lanthanide contraction and the compounds have metallic properties; for example, LaO, LaS, LaSe, and LaTe have electrical resistivities at room temperature of the order of 250 $\mu\Omega$ cm.[2,3] When the rare-earth element is divalent (Sm, Eu, Yb, and Tm), the volumes are larger by about 15% and semiconducting behaviors are then found: For example, the $4f$-$5d$ band gaps of YbO, YbS, YbSe, and YbTe are, respectively, 0.32, 1.1, 1.4, and 1.7 eV.[4] Under pressure, these divalent rare-earth monochalcogenides often exhibit a volume collapse without any structural transformation which can be discontinuous (SmS) or continuous (SmSe) and is associated with a semiconductor-to-metal transition.[2] The valence of the rare-earth element increases by less than one unit during this transition and the true trivalent state will be reached only far above.

In metallic cerium, a transition from the trivalent state to a nonmagnetic state of smaller volume is also known to occur above 1 GPa (1 GPa = 10 kbar). Therefore, in cerium monochalcogenides which are already metallic in normal conditions, a similar transition may be induced by pressure.

Such a transition has been effectively observed in CeS (Ref. 5) (fcc, $a = 5.767$ Å); a discontinuous collapse of the volume by 4.5% without any structural change occurs at 12.5 GPa and was attributed to a partial valence change of the cerium ion from a true trivalent state toward a tetravalent state.

In normal conditions, CeTe has a fcc structure of NaCl type with a lattice constant of 6.360 Å. This value indicates that cerium is in the trivalent state or very close to, as no deviation from the usual lanthanide contraction is observed. This trivalent state of the cerium is also clearly shown by L_{III} absorption edge measurements.[6]

II. EXPERIMENT

Single crystals were obtained by direct reaction of the elements in a molybdenum crucible sealed under an argon atmosphere and heated in a vacuum furnace. The temperature was first quickly raised up to 2000 °C and then slowly reduced ($\simeq$4 °C/h). Single crystals, typically $2\times2\times3$ mm^3, were cleaved from the crystallized mass. This technique avoids any contamination originating in a low-temperature treatment in a silica tube. The final composition was checked by microprobe and plasma emission analysis. The samples were always found to be very close to stoichiometry ($\pm2\%$). All the handling of elements, crystals, and samples were made in a glove box under an argon atmosphere dynamically epurated from water and oxygen contaminations.

The samples were obtained by crushing small single crystals and a fine powder of sodium or cesium chloride, used as pressure standard, was added. Acting as the pressure transmitting medium all over the investigated pressure range (0–25 GPa), silicon grease was then mixed with. In one run, it was replaced by silicon oil but the results were identical. The usual 4:1 methanol-ethanol mixture was not selected as the samples are extremely moisture sensitive.

High pressures were generated with a diamond anvil cell especially designed and built in our laboratory. The sample was placed in a 0.2-mm hole made in an Inconel X750 gasket which was fully hardened. A finely collimated x-ray beam 0.15 mm in diameter was directed on the sample along the pressure axis. A fine-focus molybdenum x-ray tube was operated at 50 kV and 8 mA and the radiation was partially filtered with a zirconium foil ($I_{K\beta}/I_{K\alpha}\simeq\frac{1}{100}$). The maximum angular dispersion is $2\theta=40°$. The diffraction pattern was recorded on a planar photographic film. This geometry is easier to handle for precise alignment and, in addition, the sample to film distance can be modified if necessary. In these experiments it was set at 25 mm. The distance from the table of the rear diamond to the front plane of the recording film was mechanically adjusted to be constant within 0.02 mm. The compression of the diamond with pressure was not taken into account (a few micrometers) but corrections were applied for the variations of the thickness of the gasket by reference to previous runs. With such a geometry, the exposure time was less than 24 h; diffraction patterns were analyzed with a low magnifying microscope (6× or 18×).

The pressure was calculated from the volume compression of the NaCl or CsCl standards using the equations of state as proposed by Decker.[7] When CsCl was added to the sample, its cell parameter was determined from the (100), (110), (211), and one of the (111), (200), or (210) lines. Fewer lines could be measured for NaCl because of some overlaps of the sample and marker lines; the (220) reflexion was used in every case in addition to one of the (111), (200), and (222) lines depending on the pressure value.

