

## High-pressure structural phase transitions in tellurium

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A new phase transition in Te from a  $\beta$ - $P_o$ -type structure to body-centered-cubic (bcc) structure has been observed at  $27 \pm 3$  GPa by using an energy-dispersive x-ray-diffraction technique at high pressures up to 40 GPa. The present structural data are compared with earlier data on the superconductivity of Te under high pressure.

The behavior of the elements under pressure has been an area of increasing interest in recent years due to the advances in diamond-anvil high-pressure techniques.<sup>1</sup> For the group-IV elements and their alloys, the experimental<sup>2-5</sup> studies showed a surprising variety of phase transitions and theoretical studies<sup>10-20</sup> using empirical or first-principles pseudopotential methods were in fact able to reproduce or even predict these phase transitions with reasonable precision. However, for the group-VI elements, the present experimental<sup>21-23</sup> and theoretical knowledge<sup>24,25</sup> is much more limited, and the challenge for the theoretical and experimental studies is much greater due to the lower symmetry of the crystal structures, known for these elements at ambient or at moderate pressures.<sup>26</sup> Since the phase diagram for oxygen and sulfur are rather complex<sup>26</sup> and Se shows structural similarities to Te, however, with apparently higher transition pressures, Te was selected for the present study.

Bridgman<sup>27</sup> was the first to observe in piston cylinder compression measurements two first-order phase transitions in Te in the pressure range up to 10 GPa. Powder x-ray diffraction measurements<sup>28</sup> on Te at 5.3 and 11.5 GPa led to the conclusion that the structure of Te at 11.5 GPa is of the  $\beta$ - $P_o$  type (space group  $D_{3d}^2$ ).<sup>28</sup> In a more recent and more detailed powder x-ray study on Te, it was shown that the first transition at 4 GPa leads from the well-known trigonal ( $\alpha$ -Te) structure Te (I) to a monoclinic phase ( $\beta \approx 92.7^\circ$ , space group  $C_2^2$ ) Te (II), with a puckered-layer-type structure.<sup>29</sup> Furthermore, a second phase transition from this monoclinic structure to an orthorhombic structure, Te (III), was noticed at 6.6 GPa in that study which covered the range up to 10 GPa.<sup>29</sup> The transition to the  $\beta$ - $P_o$ -type structure Te (IV) was, however, not observed in that study due to limitations in the pressure range.

Furthermore, the observations of a sudden change in the superconducting transition temperature  $T_c$  around 13 GPa (Ref. 30) or 15 GPa (Ref. 22) and a strong increase around 30 GPa were also related to phase transitions. Recently, new x-ray diffraction data for Te at 11.5 and 15 GPa were published<sup>23</sup> and it was concluded from these data, that a new phase of Te exists at 15 GPa; however, the structure of this phase was not determined in that study.<sup>23</sup>

This rather confusing situation stimulated the present study with the motivation to extend the phase diagram and equations of state for Te at room temperature to at

least 40 GPa, to correlate the structural data with the low-temperature superconductivity data, and to stimulate first-principles calculations of structural stabilities for this model substance at the borderline between strong covalent and weak intermolecular bonding.

The powdered samples of Te with 99.999% purity were studied under high pressure in a diamond-anvil cell by energy dispersive x-ray diffraction.<sup>31</sup> Pressure was determined with the ruby fluorescence technique<sup>32</sup> and the extended ruby pressure scale.<sup>33</sup> Liquid nitrogen was used as pressure transmitting medium in two of the present experiments and a mixture of methanol:ethanol:water in the ratio 16:3:1 was applied<sup>34</sup> in a third experiment to check on possible effects of nonhydrostatic stresses. For the same reason, data were taken not only on increasing but also on decreasing pressure. The total precision in the pressure determination with respect to the ruby scale is estimated to be better than 0.5 GPa at 40 GPa.

All the observed  $d$  spacings in the pressure range 0–10 GPa are perfectly consistent with the earlier literature data.<sup>29,35</sup> Figure 1 shows therefore only the variation of the measured lattice  $d$  spacings as a function of pressure in the range from 10.6–40 GPa. The data of the stronger peaks observed in Fig. 1 by Mao, Zou, and Bell<sup>23</sup> and Jamieson and McWhan<sup>28</sup> are also included in Fig. 1. It is clearly seen that the present data are in good agreement with these data. However, some of the “weak” diffraction peaks for Te at 15 GPa (Ref. 23) were not observed in the present study. The six observed diffraction peaks of Te (IV) in the pressure region for 10.6–25 GPa, can be indexed unambiguously on the basis of the  $\beta$ - $P_o$ -type structure. It must be emphasized that the present data do not show any other structural phase transition in the pressure region from 15–25 GPa at room temperature.

