

Melting and polymorphic transitions in liquid

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Review of the author's data, partly still unpublished, on studying of liquid tellurium and cesium are given. No proofs indicating phase transitions in liquids were found. New developments in studying the liquid-liquid phase transition are briefly described. Some relevant ethical problems are exposed in the bibliography section.

My interest to the problem of phase transformations in liquid arose many years ago, when I was deeply involved in studying the Earth structure. That time I was fascinated by the Ramsey hypothesis claiming that the seismic velocities and density discontinuities at the mantle-core boundary were a result of the phase transition of the mantle material to the metallic state¹. However, having taken into consideration that low mantle was a solid and upper core was a liquid I suggested some sort of nontrivial phase diagrams, which might satisfy necessary conditions² (Fig. 1). The point was how to realize a coexistence line for low-pressure solid and high-pressure liquid phases. As seen from Fig. 1, a phase diagram with melting maximum and a phase diagram with a first order phase transition in liquid could meet the corresponding restrictions³. Note an existence of melting maxima may mean a continuous transformation in liquid.

discover phase diagrams of the types shown in the bottom part of Fig. 1. Frankly speaking I've never expected to discover a first order phase transition in liquid. But I certainly hoped to find a maximum at the melting curve. I should mention here the Gustave Tamman hypothesis on universal melting maxima, which is certainly not true, and the wrong claim of a maximum on the Rb melting curve, made by F.Bundy. I am not going to

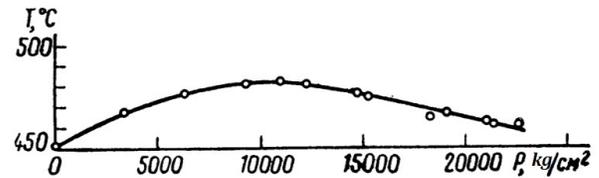


Рис. 2: The melting curve of tellurium. The first observation of melting curve maxima⁵.

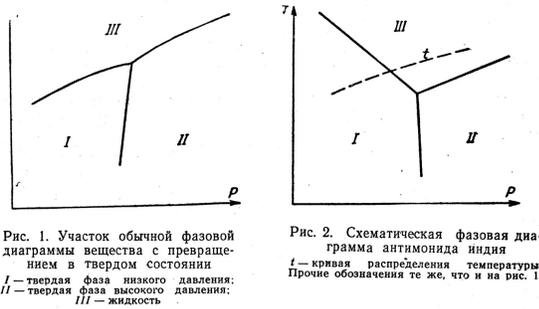


Рис. 1. Участок обычной фазовой диаграммы вещества с превращением в твердом состоянии
I — твердая фаза низкого давления;
II — твердая фаза высокого давления;
III — жидкость

Рис. 2. Схематическая фазовая диаграмма антимонда индия
t — кривая распределения температуры.
Прочие обозначения те же, что и на рис. 1

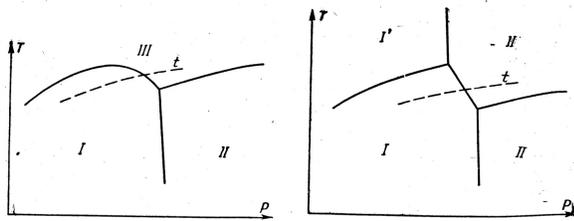


Рис. 3. Вариант предлагаемой фазовой диаграммы вещества мантии (Условные обозначения см. рис. 2)

Рис. 4. Вариант предлагаемой диаграммы состояния вещества мантии
I' — жидкая фаза низкого давления; II' — жидкая фаза высокого давления. Прочие обозначения см. рис. 2

Рис. 1: Variants of phase diagrams for one-component systems. Left lower corner: A phase diagram with a melting curve maxima, Right lower corner: a phase diagram with a first order phase transition in liquid. Reproduced from the paper, published in Russian².

