Pressure-induced valence transition in TmSe: An x-ray-diffraction study

D. Debray
*Laboratoire Léon Brillouin, Centre d'Etudes Nucléaires de Saclay,
91191 Gif-sur-Yvette, France*

A. Werner
Max Planck Institut für Festkörperforschung, 7000 Stuttgart, West Germany

D. L. Decker
Brigham Young University, Provo, Utah 84601

M. Loewenhaupt and E. Holland-Moritz
Institut für Festkörperforschung, Kernforschungsanlage, 5170, Jülich, West Germany
(Received 16 November 1981)

The pressure-volume relationship of stoichiometric TmSe has been investigated as a function of pressure up to 29 GPa by energy-dispersive x-ray-diffraction technique at room temperature. The results show a continuous valence change of Tm from the intermediate-valence state to a nearly trivalent state as the pressure reaches 5 GPa. The process of valence transition is, however, slowed down or briefly interrupted at around 2.5 GPa. A small lattice distortion apparently takes place at 10 GPa.

It is well known that nearly all monochalcogenides of the rare-earth elements Sm, Tm, and Yb show a pressure-induced semiconductor-metal transition due to the partial promotion of a $4f$ electron of the rare-earth ion into the $5d\,6s$ conduction-band states.[1] The valence state of the rare-earth ion thus changes from 2 + to intermediate, and under high pressure attains a value close to 3 +.[2,3] Since the ionic radius of the rare earth depends on its valence state, such a valence change is reflected in the pressure-volume behavior. One can thus study possible pressure-induced valence changes by investigating the pressure-volume relationship. In this paper, we report[4] the first room-temperature measurements up to 29 GPa of the pressure-volume relationship of TmSe, a well-known intermediate-valence (IV) compound in which Tm has a valence ~ 2.6 at atmospheric pressure.[5] The aim of the present study was to investigate the elastic behavior of TmSe, compare it to the known behaviors of other rare-earth monochalcogenides, and look for a possible pressure-induced valence change of Tm.

Previous magnetic measurements on TmSe have led to conflicting conclusions as to the effect of pressure on the valence state of Tm. Guertin et al.[6] concluded from magnetization measurements that the valence state of Tm changes as soon as pressure is applied and predicted complete crossover to the trivalent state for a pressure $P \gtrsim 2$ GPa. Chouteau et al.,[7] on the other hand, have reported magnetic susceptibility measurements and found no change in the valence state up to their maximum pressure of 0.8 GPa. Our results reported in this report give, for the first time, clear evidence of a continuous valence change of Tm, induced by pressure, from the IV state all the way to a nearly trivalent state. We have also observed an abnormal stiffening of the lattice, centered at about 2.5 GPa.

A polycrystalline sample of TmSe was prepared by the standard technique and checked by x-ray and neutron powder diffraction measurements. These checks showed that the sample was free from any secondary impurity phases and had the cubic NaCl-type crystal structure, characterized by a lattice parameter of 5.705(4) Å. It orders antiferromagnetically in the type-I structure with a Néel temperature of 3.30(2) K and has a saturation magnetic moment equal to $1.87(10)\mu_B$ per Tm ion. The sample can thus be characterized as stoichiometric or very nearly so. Diffraction spectra of the sample in powder form were recorded as a function of pressure up to 29 GPa by the

energy-dispersive x-ray diffraction technique at room temperature. A gasketed diamond-anvil cell was used to generate pressure which was measured from the ruby R luminescence line shift. In different pressure runs a 4:1 methanol:ethanol mixture and silicon grease were, respectively, used to cover the pressure ranges $0-9$ and $0-29$ GPa. The observed width of the ruby line showed that the pressure was hydrostatic up to about 20 GPa. The strong (200), (220), and (311) diffraction peaks were used to determine the lattice parameter as a function of pressure.