III. RESULTS

The variation of the volume of CeTe with the applied pressure is given in Fig. 1. Up to about 8 GPa, CeTe remains in a NaCl-type structure. The diffusion factors of cerium and tellurium being nearly equal, only the reflexions with even Miller indices can be observed, namely the (200), (220), (222), (400), and (420) lines. Above 8 GPa, the diffraction pattern cannot be attributed to the NaCl-type structure but can be indexed by assuming a cubic CsCl-type structure. The diffraction lines of both phases coexist over a small pressure range, between 7.5 and 8.5 GPa. Above, only the lines of the CsCl-type structure are observed. When no pressure marker is used, the (110), (200), (211), (220), and (310) lines are clearly recorded. Unfortunately, in this high-pressure range, the lattice parameters of CeTe and CsCl remain equal within 0.03 Å so CsCl cannot be used as a pressure standard. Replacing CsCl by NaCl still leaves some overlapping lines, and so only the (110) and (211) lines of CeTe could be used up to 18.5 GPa. Above this pressure, the (220) and (200) reflexions become enough separated from the NaCl lines to be used. When the pressure is released from the high-pressure range, the CsCl→NaCl transformation takes place around 3 GPa.

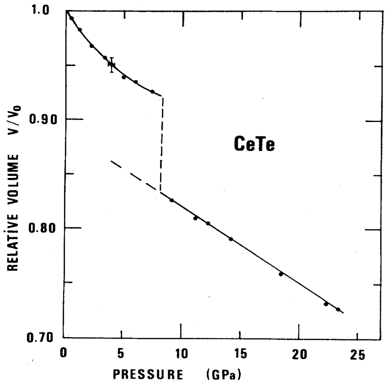

FIG. 1. Relative volume of CeTe vs pressure at room temperature.

IV. DISCUSSION

A. Compression of CeTe in the NaCl phase ($P<8$ GPa)

In this pressure range ($P<8$ GPa) the volume of CeTe decreases smoothly and the experimental data can be tentatively represented by a Murnagham equation of state[8]

$$P=\frac{B_0^{\rm I}}{B_0'^{\rm I}}\left[\left[\frac{V}{V_0^{\rm I}}\right]^{-B_0'^{\rm I}}-1\right],$$

where $B_0^{\rm I}$ is the bulk modulus of the NaCl phase at normal pressure, $B_0'^{\rm I}$ is its first pressure derivative, $V_0^{\rm I}$ is the initial volume, and V is the volume at the pressure P. A least-squares fit of the data yields $B_0^{\rm I}=52.8\pm4$ GPa and $B_0'^{\rm I}=13.6\pm2$. (See Table I.)

TABLE I. High-pressure data for CeTe. Lattice parameter at some pressures, bulk modulus at normal pressure, and its pressure derivative B_0' in the Murnagham state equation, calculated relative volume of the CsCl to the NaCl phase at normal pressure.

P (GPa)	a (Å)	Structure	B_0 (GPa)	B_0'	$\frac{V_0^{\rm II}}{V_0^{\rm I}}$
0	6.360±0.01	NaCl	52.8±4	13.6±2	0.890
8	6.192±0.01	NaCl			
8	3.773±0.01	CsCl	130 ±10	−1.3±0.3	
23.3	3.604±0.01	CsCl			

In ionic compounds the bulk modulus scales with specific volume V and ionic charges. In a particular class such as the divalent rare-earth or alkaline-earth monochalcogenides, an empirical relationship, $B_0 \propto V^{-\alpha}$ where α is a constant close to 1.15, is found to hold[4,9] (Fig. 2).

For trivalent rare-earth monochalcogenides which are then metallic, it has been argued that the electronic contribution to the bulk modulus must be very small and so a similar behavior is expected.[9] We may note that only rare-earth compounds with no $4f$ electrons (LaS, LaSe, and LaTe) or far away in the rare-earth series (ErS) verify this relationship (Fig. 2), but the cerium compounds do not. This discrepancy is also observed for the rare-earth monopnictides. In a log-log plot, the bulk moduli of CeS and Ce monopnictides, which are all also fcc, vary linearly with the molar volumes. From these experimental values, the bulk modulus of CeTe can be estimated to be about 100±10 GPa. Moreover, typical value for $B_0'^{\mathrm{I}}$ is 4±1.5 for ionic or metallic compounds. These values are quite different from the experimental values we measured ($B_0^{\mathrm{I}}=52.8$ GPa, $B_0'^{\mathrm{I}}=13.6$). This demonstrates an anomalous behavior of CeTe under pressure.