So the first thing what I had to do was to try to

describe here which way I followed to start studying the phase diagram of tellurium. What is important that a maximum on the melting curve of Te was discovered practically simultaneously in our paper⁵ (Fig. 2) and in the paper of Kennedy's group⁶. In the same paper Kennedy et al. announced a discovery of a double maximum at the melting curve of Cs. In a while the phase diagram of Te was studied in more details⁷ (Fig. 3). Later a rapid change of the slope of the Te melting curve was noticed at pressures $\sim 5\text{kb}$ ⁸ (Fig. 4) and I decided to look for a possible sharp transformation in liquid Te. The easiest way was to measure the electrical resistance of Te melt under pressure⁹. Though I should say it wasn't easy at all, because of chemical reactivity of liquid Te. It corrodes almost everything. The dependence of the electrical resistivity of liquid Te on pressure at 475 C is showed in Fig. 5. This Figure is based on the data I obtained in 1966, which never were published in this form before. As I remember it was a big disappointment for me to see just a smooth variation of the resistivity with no indication for any localized change of properties of liquid Te even in the region under suspicion. My attempts to find evidences of abnormal behavior, manifesting phase transformations in liquid Te under pressure, were not persuasive even for me⁹. Next logical step at that time was to try to find out whether the melting maxima of Cs are connected with some sort of localized transformations in liquid Cs Fig. 6. The electronic nature of the phase

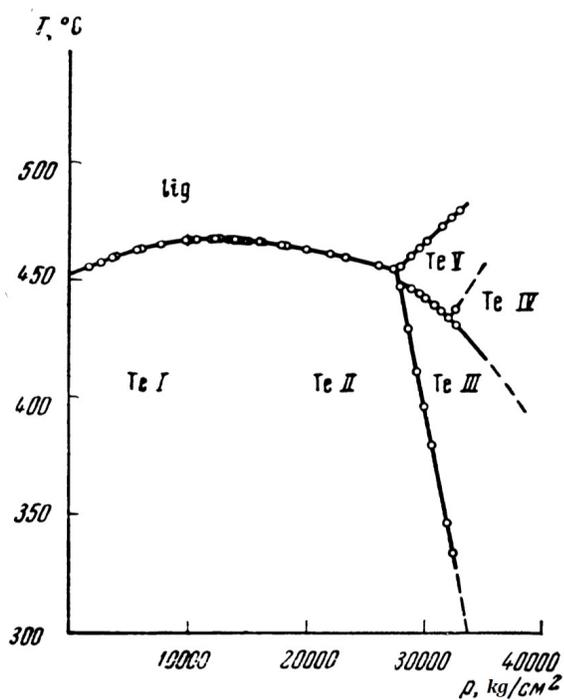


Рис. 3: The phase diagram of tellurium⁷.

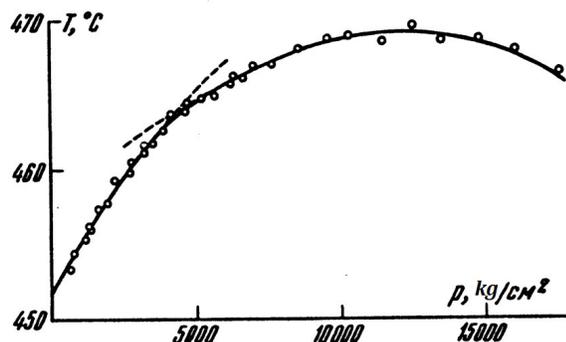


Рис. 4: The rapid change of slope of melting curve of tellurium⁸.

transformations in solid Cs gave some hope in this respect. Measuring of the electrical resistance of liquid Cs was carried out¹⁰. Analogous measurements were published a little bit earlier in¹³. Again as is seen in Fig. 7, only smooth variation of the resistivity of liquid Cs under pressure could be detected over significant pressure range. On the other hand it's obvious that resistivity of liquid and solid Cs displays quite anomalous features on compression, which could be ascribed to the continuous change of the electronic structure. A few years later we studied behavior of the thermodynamic quantities along melting curves of Cs up to 22 kb using a dilatometrical technique¹⁴ (Fig. 8). Once again we could

