SOVIET PHYSICS JETP VOLUME 22, NUMBER 2 FEBRUARY, 1966

PHASE DIAGRAM OF TELLURIUM

S. M. STISHOV and N. A. TIKHOMIROVA

Institute of Crystallography, Academy of Sciences, U.S.S.R.

Submitted to JETP editor March 3, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **49**, 618-620 (August, 1965)

The phase diagram of tellurium is investigated up to 33,000 kg/cm². Four triple points have been found. The existence of the Te II phase discovered by Kabalkina et al.[3] is confirmed. A new Te V phase is found at high temperatures and pressures.

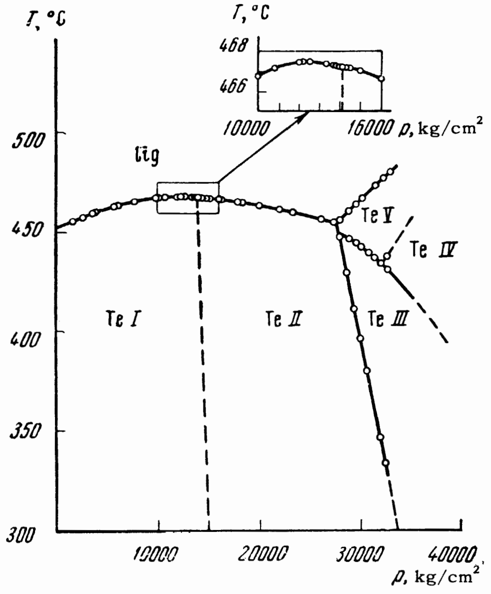
TELLURIUM is a group-VI element with semiconductor properties, used frequently as an object of research at high pressures[1-9]. We have previously investigated[8] the melting curve of tellurium up to 23,000 kg/cm². In this paper we present results of a study of the complete phase diagram of tellurium under hydrostatic pressures up to 33,000 kg/cm² by a thermal analysis method. The reproducibility errors in the measurements of the temperature and the pressure were ± 0.15°C and ± 75 kg/cm². The absolute error in the measurement of the temperature did not exceed ± 1.5°C. The influence of the pressure on the thermocouple readings was disregarded. The values of pressure above 15,000 kg/cm² are possibly somewhat undervalued, owing to the large deviation from the linearity in the pressure dependence of the electric resistance of manganin. The experimental technique will be described in detail in a later paper.

The results of the study of the phase diagram of tellurium are shown in the figure. It can be seen from the figure that the phase diagram of tellurium is rather complicated and has the following singularities: 1) a maximum on the melting curve of the Te I phase, with coordinates T = 467.5°C and p = 12,400 kg/cm²;[1] 2) a weakly pronounced inflection of the melting curve beyond the maximum at T = 467.0°C and p = 14,200 atm. This inflection, obviously, corresponds to the place where the Te phase transformation boundary crosses the melting curve, i.e., it is a triple point. (This crossing was observed by an x-ray method by Kabalkina et al.[3] at 15,000–20,000 kg/cm² and room temperature.) The thermal effects corresponding to the Te I–Te II transition were too small to be registered, so that the Te I–Te II equilibrium point has been drawn using the data of Kabalkina et al.[3] and the coordinates of the triple point observed by us.

In addition, three additional triple points:

TeII — TeV — liq at $T = 454.0°$ C, $p = 27800$ atm[2];
TeII — TeIII — TeV at $T = 449.0°$ C, $p = 28000$ atm;
TeIII — TeIV — TeV at $T = 433.0°$ C, $p = 32200$ atm

were obtained. The Te II–Te III equilibrium curve undoubtedly corresponds to the transition noted by Bridgman[1] at room temperature and 45,000 kg/cm² since extrapolation of this curve gives a value of 44,700 kg/cm² at this temperature. It must



Phase diagram of Te up to 33,000 kg/cm².

---

[1] The values of the melting curve of Te cited by us previously[8] were too high because of an incorrect conversion of the melting points to absolute values.

[2] The coordinates of the triple point TeII – TeV – liq and the position of the liquidus after the triple point found by Kennedy and Newton[9] who investigated the Te diagram up to 50,000 kg/cm² under quasihydrostatic conditions do not agree with our data. In addition they were unable to register the boundaries of solid-phase transitions.

be noted that the Te II—Te III transition at rising temperature takes place with a slight degree of superheat (~ 0.5°), while in the reverse Te III–Te II transition we observe a strong supercooling, reaching 30°C. Knowing the volume discontinuity in this transition, $\Delta v = 0.0058\ \mathrm{cm}^2/\mathrm{g}$ at $T = 20°\mathrm{C}$, and the slope of the equilibrium curve, we can easily calculate the heat of the Te II–Te III transition, which turns out to be 1.58 cal/g. Bridgman's measurements[4,5] and Bardeen's calculations[7] have shown that this is a phase transition into the metallic state.