The large volume reduction of CeTe, at least at low pressure in comparison with a normal rare-earth compound indicates clearly that an additional electronic contribution is present in the free energy. The most straightforward explanation for this additional term is to consider that pressure induces a continuous change of the valence of the cerium ions. The high value of the derivative $B_0'^{\mathrm{I}}$ shows that most of this electronic transition takes place in the lower-pressure range, below 5 GPa. At 8 GPa the difference between the variations of the volume from the normal pressure for CeTe and a normal rare-earth compound calculated following the Murnagham equation with $B_0^{\mathrm{I}}=100$ GPa and $B_0'^{\mathrm{I}}=4$ is approximately equal to 2%. This value is smaller than the value of $\Delta V/V$ equal to 4.5% found in CeS at the first-order transition occurring at 12.5 GPa (Ref. 5), where the corresponding valence change was estimated to be about 50%. However, with the ionic radius of sulfur being significantly smaller than the tellurium radius (1.84 Å instead of 2.21 Å), a larger value of $\Delta V/V$ is expected in CeS for a similar valence change. As we shall see later, a detailed comparison between the volume jumps of CeTe and PrTe leads to a valence of 3.3 at the critical pressure.

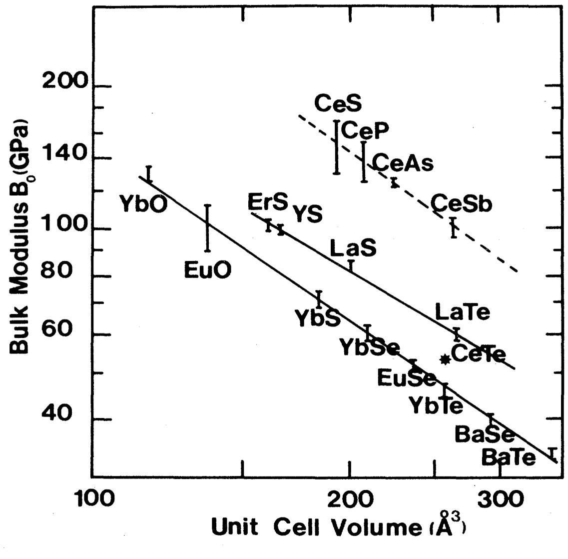

FIG. 2. Bulk-modulus behavior with unit-cell volume (log-log scale) for divalent and trivalent rare-earth or alkaline-earth monochalcogenides and cerium monochalcogenides or monopnictides.

B. NaCl-CsCl transformation

From our measurements it clearly appears that CeTe undergoes a sharp discontinuous phase transition from a NaCl- to a CsCl-type structure at about 8±1 GPa. The hysteresis found when pressure is released from the high-pressure range is another evidence of the first-order nature of this transformation. The relative volume change at the transition is 8.5%; this value is significantly smaller than found for the similar compound PrTe (11.5%) which undergoes the same crystallographic transformation at 9 GPa.[10]

The variation of the coordination number from 6 in the NaCl structure to 8 in the CsCl structure leads to an increase of the cerium-tellurium distance from 3.10 to 3.27 Å ($\frac{1}{2}a_{\mathrm{NaCl}}$ to $\sqrt{3/2}a_{\mathrm{CsCl}}$), which can be interpreted as an increase of the cerium radius by 0.17 Å as the anionic radius can be taken as independent of the crystal structure.[11] This variation of the effective cerium radius is too large to come only from the change of the coordination number because, from Shannon and Prewitt,[11] only an increase of 0.11 Å can take place at this crystallographic transition. Moreover, such a difference is not found in PrTe for which the increase of the ionic radius of praesodymium was measured to be 0.14 Å (Ref. 10), in agreement with the calculated value, 0.13 Å. Therefore we may infer that the size of the cerium ion is significantly larger in the CsCl phase than in the NaCl phase; a possible explanation could be a variation of the actual valence of the cerium ion.