Figure 1 shows the reduced volume V/V_0 as a function of pressure, where V is the unit-cell volume at pressure P and V_0 that at zero pressure. V and V_0 were calculated from the experimentally observed lattice parameters. We have found no evidence for a distinct structural phase transition up to the maximum pressure of 29 GPa. It should, nevertheless, be noted that the uncertainty in the V/V_0 data in the pressure range $P > 10$ GPa is nearly constant and three times larger than that for the range $P < 8$ GPa. This appreciable difference in the standard deviations of the data in the two pressure ranges possibly reflects a small distortion of the NaCl lattice for pressures greater than 10 GPa.

To get information about the elastic behavior of TmSe we have calculated the instantaneous bulk modulus B as a function of pressure. This is shown in Fig. 2. Values of B were obtained from a second-order polynomial fit of the experimental V/V_0 data shown in Fig. 1. The fitting was carried out in segments of m consecutive data points

$(m=6,7,8)$ such that the nth segment $(n=1,2,3,\ldots)$ contained from the nth up to the $(n+m-1)$th data point. The bulk modulus is found to behave linearly up to about 2 GPa and then rise rapidly. This is followed by an abnormal softening at $P \sim 2.5$ GPa. Finally, beyond 5 GPa the bulk modulus regains linear behavior with a much smaller slope.

Neglecting, as a first step, the anomalous lattice stiffening centered around 2.5 GPa, one can distinguish in Fig. 2 two pressure regions with different behavior of B: (I) $P < 5$ GPa and (II) $P > 5$ GPa. In both these regions B varies almost linearly with pressure, but with different slopes, and can be expressed as

$$B(P) = B_0 + B_0' P \ . \tag{1}$$

B_0 and B_0' for the two pressure regions could be obtained directly from Fig. 2 and are as follows: $B_0^{\mathrm{I}} = 39(2)$ GPa, $B_0'^{\mathrm{I}} = 12(2)$ and $B_0^{\mathrm{II}} = 95(4)$ GPa, $B_0'^{\mathrm{II}} = 2.6(3)$. We have also fitted the V/V_0 data in these two pressure regions with the first-order Murnaghan equation of state[8]:

$$P = \frac{B_0}{B_0'} \left[\left[\frac{V_0}{V} \right]^{B_0'} - 1 \right] , \tag{2}$$

which is valid for a linear behavior of B as given by Eq. (1). The fitting was done in the range $0-1.6$ GPa for region I and $10-29$ GPa for region II. Note that in region I, B_0 and B_0' are fit parameters and V_0 $(=V_0^{\mathrm{I}})$ is the actual unit-cell volume at atmospheric pressure. For region II, however, V_0 $(=V_0^{\mathrm{II}})$ is the zero-pressure unit-cell volume of TmSe in the state characteristic for
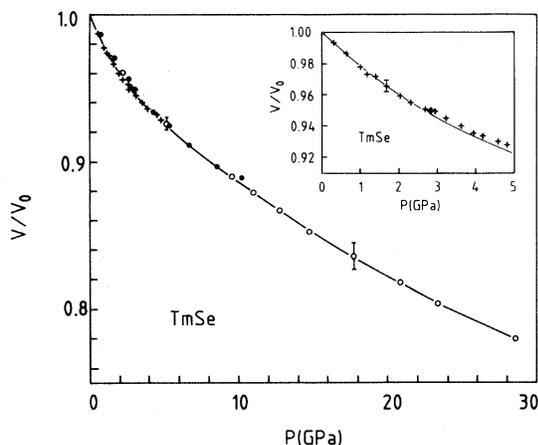

FIG. 1. Pressure-volume data of stoichiometric TmSe at room temperature. Different symbols indicate the data of different runs. The solid line is an eye guide.
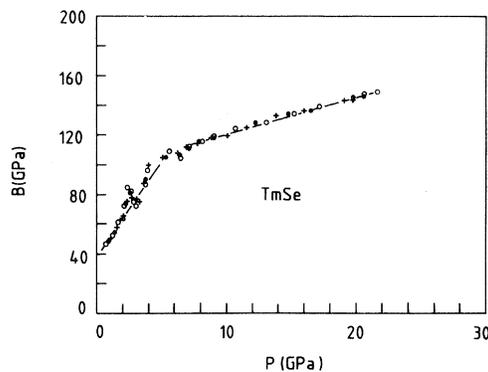

FIG. 2. Bulk modulus B of stoichiometric TmSe as a function of pressure from polynomial fit of data of Fig. 1. The symbols $\bigcirc$, $\bullet$, and $+$ represent, respectively, six, seven, and eight data-point fits. See text for details. The solid line is an eye guide.