The Te III–Te IV equilibrium curve obviously corresponds to the transformation observed by Bridgman[2] at 70,000 $\mathrm{kg/cm}^2$ and room temperature.

The high-temperature phase Te V observed by us was never registered before. The heats of the Te III–Te V and Te III–Te IV transitions are approximately half the heat of the Te II–Te III transition. This indicates that the phases Te IV and Te V differ little from Te III. This is also evidenced by the jump in volume in this transition, which was obtained by Bridgman[2] at room temperature and found to be only 0.7%.

As is well known, the atoms in the crystal structure of Te form helical chains that stretch along the c axis. The interatomic distances in the chain are smaller than in the corresponding distances between the atoms of the neighboring chains[12]. The character of the crystalline structure of Te indicates that the principal role is played here by the valent state p^2. The other pair of p-electrons of Te plays a small role in the bond. To explain the semiconducting properties of Te and the distances between the chains in its structure, it is necessary to take into account the role of other valent states, namely pd, p^3d^3, and obviously d^2sp^3, inasmuch as the coordination polyhedron of Te is close to an octahedron. With increasing pressure, the Te crystal compresses along the a axis and stretches along the c axis[6]. It is obvious that in this case the helical chains of Te straighten out, and the arrangement of the bonds in the chain tends in the limit to become linear. In all probability, an appreciable role is being assumed here by the linear component of the pd bond. This is favored by the decrease in the width of the forbidden band of Te under pressure[5,7], which in this case denotes the coming together of the energies of the filled p-subband and the free d-band[10]. At 15,000–20,000 $\mathrm{kg/cm}^2$ the original structure of Te changes into a layered structure of the arsenic type. Owing to the trigonal-pyramidal configuration of the bonds, this structure can be ascribed a predominating valent state p^3. It is probable that the four p-electrons of Te provide in this case three σ-bonds and one resonating π-bond which is weak at the given configuration. However, it is necessary for this purpose that the initially-split two lower p-subbands join together, which is probably the reason for the phase transition in question.

In a structure of the arsenic type Te II behaves under pressure in a manner different from antimony[11], which also crystallizes in this structure, namely, the ratio c/a in antimony decreases continuously with pressure, the lengths of the bonds become equalized, and the structure itself tends to primitive cubic, whereas as in Te the ratio c/a increases with increasing pressure[3].

This fact appears to be paradoxical in the presence of strong bonds in the corrugated layer of Te atoms and weak bonds between the layers. However, if we take into account the possible valent state dp^2 with planar configuration and its increased role under pressure, we conclude that pressure causes the corrugated layers of Te atoms to become slightly rectified, leading to stronger double bonds, which in turn lead to an additional reduction in the interatomic distances. In the limit this process would lead to a structure of the type of β graphite. However, at 45,000 $\mathrm{kg/cm}^2$ the forbidden band in tellurium vanishes[7] and a new structure appears, which could not yet be identified, but which, unlike in antimony, is not primitive cubic[3].

---

[1] P. W. Bridgman, Phys. Rev. **48**, 893 (1935).

[2] P. W. Bridgman, Proc. Amer. Acad. Arts Sci. **74**, No. 13, 1942.

[3] Kabalkina, Vereschagin, and Shulenin, JETP **45**, 2073 (1963), Soviet Phys. JETP **18**, 1422 (1964).

[4] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **72**, No. 4, 1938.

[5] P. W. Bridgman, ibid. **81**, 165 (1952).

[6] P. W. Bridgman, ibid. **77**, 187 (1949).

[7] J. Bardeen, Phys. Rev. **75**, 1777 (1949).

[8] N. A. Tikhomirova and S. M. Stishov, JETP **43**, 2321 (1962), Soviet Phys. JETP **16**, 1639 (1963).

[9] G. C. Kennedy and R. C. Newton, Solids Under Pressure, New York, 1963.

[10] Blacksmore, Long, Nemura, and Nussbaum, Progress in Semiconductors, London, **6**, 1962.

[11] L. F. Vereshchagin, and Shulenin, JETP **47**, 414 (1964), Soviet Phys. JETP **20**, 274 (1965).

[12] A. J. Bradley, Phil. Mag. **48**, 477 (1924).

Translated by J. G. Adashko
79