Assuming a linear relationship between valence and lattice parameter it is possible to give an estimate of the valence or, at least, its variation at the transition. According to a Vegard's law, the variation of the cerium radius at the transition is given by

$$\begin{aligned} r^{3+y}_{\mathrm{Ce^{VIII}}} - r^{3+x}_{\mathrm{Ce^{VI}}} &= 0.17\ \text{Å} \\ &= r^{3+}_{\mathrm{Ce^{VIII}}} - r^{3+}_{\mathrm{Ce^{VI}}} + x(r^{3+}_{\mathrm{Ce^{VI}}} - r^{4+}_{\mathrm{Ce^{VI}}}) \\ &\quad - y(r^{3+}_{\mathrm{Ce^{VIII}}} - r^{4+}_{\mathrm{Ce^{VIII}}})\ , \end{aligned}$$

where $r^{3+}_{\mathrm{Ce^{VI}}}=1.034$ Å, $r^{3+}_{\mathrm{Ce^{VIII}}}=1.14$ Å, $r^{4+}_{\mathrm{Ce^{VI}}}=0.85$ Å, $r^{4+}_{\mathrm{Ce^{VIII}}}=0.97$ Å. x and y are the proportions of the 4+ state in the NaCl and CsCl phases, respectively; r_{Ce} is the ionic radius of cerium with different coordination numbers (roman figure) and oxidation states (superscript). The values from Shannon and Prewitt[11] have been used except for $r^{4+}_{\mathrm{Ce^{VI}}}$ which is quoted as unreliable and has then been obtained by substracting 0.12 Å to $r^{4+}_{\mathrm{Ce^{VIII}}}$ which is the usual radius variation due to a decrease by two of the coordination number.[11]

So we deduce $x-y=+\frac{1}{3}$. Then the cerium valence *decreases* by about 0.3 when CeTe undergoes the NaCl$\rightarrow$CsCl phase transition leading to a reentrant valence behavior. It directly follows that just before the transition the actual valence of cerium is at least 3.3.

In ionic compounds the pressures needed to induce structural transitions increase when the cation radii decrease. This applies particularly to divalent rare-earth monotellurides. For SmTe and EuTe the NaCl-CsCl phase transformation occurs at about 10 GPa, but it has not been observed in YbTe up to 30 GPa.[2]

The metallic tellurides such as CeTe or PrTe undergo also the NaCl-CsCl crystallographic transformations and the threshold pressures also increase when the sizes of the unit cell are reduced: It occurs at 8 GPa for CeTe but at 9 GPa for PrTe.[10] These transition pressures are much lower in metallic rare-earth monotellurides than in ionic semiconducting tellurides of same lattice constant: YbTe and CeTe have indeed the same lattice parameter (6.36 Å), but the latter is metallic and the transformation pressure is reduced to 8 GPa.

This lowering of the NaCl-CsCl transition pressure in metallic tellurides can be evidenced by considering a thermodynamic cycle involving four different forms (metallic or ionic bonding in the NaCl and CsCl structures). Assuming that the ratio of the dissociation energies of the metallic or ionic forms found for monoxides[1] applies also here, a decrease by about 30 GPa for the metallic NaCl-CsCl transition pressure is obtained which seems to account well for the experimental results.

C. Compression of CeTe in the CsCl phase ($P>8$ GPa)

The smooth compression curve in this higher-pressure range ($P>8$ GPa) can also be tentatively fitted by a Murnagham state equation which has now a third unknown parameter V_0^{II}, the volume the CsCl phase would have at normal pressure. We then obtain, by a least-squares fit, $B_0^{\mathrm{II}}=130$ GPa, $B_0'^{\,\mathrm{II}}=-1.3$, and $V_0^{\mathrm{II}}/V_0^{\mathrm{I}}=0.890$. The first pressure derivative $B_0'^{\,\mathrm{II}}$ of the bulk modulus is negative and not in agreement with a normal behavior for which B' is positive and close to four. This anomalous behavior could be ascribed to a continuous increase of the valence under pressure as in the NaCl structure but nonlinear effects are less pronounced as cerium ions have more space in the CsCl structure, the first neighbors being further apart. In order to get some idea about the electronic contribution to the bulk modulus, we choose the following values for a normal CeTe with a CsCl lattice:

$$\frac{V_0^{\mathrm{II}}}{V_0^{\mathrm{I}}}=0.885\ ,$$

which is the value found for PrTe where no electronic transition was detected;

$$B_0'^{\,\mathrm{II}}=+4\ ,$$

which is the normal value for rare-earth monochalcogenides. These values lead to about 105 GPa for B_0^{II} in order to get the observed volume at the transition pressure of 8 GPa. Then the volume difference at 25 GPa coming from the electronic contribution is about 2.5% of the same order of magnitude than that found in the NaCl phase.