Figure 1 shows very clearly the disappearance of the (101), (110), (012), and (300) peaks of Te (IV) along with the appearance of the well-separated (110) peak of a bcc phase, Te (V), which make the Te (IV  $\rightarrow$  V) phase transition quite pronounced. Besides the (110), (200), and (211) peaks, the (220) reflection of the bcc phase of Te (V) was also observed in some experiments. It can be noticed, furthermore, that this transition is of first order, with coexistence of both phases over a narrow pressure range and also with some hysteresis between increasing and decreasing pressure experiments.

The atomic volume of Te under pressures up to 12 GPa is shown in Fig. 2. Close agreement is observed with

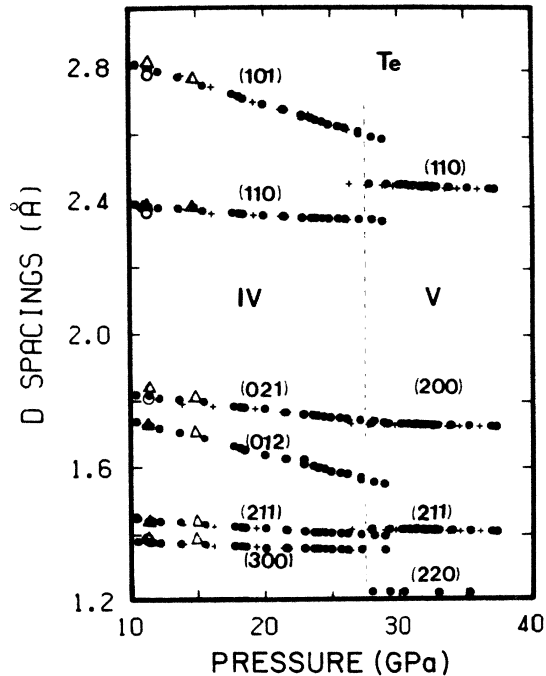


FIG. 1. Lattice spacings ( $d_{hkl}$ ) for Te in phases IV and V. Solid circles and crosses indicate data collected in increasing and decreasing pressure cycles, respectively. Triangles and open circles represent data from Refs. 23 and 28.

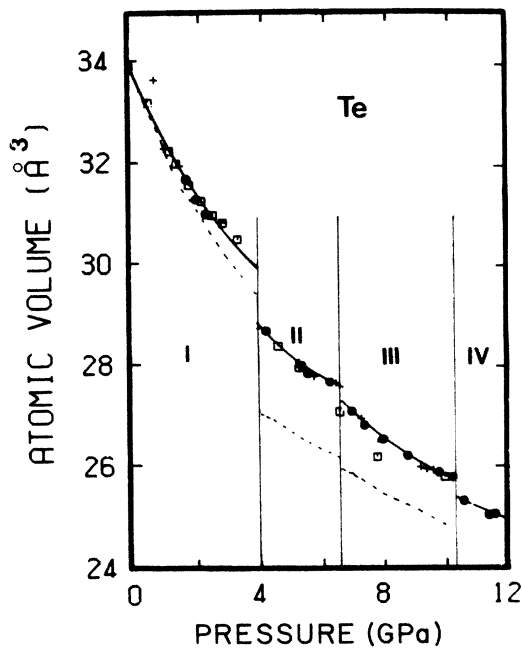


FIG. 2. Atomic volume of Te at room temperature for pressures up to 12 GPa. Solid circles and crosses represent data collected in increasing and decreasing pressure cycles, respectively. Squares indicate, in the 0–4 GPa range, data from Ref. 35 and, in the 4–10 GPa range, data from Ref. 29, respectively. The dashed curve illustrates the data from Ref. 27. The solid lines represent the least-squares fit of first-order Murnaghan EOS's.

respect to the earlier single-crystal data<sup>35</sup> for Te (I) as well as with the powder x-ray data<sup>29</sup> for Te (II). There is, however, a distinct disagreement with respect to the earlier piston-cylinder data,<sup>27</sup> and this discrepancy had been noticed before.<sup>28</sup> However, the transitions from phase Te (I) to Te (II) and from Te (II) to Te (III) are found in close agreement with respect to the piston-cylinder study<sup>27</sup> at 4.0 and 6.8 GPa, respectively, but with volume discontinuities of only 5 and 1.7%.

The phase transition from orthorhombic Te (III) to  $\beta$ - $P_o$ -type Te (IV) is located for the first time in this study. On compression, it was observed at 10.6 GPa and on decreasing pressure, the phase III was completely recovered at 9.6 GPa, but no detailed study was performed on the hysteresis of this phase transition. The effect of pressure on the atomic volume of Te in the more extended pressure range from 10–40 GPa is represented in Fig. 3 which illustrates again that the phase transition between  $\beta$ - $P_o$ -type Te (IV) and bcc Te (V) is observed at  $27 \pm 3$  GPa with a volume discontinuity of about 2% and a slight hysteresis with increasing and decreasing pressure experiments.