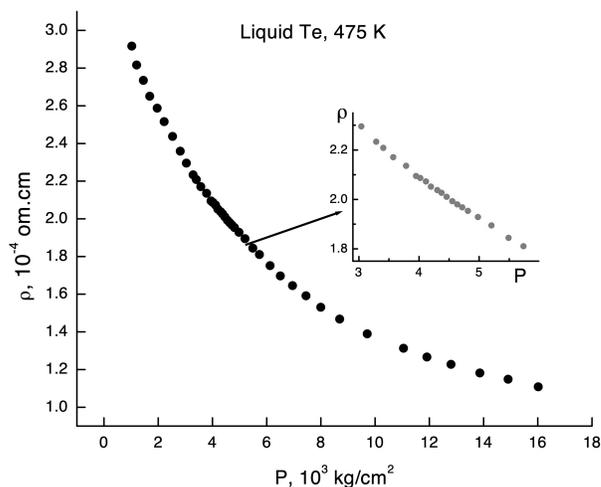


Рис. 5: The resistivity of liquid Te at high pressure⁹.

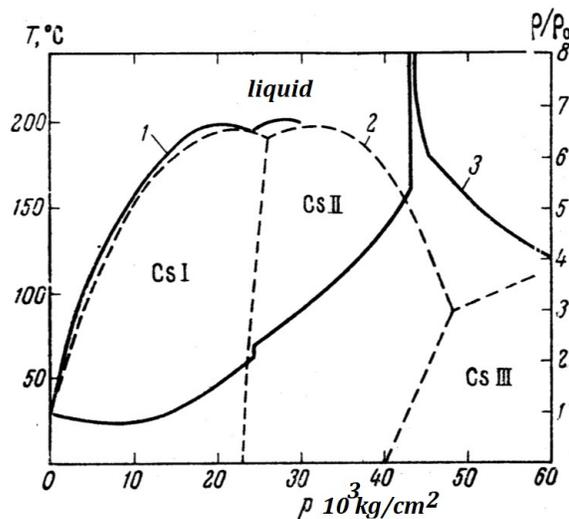


Рис. 6: The phase diagram of cesium and the resistance curve of solid cesium, (1)¹⁰, (2)¹¹, (3)¹².

not find any localized anomaly, which might indicate the phase transition in liquid, though there is no doubt that a continuous transformation in liquid Cs occurred in the significant range of pressure. The same conclusions were made upon completion of studying the equation of state of liquid Cs¹⁵ (Fig.9). My involvement in the anomalous melting study was described in the review paper of 1968¹⁶. So I must say that my personal experience didn't favor the existence of phase transitions in liquids. Of course it wasn't mean that they didn't exist.

Anyway in 1989 twenty years later since publication of my review¹⁶ a paper, claiming a sharp phase transition in liquid selenium was published in JETP Letters (see translation in¹⁷)¹⁸. Somewhat later the same team published a paper²⁰, describing their would be discovery a first order phase transition in liquid

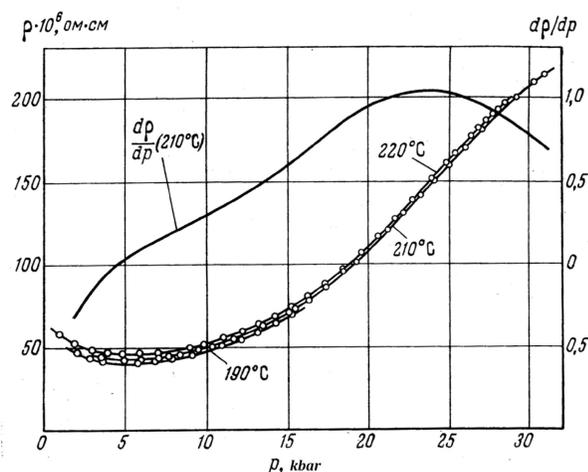


Рис. 7: The resistivity of liquid cesium at high pressure after¹⁰.