V. CONCLUSION

We have shown that CeTe exhibits a quite unusual behavior when high pressure is applied which cannot be understood by assuming that cerium is a normal trivalent rare-earth ion. The bulk modulus B_0^{I} of the NaCl phase has a too low value when compared with other cerium compounds and its first pressure derivative $B_0'^{\,\mathrm{I}}$ has, on the contrary, a much larger value than usually found. These two features are displayed in monochalcogenides when the rare-earth element is in an intermediate valence state and undergoes a continuous valence change toward a higher valence state with a smaller volume.[12]

In CeTe we can also invoke a similar valence change with pressure; the valence variation has been determined from the values of the cerium-tellurium distances in both NaCl and CsCl phases at the transition. Assuming a Vegard's law, a minimum value of 3.3 has been calculated for the valence in the lower-pressure phase just prior to the transition. Such a procedure leads to an overestimate[13] of the valence in comparison with taking a linear relationship between the bulk modulus and the valence. It is worth noticing that this value of the valence is commonly found in many cerium compounds. Anyway, to get such a valence change with such a relatively small pressure, CeTe must be at normal pressure already in an intermediate-valence regime or very close to. Such a conclusion is difficult to accept because neutron diffraction experiments have shown that CeTe is magnetic at low temperatures and orders antiferromagnetically below $T_N\simeq 2$ K with a type-II structure. Moreover, the value of the magnetic moment was found to be only $0.2\mu_B$ which is much smaller than the moment expected for a Γ_7 doublet ground state ($0.7\mu_B$).[14,15] Another possible explanation is to consider that this moment reduction is actually induced by a Kondo effect and then CeTe would be just at the borderline between a mixed and a pure Kondo state.[16] Then the high-pressure results can be understood by an increase of the Kondo temperature with pressure according to Lavagna *et al.*[17] and Allen *et al.*[18] Indeed they describe the γ-α transition in cerium compounds as being due to the disappearance of magnetism associated with a very high Kondo temperature and not to a valence change. In a Kondo lattice, the Kondo exchange interaction J is strongly enhanced by a volume decrease and then the Kondo temperature must increase very largely with pressure as it depends exponentially on J. Actually, this Kondo coupling gives a negative contribution to the bulk modulus and a first-order transition can result at low temperatures; however, above a critical temperature the transition becomes continuous. This can be an interpretation for the experiments reported here about CeTe. At low pressures the bulk modulus B is significantly reduced but its pressure derivative is very high so that B increases very rapidly with pressure and a continuous volume decrease takes place. No isostructural first-order transition is then found which indicates that the critical temperature in CeTe would be below room temperature. In the NaCl low-pressure phase the transition could be similar to the γ-α transition in pure cerium above the critical temperature of 550 K.

So under high pressures we may infer the existence of a first-order transition at low temperatures, and, in addition, a reduction of the magnetic moment associated with the increase of the Kondo coupling would be observed in the NaCl phase by neutron diffraction experiments.

The NaCl lattice becomes unstable under high pressures as shown by the NaCl-CsCl transitions observed in rare-earth tellurides and especially in PrTe. This structural transition is also observed in CeTe but the volume discontinuity is significantly smaller than in PrTe, indicating a larger cerium ionic radius in the high-pressure CsCl phase. In this phase the cerium ions have more space to extend and the experimental results can be accounted for by assuming that the cerium valence goes back by 0.3. Another possible explanation is that the Kondo effect responsible for the anomalous volume decrease in the NaCl phase is strongly reduced at the transition leading then to the observed relative volume change. A reentrant behavior should be observed at the transition, but again the increase of the Kondo coupling with pressure would take place in the CsCl phase giving a negative contribution to the bulk modulus. This is effectively what is observed as the bulk modulus decreases slightly with pressure instead of increasing.

Pressure experiments have shown that cerium in CeTe is not a normal trivalent rare-earth ion already at normal pressure. The assumption of CeTe being in a mixed Kondo regime, close to the instability region, is consistent with the observed behavior; however, a valence change cannot be discarded by pressure-volume measurements.

Note added in proof. Recent values for the bulk modulus of CeAs (Ref. 19) and CeSb (Ref. 20) are considerably lower than previously published and come close to the trivalent rare-earth monochalcogenide line. However, the bulk modulus of CeTe is much lower than expected from CeS and is also lower than the bulk modulus of LaTe. In addition, the B' value being very high and anomalous, all the above discussion stays valid.

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