$P > 5$ GPa and has been treated as a third fit
parameter. It should be remembered that $V_0^I \neq V_0^{II}$.
B_0 and B_0' for the two pressure regions and V_0^{II}
were obtained from the fits. The values are as fol-
lows: $B_0^I = 38(1)$ GPa, $B_0'^I = 11(1)$, $B_0^{II} = 93(1)$ GPa,
$B_0'^{II} = 2.7(2)$, and $a_0^{II} = (V_0^{II})^{1/3} = 5.655(5)$ Å. These
are in very good agreement with those obtained
from Fig. 2 using Eq. (1). The values of B_0^I and
$B_0'^I$ also agree very well with those found by recent
neutron diffraction measurements.[9] B_0^I is, how-
ever, about 50% higher than that deduced from
sound velocity measurements.[10]

The elastic behavior of TmSe, as depicted in Fig.
2, can now be compared to that of other rare-earth
monochalcogenides which undergo a pressure-
induced valence change. This is done in Fig. 3,
where we have reproduced the data of Fig. 2 for
TmSe, neglecting the anomaly at $P \sim 2.5$ GPa.
The bulk modulus B is shown as function of re-
duced volume V/V_0 instead of pressure, since the
former is a more fundamental physical parameter.
We have also shown in Fig. 4 the Anderson-Nafe
empirical relationship,[11] $B_0 \sim V_S^{-x}$ (V_s is the specif-
ic volume M/ρ, where M is the molecular weight
and ρ the density) for divalent and trivalent rare-
earth monochalcogenides, indicated, respectively,
by the solid lines R^{2+} and R^{3+}. The R^{2+} line is
based on the data of Jayaraman et al.[2,3] and R^{3+}
on those of Molnar et al.[12] as well as Jayaraman
et al.[13]. The above empirical law is found to hold
for a particular class of compounds, where the
value of x and the constant of proportionality
depend on the class of compound. Figure 4 can
thus be used to obtain information about the
valence state of the rare earth in a rare-earth
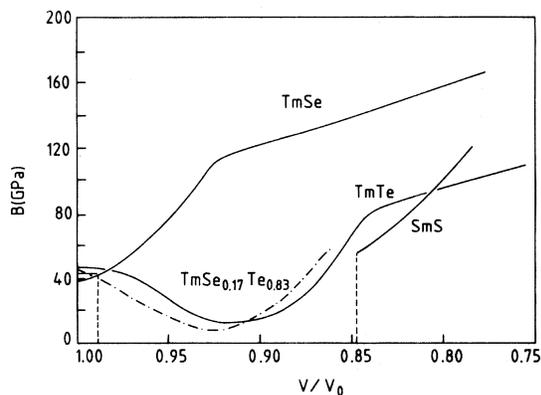monochalcogenide.