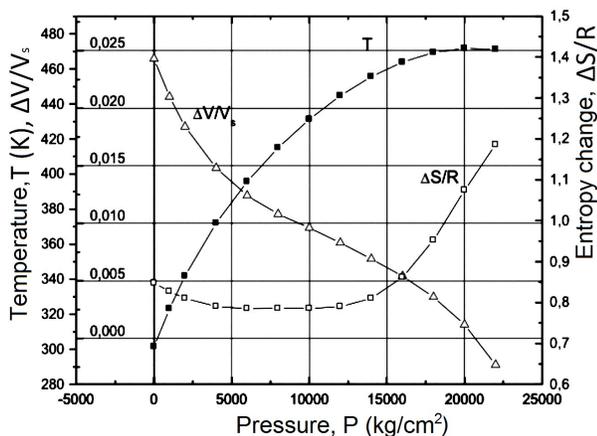


Рис. 8: The melting properties of cesium¹⁴.

tellurium. Note that in both case authors^{17,20} employed so called thermobaro analysis (TBA) to estimate the volume change making use the difference in the pressure dependence of the EMFs of two types of thermocouples. This technique is absolutely not reliable in conditions of non hydrostatic pressure and strong temperature gradient. In fact, the mentioned conclusions on phase transitions in liquid selenium and tellurium didn't find the solid confirmations when probing with the adequate tools like EXAFS, X-ray diffraction, X-ray absorption²¹⁻²⁵, carried out mainly by O.Shimomura group in Japan. However, there arose in 1999 some hope that the first order phase transitions in liquid might exist. This hope was based on paper²⁶ reporting a first order phase transition in liquid carbon between sp and sp_3 states from the classical molecular dynamics study. Unfortunately, this hope vanished when the quantum molecular dynamics was applied to the same problem. No phase transitions in liquid carbon was found²⁷.

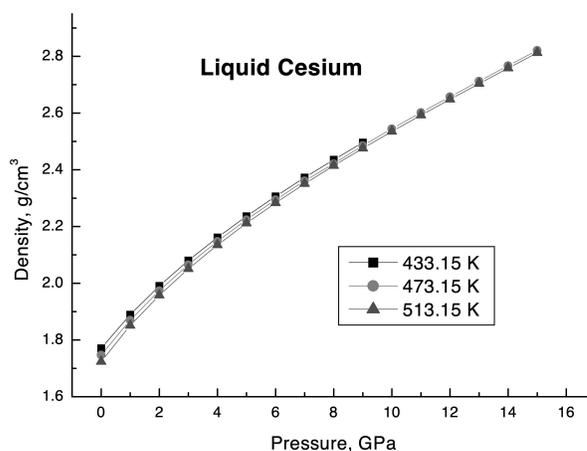


Рис. 9: Density variation of liquid cesium at high pressure¹⁵.

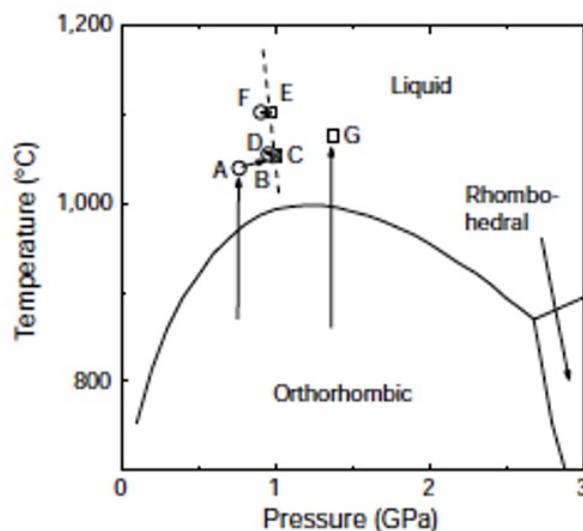


Рис. 10: Location of the liquid-liquid phase transition on phase diagram of phosphorus.²⁸

Meanwhile the Japanese group didn't give up hope and continue their pursuit. Finally they finished up with the sensational discovery of the first order phase transition in liquid phosphorus at pressure about 1 GPa²⁸. The transition occurred between the molecular liquid of tetrahedral P_4 molecules and the polymeric liquid. Later on this transition was studied with more details in paper²⁹ (see Fig.11).

