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PHASE TRANSITIONS IN TeO_4 *AT HIGH PRESSURES*

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The effect of high pressure on the structure of the tetragonal phase TeO_2 I is investigated. The structure was investigated by x-ray diffraction at room temperature and at pressures up to 100 kilobars in a special x-ray camera having an amorphous-boron wafer as its fundamental feature. At $p > 30$ kbar TeO_2 I undergoes a reversible phase transition of the first kind. The data indicate that the high-pressure phase TeO_2 II possesses an orthorhombic lattice cell with the parameters (at 60 kbar) $a = 4.22$ Å, $b = 4.84$ Å, $c = 3.67$ Å, $z = 2$, $\rho = 7.07$ g/cm^3, and a Pnnm Fedorov group; the $CaCl_2$ type of structure is indicated. The effects of pressure on the unit cell parameters of TeO_2 I and TeO_2 II are calculated.

VAST quantities of data on phase transitions in solids at high pressure have already been accumulated; as experimental capabilities are enlarged new information is constantly added. A guiding principle is desirable in any search for new transitions, in order to know what compounds it would be best to investigate first of all.

Goldschmidt suggested some time ago that the coordination numbers should increase at high pressures. Numerous experimental confirmations of this hypothesis are already known. It has also been noted (Table I) that the high-pressure phase of an ionic compound has in some cases the same structure as the low-pressure compound that is obtained by replacing the cation with an element having a lower place in the same group or subgroup of the periodic system. Consequently, for these simple compounds the influence of cation size on the structure is qualitatively equivalent to a high-pressure effect; an increase of cation size, like increased pressure, results in a new type of structure associated with a higher coordination number.

Table I

High-pressure phase	Low-pressure phase	Type of structure
$FeVO_4$[1]	$FeNbO_4$	Disordered orthorhombic wolframite
$CrVO_4$[2]	$CrNbO_4$	rutile
$AlAsO_4$[3]	$AlSbO_4$	rutile
SiO_2[4]	GeO_2	rutile
RbI[5]	CsI	CsCl
RbCl[5]	CsCl	CsCl
ZnO[6]	CdO	NaCl

In view of the foregoing discussion, one possible procedure in a search for new phase transitions would be to investigate compounds having the same anion but different cations belonging to a single group or subgroup of the periodic system. Compounds on the boundary between two types of structure are naturally selected. If we consider the series CO_2-SiO_2-GeO_2-SnO_2-PbO_2, for example, we observe that as the cation size increases the molecular structure with the coordination number

Table II

hkl	d_{calc},Å	d_{exp},Å	*I*	*hkl*	d_{calc},Å	d_{exp},Å	*I*
110	3.20_7	3.20_2	Strong	211	1.74	1,73	Weak
011	2.93_4	2.93_3	Strong	112	1.60_5	1.61	Medium
101	2.81	2.80_6	Strong	220	1.60_4		
020	2.40	2.42	Weak	130	1.50	1,50	Weak
111	2.39			031	1.48		
200	2.14	2.09	Weak	131	1.39	1,41	Weak
120	2.10			310	1.38		
210	1.96	1.96	Weak	301	1.34	1,32	Weak
002	1.85	1.84	Strong	311	1.28	1.27	Weak
121	1.83						

two changes to the rutile structure with coordination number six. It is plausible to expect that at high pressures, in addition to the observed transitions in SiO_2,[4, 7] a transition can also occur, with increase of the coordination number, in CO_2. In the MO series where M = Be, Mg, Ca, and Sr a transition to NaCl structure is evidently possible in BeO. The same considerations suggest investigations of BeS, BeSe, and MgTe. In the series AF_2 (A = Be, Mg, Ca, Sr) we can expect to observe polymorphic transitions in BeF_2 and MgF_2.1)

The foregoing discussion is, of course, qualitative in character; therefore it is impossible to predict at what pressure a phase transition will occur, or whether it will be reversible. Some discussion of the second question can be found in the literature.

In view of the foregoing discussion the oxides of elements in group VI B (SO_2, SeO_2, TeO_2, and PoO_2) are of great interest. These compounds exhibit extremely diversified structures, from the typical molecular structures of SO_2[9] and SeO_2[10] to the ionic structure of PoO_2.2) The coordination numbers here vary from two (SO_2) to eight (PoO_2); therefore phase transitions of SO_2, SeO_2, and TeO_2 could reasonably be expected to occur at high pressures.