The main features of the elastic behavior of a
rare-earth monochalcogenide going from the 2 +
valence state of the rare earth to a new stable state,
nearly 3 + , can be understood by taking TmTe as
the representative case[2] (Fig. 3). Starting at
$V/V_0 = 1$, when Tm is in the divalent state, we ob-
serve a nearly constant bulk modulus for small de-
crease in the volume. The B_0 of this range falls
neatly on the R^{2+} line of Fig. 4 as indicated by
TmTe(I). Around $V/V_0 \sim 0.98$ a continuous
valence transition sets in. Since the change of
valence of Tm from 2 + toward 3 + is accom-
panied by a decrease of the ionic radius, this re-
sults in a softening of the lattice, leading to a rapid
decrease of B. A broad minimum in B follows,
centered around $V/V_0 \sim 0.92$ at which point the
semiconducting gap disappears, the material be-
comes metallic,[1] and Tm attains the IV state. In
the range $0.92 > V/V_0 > 0.84$ the valence change
continues, but B now shows a rapid, monotonous
increase with decrease in volume. Finally, for
$V/V_0 < 0.84$, B shows a linear behavior with
$B_0 = 71.6$ GPa and $B_0' = 2.5$ [Eq. (1)]. This
behavior is typical of a rare-earth monochal-
cogenide in a stable valence state for which the
value of B_0' lies between 3 and 5. The B_0 value,
represented in Fig. 4 by TmTe(II), indicates that
the valence of Tm is nearly 3 + in the range
$V/V_0 < 0.84$. The ternary monochalcogenide
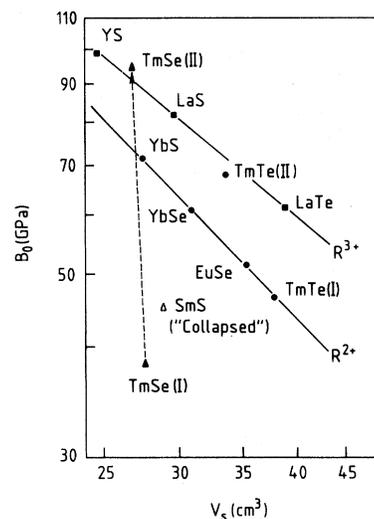$TmSe_{0.17}Te_{0.83}$ shows an elastic behavior identical

FIG. 3. Bulk modulus B as a function of reduced
volume for some rare-earth monochalcogenides at room
temperature.

FIG. 4. Anderson-Nafe plots for rare-earth mono-
chalcogenides. The lines R^{2+} and R^{3+} correspond,
respectively, to the 2 + and 3 + valence state of the
rare earth.

to that of TmTe, except that data[14] for sufficiently high pressures are not yet available. SmS exhibits a different behavior in the initial stage in the sense that the transition to the IV state is of first order[3,15] and is accompanied by a volume collapse from $V/V_0=0.985$ to 0.845. From there on, however, the elastic behavior[16] is similar to that of TmTe and $TmSe_{0.17}Te_{0.83}$, as discussed above. Indeed, high-pressure magnetic susceptibility[15] and Mössbauer measurements[17] show that the valence of Sm in the "collapsed" phase of SmS changes continuously toward 3 + with decrease in volume.

The preceding discussion shows clearly that the IV state of a rare-earth monochalcogenide is characterized by a low value of the bulk modulus B_0 and a high positive value of its first pressure derivative B_0'. It also suggests that a high value of B_0' is characteristic of a continuous valence change of the rare earth from the IV state toward a higher valence. Similar conclusion has also been drawn by others.[18] The elastic behavior of TmSe, as shown in Fig. 3, satisfy these characteristics and closely resembles that of TmTe in the range $V/V_0<0.92$. So the bulk modulus of TmSe in the pressure region I indicates a continuous valence change of Tm from the intermediate state to a new state with a stable valence close to 3 + in region II. We arrive at the same conclusion from an examination of Fig. 4, where we have plotted the values of B_0 and V_S for TmSe in the low- and high-pressure regions, designated as TmSe(I) and TmSe(II), respectively. Note that TmSe(I), which refers to TmSe at atmospheric pressure in the IV state, and "collapsed" SmS both lie well below the R^{2+} line, indicating their soft elastic nature. TmSe(II) is located close to the R^{3+} line, suggestive of a nearly trivalent state of Tm, as is the case for TmTe(II).