Since then quite a number of theoretical calculations based on first principals were performed, describing of the liquid-liquid transition in phosphorus (see one of the last paper³⁰ and corresponding references therein). The melting curve of phosphorus at high pressures, which was studied some years ago³¹ (see also Fig.10), was revised quite recently^{32,33} (Figs.12,13) with somewhat controversial results. It is interesting to note that the part of the diagram in Fig.13 is almost equivalent to the

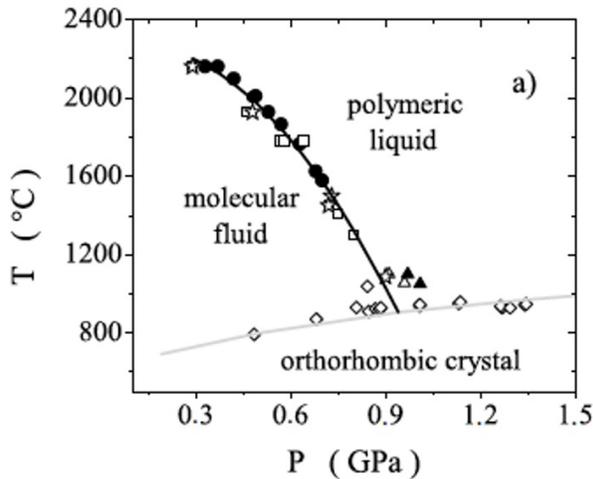


Рис. 11: Partial phase diagram of phosphorus²⁹. Phase transition line between two liquid phase, which probably ends in the critical point, is shown.

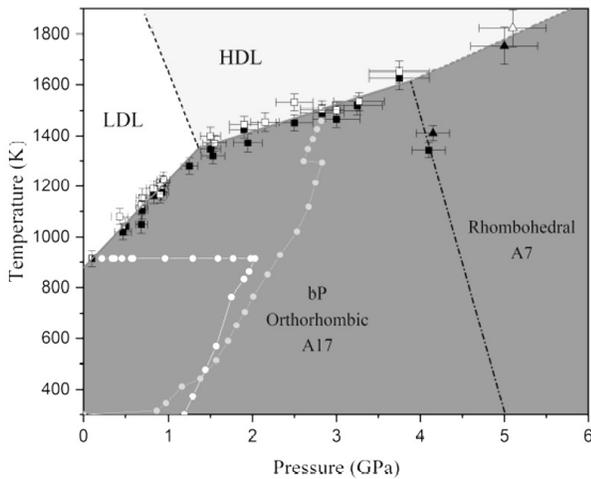


Рис. 12: Melting line of black phosphorus after.³²

schematic phase diagram with a phase transition in liquid suggested in Ref.²(see Fig.1).

It became clear after the exciting discovery in liquid phosphorus that the liquid-liquid phase transitions probably could be found most exclusively in substances with molecular structures. So the first order phase transition was recently discovered in liquid sulfur, corresponding transformation the S_8 cyclic molecules to a polymeric liquid³⁴. The transition in sulfur ended up in a critical point at high temperatures as it occurred in phosphorus. Note that the critical points on the liquid-liquid transition lines belong to the liquid-gas class since there are no symmetry limitations. Then the obvious candidate for that kind phenomena is liquid hydrogen at the metallization transition (see for instance³⁵). However, so far the experimental data are too controversial to make a positive conclusion.