The present work is devoted to investigating the influence of high pressure on the structure of TeO_2, which is known to have two modifications: orthorhombic structure (found in nature in the form of the mineral tellurite) and the more close packed tetragonal structure (obtained artificially). The orthorhombic structure of TeO_2[12] resembles the structure of brookite. The tetragonal phase[13] has the cell parameters a = 4.796 Å, c = 7.626 Å, z = 4, and the space group $P4_12_12$ or $P4_32_12$. A thorough study of this structure by means of neutron diffraction has enabled us to fix the positions of all the atoms in the unit cell. It was established that each Te atom forms a covalent bond with four O atoms, two of which are separated from the Te atom by the distance 1.91 Å, and the other two by the distance 2.09 Å. Each O atom is bound to two Te atoms. The coordination polyhedron of tellurium is a strongly distorted square pyramid with a Te atom at its vertex.

We made an x-ray study of the structure of TeO_2 (tetragonal phase) at room temperature and pressures up to 100 kbar. The fundamental feature of our special x-ray camera was an amorphous boron wafer with a channel for the sample.[14] The pressure calibration of the camera, performed by an x-ray method, was based on the compressibility of NaCl, using Bridgman's data.[15] X-ray patterns were obtained with molybdenum radiation. Absorption was reduced by diluting the samples with amorphous boron in the proportion $^2/_3$ B + $^1/_3$ TeO_2.

The experiments showed that the tetragonal TeO_2 phase undergoes a reversible phase transition at $p \cong 30$ kbar. The data (Table II) indicate that the high-pressure phase has an orthorhombic cell with the parameters (at 60 kbar) a = 4.22 Å, b = 4.84 Å, c = 3.67 Å, z = 2, ρ = 7.07 g/cm^3, and the Pnnm Fedorov group. On this basis we postulate that TeO_2 II has the structure of $CaCl_2$. The parameters of the TeO_2 I and TeO_2 II cells have the simple relations $a_{II} = a_I - \Delta_1$, $b_{II} = a_I + \Delta_2$, $c_{II} = c_I/2$.

In the phase transition the original tetragonal cell is transformed into an orthorhombic cell through deformation of the aa square (by the contraction of one pair of sides and the stretching of the other sides); at the same time the parameter c is reduced approximately one-half. The rhombic distortion accordingly leads to splitting of the

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1)In the case of BeF_2 a transition to rutile structure is anticipated, although thus far a transition to coesite has been observed,[8] and for MgF_2 a transition from rutile to α-PbO_2 structure or to another intermediate stage between rutile and CaF_2 structure.

2)The low-temperature modification of PoO_2[11] has the structure of CaF_2, with the Po-O distance equal to the sum of the ionic radii. The structure of the high-temperature phase has not been investigated completely.

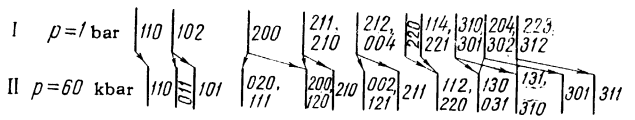

FIG. 1. Scheme of the x-ray patterns of TeO_2I and TeO_2II, obtained at the pressures I – 1 bar, II – 60 kbar. The arrows indicate line splitting that accompanies the phase transition.

lines; this is observed in the x-ray patterns obtained when $p \geq 25-30$ kbar. Each line of TeO_2 I with the indices $h_1k_1l_1$ becomes two lines, with $h_1k_1l_2$ and $k_1h_1l_2$, where $l_2 = l_1/2$ (Fig. 1). Since the $CaCl_2$ structure is a distorted rutile type, we may conclude that at high pressures TeO_2 is of the rutile type, with a change to coordination number six.

A detailed x-ray study enabled us to calculate the influence of high pressures on the unit-cell parameters of TeO_2 I and TeO_2 II (Figs. 2 and 3). An interesting result was obtained for the first phase (Fig. 2); at high pressures the cell is elongated along $\bar{c}$ and contracted along $\bar{a}$ ($\Delta c/c < 0$); at $p = 20$ kbar $\Delta a/a \cong 2.0\%$ and $-\Delta c/c \cong 2.0\%$. Accordingly, the ratio c/a increases with pressure. In the TeO_2 II phase the linear compressibilities $\Delta a/a_0$, $\Delta b/b_0$, and $\Delta c/c_0$ are positive, but their magnitudes decrease markedly as p increases. On the curve representing the pressure dependence of the unit-cell volume (Fig. 4) there is a distinct jump of ~7% at 30 kbar corresponding to the phase transition $TeO_2 \text{ I} \rightarrow TeO_2 \text{ II}$.