We have, so far, looked for similarities between TmSe and other rare-earth monochalcogenides, neglecting in the process the fairly pronounced peak in B located at around 2.5 GPa and shown in Fig. 2. The inset in Fig. 1 shows how this anomaly results. The solid line represents fit of the data with Eq. (2) up to 1.6 GPa. Note that for pressures higher than 2.3 GPa the data points lie consistently above the solid line representing the Murnaghan equation of state. This produces a stiffening of the lattice followed by softening which gives rise to the peak around 2.5 GPa. Though the effect is small, it has been consistently reproducible in independent pressure runs. Moreover, recent high-resolution neutron diffraction measurements[9] on TmSe in the range up to 2.6 GPa clearly show a stiffening of the lattice, starting at 2.0 GPa. A possible explanation of the peak in B may be the presence of an energy barrier, which hinders the process of valence change, and subsequent overcoming of it at higher pressure. The existence of such a barrier can be qualitatively understood if one assumes the presence of a gap or a quasigap in the conduction band of TmSe, with the Fermi energy lying below the bottom edge of the gap but close to it. Indeed, there is a general consensus amongst theoreticians that such a gap exists in an IV material.[19]

In conclusion, we have presented first clear evidence of pressure-induced valence change of Tm in TmSe from the IV state to a nearly trivalent state. The present work also shows, for the first time, the presence of an energy barrier to the process of valence transition and subsequent overcoming of it. Further high-pressure work is, however, needed to establish this feature unequivocally.

[1]A. Jayaraman, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner and L. R. Eyring (North-Holland, Amsterdam, 1979), Vol. 2, p. 575, and references therein.

[2]A. Chatterjee, A. K. Singh, and A. Jayaraman, Phys. Rev. B **6**, 2285 (1972).

[3]A. Jayaraman, A. K. Singh, A. Chatterjee, and S. Usha Devi, Phys. Rev. B **9**, 2513 (1974).

[4]A preliminary report of this work can be found in *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 183.

[5]M. Loewenhaupt and E. Holland-Moritz, J. Magn. Mater. **9**, 50 (1978); H. Launois, M. Rawiso, E. Holland-Moritz, R. Pott, and D. Wohlleben, Phys. Rev. Lett. **44**, 1271 (1980).

[6]R. P. Guertin, S. Foner, and F. P. Missel, Phys. Rev. Lett. 37, 529 (1976).

[7]G. Chouteau, F. Holtzberg, O. Pena, T. Penney, and R. Tournier, J. Phys. (Paris) 40, C5-361 (1979).

[8]F. D. Murnaghan, Proc. Nat. Acad. Sci. U. S. A. 30, 244 (1944).

[9]D. Debray (unpublished).

[10]H. Boppart, A. Treindl, P. Wachter, and S. Roth, Solid State Commun. 35, 483 (1980).

[11]O. L. Anderson and J. L. Nafe, J. Geophys. Res. 70, 3151 (1965).

[12]S. Von Molnar, R. Penney, and F. Holtzberg, J. Phys. (Paris) Colloq. C4-241 (1976).

[13]A. Jayaraman, B. Batlogg, R. G. Maines, and H. Bach, Phys. Rev. B (in press).

[14]H. Boppart, P. Wachter, B. Batlogg, and R. G. Maines, Solid State Commun. 38, 75 (1981).

[15]M. B. Maple and D. Wohlleben, Phys. Rev. Lett. 27, 511 (1971).

[16]R. Keller, G. Güntherodt, W. B. Holsapfel, M. Dietrich, and F. Holtzberg, Solid. State Commun. 29, 753 (1979).

[17]J. M. D. Coey, S. K. Ghatak, M. Avignon, and F. Holtzberg, Phys. Rev. B 14, 3744 (1976).

[18]H. E. King, Jr., S. J. La Placa, T. Penney, and Z. Fisk, in Valence Fluctuations in Solids, Ref. 4, p. 333.

[19]R. M. Martin and J. W. Allen, in Valence Fluctuations in Solids, Ref. 4, p. 85; B. Brandow, Solid State Commun. (in press).