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

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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 5d6s 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 \(\sim 2.6\) 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 \etal\(^6\) 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 \(P \geq 2\) GPa. Chouteau \etal\(^7\), 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)μ\(_B\) 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 \( V_0 \) 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 \( n \)th segment \( (n=1,2,3,\ldots) \) contained from the \( n \)th 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: \( B_0^I = 39(2) \) GPa, \( B'_0^I = 12(2) \) and \( B_0^{II} = 95(4) \) GPa, \( B'_0^{II} = 2.6(3) \). We have also fitted the \( V/V_0 \) data in these two pressure regions with the first-order Murnaghan equation of state:\n
\[
P = \frac{B_0}{B'_0} \left[ \frac{V_0}{V} - 1 \right], \tag{2}
\]

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 \( V_0 (= V_0^I) \) is the actual unit-cell volume at atmospheric pressure. For region II, however, \( V_0 (= V_0^{II}) \) is the zero-pressure unit-cell volume of TmSe in the state characteristic for

![FIG. 1](image1.png)  
**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](image2.png)  
**FIG. 2.** Bulk modulus \( B \) of stoichiometric TmSe as a function of pressure from polynomial fit of data of Fig. 1. The symbols ○, ●, 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 $V_0$ were obtained from the fits. The values are as follows: $B_0^I = 38(1)$ GPa, $B_0^{II} = 11(1)$, $B_0^I = 93(1)$ GPa, $B_0^{II} = 2.7(2)$, and $a_0^{II} = (V_0^I)^{1/3} = 5.655(5)$ 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. $B_0$ is, however, about 50% higher than that deduced from sound velocity measurements.

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 $B_0$ is shown as function of reduced 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, $B_0 \sim V_0^{1-2x}$ ($V_0$ is the specific volume $M/\rho$, where $M$ is the molecular weight and $\rho$ 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. and Jayaraman et al. 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 (Fig. 3). Starting at $V/V_0 = 1$, when Tm is in the divalent state, we observe a nearly constant bulk modulus for small decrease 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 accompanied by a decrease of the ionic radius, this results 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 becomes metallic, 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 monochalcogenide 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 TmSeO.17TeO.83 shows an elastic behavior identical.

**FIG. 3.** Bulk modulus $B_0$ as a function of reduced volume for some rare-earth monochalcogenides at room temperature.

**FIG. 4.** Anderson-Nafe plots for rare-earth monochalcogenides. 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\textsuperscript{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\textsuperscript{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\textsuperscript{16} is similar to that of TmTe and TmSe\textsubscript{0.575}Te\textsubscript{0.425}. As discussed above. Indeed, high-pressure magnetic susceptibility\textsuperscript{15} and Mössbauer measurements\textsuperscript{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.\textsuperscript{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 range 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 $V_0$ 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 $R^{3+}$ 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 Mur-naghan 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\textsuperscript{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 quasi-gap 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.\textsuperscript{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.

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PRESSURE-INDUCED VALENCE TRANSITION IN TmSe: . . .

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