It is noteworthy that long before the phase transition is initiated at $p = 20$ kbar the TeO_2 I lines are noticeably broadened; the original structure is apparently rearranged. At $p \cong 25-30$ kbar the lines begin to split; this corresponds to the orthorhombic distortion. The lines of TeO_2 II appear; the new lines exhibit intensities that increase with the pressure and thus indicate the presence of two-phase regions. Therefore the $TeO_2 \text{ I} \rightarrow TeO_2 \text{ II}$ transition is not instantaneous, but begins at 25–30 kbar and terminates at 40–45 kbar. It could be assumed logically that the phase transition in TeO_2 passes through a rutile stage. Indeed, in TeO_2 I the four tellurium atoms of the unit cell occupy special sites on the binary axes (the space group $P4_12_1$ or $P4_32_1$): $xx0$, $\bar{x}\bar{x}\,{}^1/_2$, ${}^1/_2 - x\,{}^1/_2 + x\,{}^1/_2$, ${}^1/_2 + x\,{}^1/_2 - x\,{}^3/_4$; the eight oxygen atoms occupy the usual sites xyz, $\bar{x}\bar{y}\,{}^1/_2 + z$, ${}^1/_2 - y\,{}^1/_2 + x\,{}^1/_4 + z$, ${}^1/_2 + y\,{}^1/_2 - x\,{}^3/_4 + z$, $yx\bar{z}$, $\bar{y}\bar{x}\,{}^1/_2 - z$, ${}^1/_2 - x\,{}^1/_2 + {}^{61}/_4 - z$, ${}^1/_2 + x\,{}^1/_2 - y\,{}^3/_4 - z$. The coordinates of the atoms are:[13] For Te, $x = 0.020$; for 0, $x = 0.142$, $y = 0.268$, $z = 0.182$.

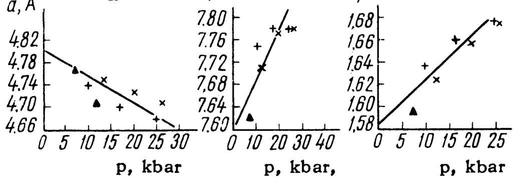

FIG. 2. Pressure dependences of the parameters a, c, and c/a in the TeO_2I phase.

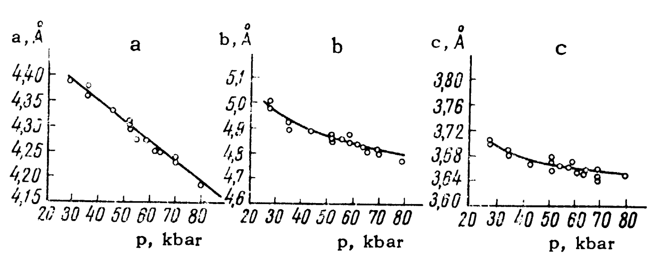

FIG. 3. Pressure dependences of the parameters a, b, and c in the TeO_2II phase.

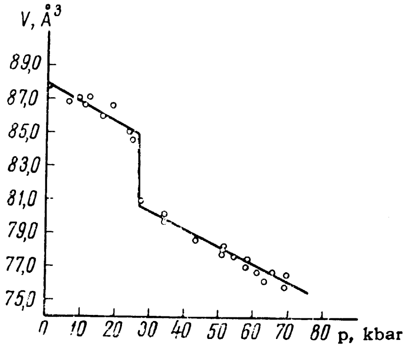

FIG. 4. Pressure dependence of the unit cell volume V in TeO_2I and TeO_2II phases.

To transform to the rutile structure it is sufficient to shift the atoms to the positions $x_{Te} = 0$, $x_0 = y_0$, $z_0 = 0.250$ (on the coordinate axes of TeO_2 I), while reducing the cell size one-half in the c direction ($c_{rutile} = c_I/2$). This transition is, of course, not accompanied by any volume jump. The next stage in this transition scheme is the orthorhombic distortion of the rutile structure, resulting from displacements of the oxygen atoms accompanied by the volume jump. In the resulting orthorhombic phase (the $CaCl_2$ type) the two Te atoms occupy the centers of symmetry 000 and ${}^1/_2{}^1/_2{}^1/_2$, while the four O atoms are located on mirror-symmetry planes at $xy0$, $\bar{x}\bar{y}0$, ${}^1/_2 - x\,{}^1/_2 + y\,{}^1/_2$, and ${}^1/_2 + x\,{}^1/_2 - y\,{}^1/_2$.