- * Electronic address: stishovsm@lebedev.ru
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 - ² S.M. Stishov, Geochemistry, 11, 989 (1962)
 - ³ It is curious that Fig.1 was almost completely reproduced in the much later paper⁴. Accidental coincidence was of cause possible but not highly probable.
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 - ⁵ N.A. Tikhomirova and S.M. Stishov, JETP, 43, 2321 (1962)
 - ⁶ G.C. Kennedy and R.C. Newton, in Solids under Pressure, edited by W.Paul and D.M. Warschauer, McGraw book Company, Inc., New York (1963)
 - ⁷ S.M.Stishov, N.A. Tikhomirova, JETP, 49, 618 (1965)
 - ⁸ S.M. Stishov, N.A. Tikhomirova, and E.Yu. Tonkov, JETP letters, 4, 161 (1966)
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 - ¹¹ G.C. Kennedy, A.Jayaraman, and R.C. Newton, Phys.Rev.126, 1363 (1962)
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 - ¹³ A. Jayaraman, R.C. Newton, and J.M. McDonough, Phys.Rev. 159, 527 (1967)
 - ¹⁴ I.N. Makarenko, V.A. Ivanov, and S.M. Stishov, JETP Letters, 18, 320 (1973)
 - ¹⁵ I.N. Makarenko, A.M. Nikolaenko, and S.M. Stishov, unpublished
 - ¹⁶ S.M. Stishov, Usp.Fiz.Nauk 96, 467 (1968)
 - ¹⁷ V. V. Brazhkin, R. N. Voloshin, and S. V. Popova, Soviet Phys. J. Exper. Theor. Phys. Lett. 50, 424 (1990).
 - ¹⁸ In the publication¹⁷ no references was made to paper², where an idea on phase transitions in liquids was proposed for the first time. Also all my group publications were ignored. Instead, authors of ¹⁷ cited Ubbelodde book¹⁹, which didn't contain any relevant information,

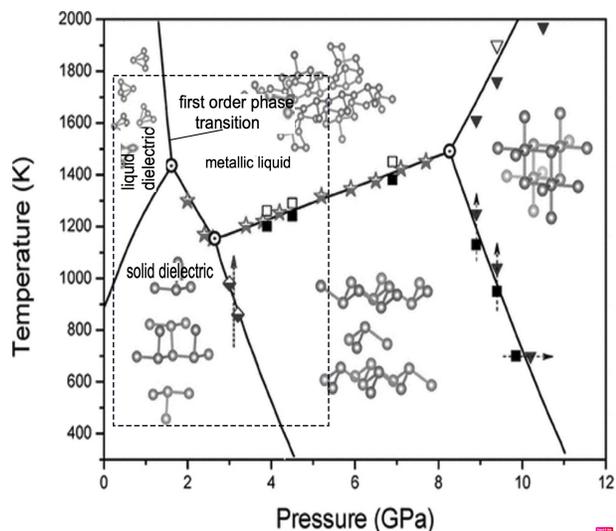


Рис. 13: Phase diagram of phosphorus after.³³ It is amazing that the part of the diagram concluded in the rectangle is much similar to the diagram at the low right corner of Fig.1.

but contained three references to our papers, including the review of 1968¹⁶. Unluckily authors of Ref.¹⁷ could not find time to read it? All this sounds like concealing the fact of borrowing the idea "without permission". It is fanny and symptomatic that out of enormous literature references in the Ubbelohde book, which I found in the library, only those three of them appeared to be enlightened in yellow. Someone worked hard. So all of this is an example of shameless plagiarism.

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- ²⁰ V V Braznkin, R N Voloshin, S V Popova and A G Umnov, *J.Phys.Condens. Matter*, 4, 1419 (1992)
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- ²⁸ Yoshinori Katayama, Takeshi Mizutani, Wataru Utsumi, Osamu Shimomura, Masaaki Yamakata, Ken-ichi Funakoshi, *Nature*, 403, 170 (2000)
- ²⁹ G. Monaco, S. Falconi, W. A. Crichton, and M. Mezouar, *Phys.Rev.Lett*, 90, 255701 (2003)
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- ³² Hermann Muhammad1, Mohamed Mezouar1*, Gaston Garbarino1, Laura Henry2, Tomasz Poręba1, Matteo Ceppatelli3,4, Manuel Serrano-Ruiz4, Maurizio Peruzzini4, Frédéric Datchi5, arXiv:2311.17683
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- ³⁵ Carlo Pierleonia, Miguel A. Moralesb Giovanni Rilloc Markus Holzmannnd, and David M. Ceperley, *PNAS*,113, 4953 (2016)