The pressure-volume data for the different phases are fitted to a first-order Murnaghan equation of state (EOS) of the type

$$(V/V_r) = \left[ \frac{B'_r}{B_r}(p - p_r) + 1 \right]^{-1/B'_r}, \quad (1)$$

where  $V_r$ ,  $B_r$ , and  $B'_r$  represent the volume per atom, bulk modulus, and its pressure derivative at the reference pressure  $p_r$ . The values of these parameters listed in Table I represent the results obtained from the least-squares fit. The values of  $p_r$  were chosen thereby in the middle of the

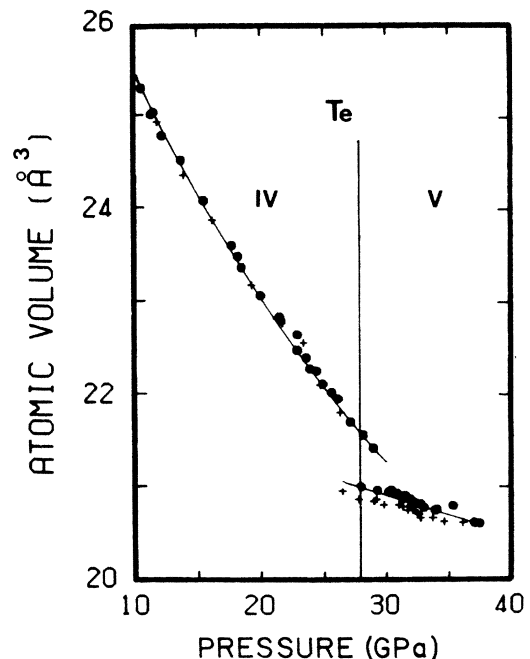


FIG. 3. Atomic volume of Te at room temperature in phases IV and V. The meaning of the symbols is the same as in Fig. 2.

TABLE I. Values of the parameters  $P_r$ ,  $V_r$ ,  $B_r$ , and  $B_r'$  obtained from the least-squares fits of pressure-volume data to Eq. (1).

Phases	$P_r$ (GPa)	$V_r$ ( $\text{\AA}^3$ )	$B_r$ (GPa)	$B_r'$
I	2.0	31.3(1)	24(2)	2.3(2)
II	5.0	28.0(1)	54(7)	4.0(5)
III	8.5	26.2(1)	57(6)	4.0(5)
IV	17.5	23.60(5)	115(8)	2.0(2)
V	33.0	20.65(4)	425(40)	5.0(8)

stability region of each phase to obtain minimum uncertainties in  $B_r$ . The rather low values of  $B_r'$  for Te (I) and Te (IV) may point to special electronic rearrangements in these phases under pressure, whereas the larger value for Te (V) is typical for materials with stable electronic configurations.<sup>36</sup>

For first-principles calculations of structural stabilities, the present results may serve as an ideal set of data, presenting transitions from a semiconducting phase, Te (I), characterized by covalently bonded helical chains with weak interchain interactions<sup>37</sup> to a low-symmetry layer-type metal, Te (II), higher symmetry layer-type metal, Te (III), and finally with a sequence of two first-order phase transitions to a typical metallic structure Te (V).

For the comparison of the present structural data with the earlier determinations<sup>22,30</sup> of  $T_c(P)$ , it should be recalled that the change in pressure was applied in all these

earlier studies also at room temperature and it is very typical for this type of experiment to quench the room-temperature phases on cooling to liquid-helium temperatures. Moreover, the pressure scales are usually more uncertain at low temperatures.<sup>22,30</sup> Keeping this in mind, the first increase in  $T_c$  between 4 and 6 GPa in the study of Ilina<sup>30</sup> seems to represent the behavior of phase II, the decrease between 6 and 12 GPa covers the range of phase III and the next increase above 12 GPa may reflect the appearance of phase IV. The broadening of the transition curves at the transition to phase V in the extended high-pressure study<sup>22</sup> seems to be typical for phase mixtures with the possibility of small contributions from phase V showing up already at 16 GPa and with a completion of the IV-V transition in that study only at 30 GPa.<sup>22</sup> With this interpretation,  $T_c$  increases from a value of about 1 K in phase IV to about 6.5 K in phase V, and its pressure dependences in the phases IV and V still remain ill determined. The high  $T_c$  of 8.5 K (Ref. 30) in the highly doped *p*-type Te needs further experimental studies for its correlations with our structural data.

A more detailed investigation on the high-pressure phases of Te and a comparison with Se under high pressure are in progress.

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