In order to prove experimentally that the proposed transition scheme is realistic we would have to record the existence of the rutile phase; this would be difficult because the diffraction patterns of the two phases are similar.[3] In contrast with

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[3] This similarity evidently was responsible for the original attribution of rutile structure to TeO_2.[16]

rutile the TeO_2 I patterns contain several additional weak lines that can be observed, for example, in Debye crystallograms produced with Cu K_α radiation in a camera of 114-mm diameter. When Mo K_α radiation is used (with the same camera) these lines are superposed on strong lines and the difference between rutile and TeO_2 I disappears. Therefore the conditions of high-pressure experimentation would make it impossible to record the intermediate stage.

We shall now consider how the interatomic bonds are changed by the TeO_2 I → TeO_2 II transition. The coordinates of the oxygen atoms must be known before the Te – O distance in the TeO_2 II phase can be calculated. These coordinates cannot be determined even from a large number of x-ray diffraction patterns, because the tellurium atoms scatter x-rays much more strongly than the oxygen atoms. Assuming $x_0 = 0.275$ and $y_0 = 0.325$ (the coordinates of chlorine in $CaCl_2$[17]), we obtain for TeO_2 II a distorted octahedron that is compressed diagonally, with two oxygen atoms considerably closer to a tellurium atom than the other four of the six oxygen atoms that surround the tellurium atom. At 60 kbar the Te – O distance would be 1.97 Å for the first two and 2.26 Å for the others. (The second distance is the sum of the tellurium and oxygen ionic radii.) If the assumed coordinates x_0 and y_0 are close to the true values, the foregoing result indicates that the phase transition is accompanied by a partial replacement of covalent bonds by ionic bonds (leaving two covalent bonds along with four ionic bonds).

Neglecting the orthorhombic distortion and assuming rutile structure for TeO_2 II with the cell parameters (at 60 kbar) $a = 4.55$ Å and $c = 3.67$ Å $[a = (a_{rhomb} + b_{rhomb})/2]$, and also assuming $x = 0.306$ for the oxygen atoms (by analogy with SnO_2[18] and other representatives of this structural type), we again obtain a distorted TeO_2 octahedron; two Te – O distances will be 1.96 Å and the four others will be 2.20 Å.

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[1] F. Laves, A. P. Young, and C. M. Schwartz, Acta Cryst. **17**, 1476 (1964).

[2] A. P. Young and C. M. Schwartz, Acta Cryst. **15**, 1305 (1962).

[3] A. P. Young, C. B. Sclar, and C. M. Schwartz, Z. Krist. **118**, 223 (1963).

[4] S. M. Stishov and S. V. Popova, Geokhimiya **10**, 837 (1961).

[5] L. F. Vereshchagin and S. S. Kabalkina, DAN SSSR **113**, 797 (1957).

[6] C. H. Bates, W. B. White, and R. Roy, Science **137**, 993 (1962).

[7] L. Coes, Science **118**, 131 (1953).

[8] R. Roy and F. Dachille, Z. Krist. **111**, 451 (1959).

[9] B. Post, R. S. Schwartz, and I. Fankuchen, Acta Cryst. **5**, 372 (1952).

[10] J. D. McCullough, J. Am. Chem. Soc. **59**, 789 (1937).

[11] A. W. Martin, J. Phys. Chem. **58**, 911 (1954).

[12] T. Ito and H. Savada, Z. Krist. **102**, 13 (1940).

[13] J. Leciejewicz, Z. Krist. **116**, 345 (1961).

[14] S. S. Kabalkina and Z. V. Troitskaya, DAN SSSR **151**, 1068 (1963), Soviet Phys. Doklady **8**, 888 (1964).

[15] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1945).

[16] W. H. Zachariasen, SB **1**, 211 (1931).

[17] Döll and Klemm, Z. Anorg. Allgem. Chemie **241**, 244 (1936).

[18] W. H. Baur, Acta Cryst. **9**, 515 (1956).

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