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Thermodynamic properties of liquid cesium: searching for anomalies

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The polymorphism of liquid cesium at atmospheric pressure in the temperature range of ~ 590 K in the form of a second-order phase transition, announced in the late 90s, is not confirmed in new experimental works and in computer simulations of its properties. At the same time, the question whether the change in the properties of liquid cesium with a decrease or increase in density up to two times is monotonous or is accompanied by various anomalies needs further research.

Keywords: liquid cesium, polymorphism, second-order phase transition, density, adiabatic thermal pressure coefficient, structure

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Introduction

Phase transitions in disordered liquid media (liquid-liquid phase transitions, LLPT) have become an important research topic in the last 20–30 years. Papers on this subject have been reviewed, e.g., in 2018 by M.A. Anisimov et al. in „Thermodynamics of fluid polyamorphism“ [1]. Earlier critical reviews of the experimental and theoretical data on the problem of phase transitions in liquids have been presented in [2,3]. The majority of studies of single-component systems are focused on first-order phase transitions (FPTs) with two phases coexisting. In the present study, we consider another option: second-order phase transitions (SPTs). As was noted by I.I. Novikov, the SPT curve is the stability boundary for both phases that is „formed by the spinodals of both phases merged into a single line“ [4].

Liquid sulfur is a classic example of an SPT, which is observed in it at atmospheric pressure and a temperature of 159°C. This phenomenon has been studied extensively. In accordance with the definition of an SPT, the first derivatives of the thermodynamic potential at $p = \text{const}$ (density $\rho = 1/v$ and entropy s) are the same for both phases, while the second derivatives change abruptly: coefficient of thermal expansion (CTE) $\alpha = 1/v(dv/dT)_p$, compressibility factor $\beta = -1/v(dv/dp)_T$, and heat capacity $c_p = T(ds/dT)_p$. The Ehrenfest equations hold true on the SPT curve. One version of these equations is as follows [5]:

$$dp/dT = -(\alpha'' - \alpha')/(\beta'' - \beta'),$$

$$T(dp/dT)^2 = -(c_p'' - c_p')/v(\beta'' - \beta'). \quad (1)$$

It is important to stress that the Ehrenfest equations characterize the relation between the jumps of second derivatives in much the same way as the Clausius–Clapeyron relation for an FPT serves as an interlink between the jumps of

density and entropy of coexisting phases. Near the SPT curve, CTE, compressibility, and heat capacity undergo significant changes on either side. These changes presignify a phase transition. The characteristic pattern of variation of the density and heat capacity of sulfur near an SPT on either side of 159°C is shown in Fig. 1, which was taken from [6].

The p – T dependence of the polymerization curve on pressure where an SPT occurs for sulfur was examined in [7]. In the initial section, derivative $dT/dp = -0.18 \text{ K}\cdot\text{GPa}^{-1}$, which provides an opportunity to match the experimental data on heat capacity and CTE of coexisting phases using dependences (1). Tellingly, the dependences of heat capacity for liquid sulfur before and after 433 K are provided in the fundamental reference book on thermodynamic properties of substances published in 1978 [8] (see Vol. 1, Book 1, Chapter 12), but this temperature interval is omitted in the table of parameters in Book 2.

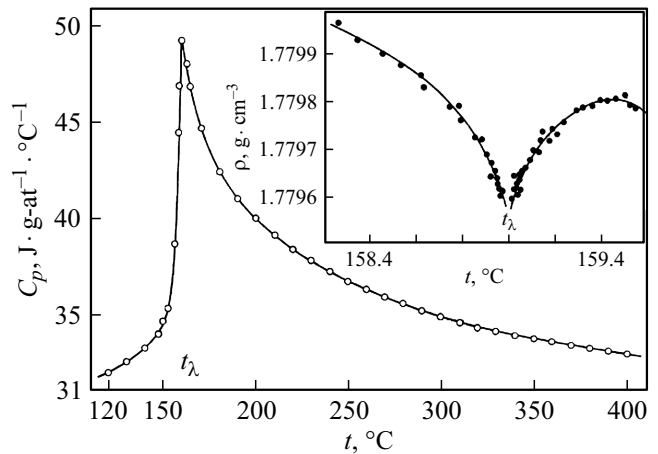


Figure 1. Pattern of variation of the density and heat capacity of liquid sulfur on either side of the SPT temperature.

Deviations $\Delta = \rho_{\text{exper}} - \rho_{\text{calc}}$ of experimental ρ_{exper} values from the approximating second-order polynomial (ρ_{calc}) at temperatures of 578–608 K at the cooling stage

T, K	578.5	583.2	588.0	593.0	598.0	603.2	608.5
$\rho_{\text{exper}}, \text{kg}\cdot\text{m}^{-3}$	1689.8	1682.7	1677.6	1679.7	1674.3	1673.8	1667.5
$\Delta, \text{kg}\cdot\text{m}^{-3}$	4.0	-0.3	-2.9	2.0	-0.7	1.7	-1.6

In the latter half of the past century, the thermophysical properties of liquid-metal coolants (specifically, alkali metals) have been studied extensively. The authors of several studies into the thermodynamic properties of liquid cesium have noted certain features (anomalies) of the temperature dependence of density of saturated liquid and interpreted them as signs of an SPT [9–11]. In the present study, we analyze these reports against the backdrop of concepts of the sulfur SPT that were mentioned above.

1. Experimental data on the density and the adiabatic thermal pressure coefficient of liquid cesium

Working in 1965–70 at the newly formed Institute of Thermophysics of the Siberian Branch of the Academy of Sciences in Novosibirsk, A.S. Basin and A.N. Solov'ev have conducted meticulous measurements of the density of liquid lead, gallium, and cesium using an X-ray absorption setup. The measurements for cesium were carried out at 30 points within the 307–1125 K interval [12]. Experimental data on the density of high-purity liquid gallium in the 296–1408 K temperature interval in this study were „interpolated by sections of three straight lines.“The deviations of experimental points from fitting dependences did not exceed $\sim 0.1\%$. The authors noted that drastic changes in CTE were observed in the region of intersection of lines at 505 and 1020 K and that „such breaks should be visible in the temperature dependences of other properties.“We are dealing here with the problem of a continuous or discontinuous change in the thermodynamic properties and, specifically, with the issue of when the intersecting lines of characteristics on isolines may substitute the actual continuous dependences.

Using the penetrating radiation method, A.S. Basin has later conducted comprehensive measurements of the density of liquid cesium on 0.6–20 atm isobars at temperatures up to 1260°C (approximately 220 experimental points). The obtained results were reduced to the saturation curve and approximated by second-order polynomial

$$\rho = 1.747 - 0.056x - 6.2 \cdot 10^{-4}x^2 \text{ g} \cdot \text{cm}^{-3},$$

$$x = (t - 200)/100 \quad (2)$$

with a scatter of points of $\sim 0.2\%$ about the fitting dependence [9,13]. In his penetrating-radiation experiments

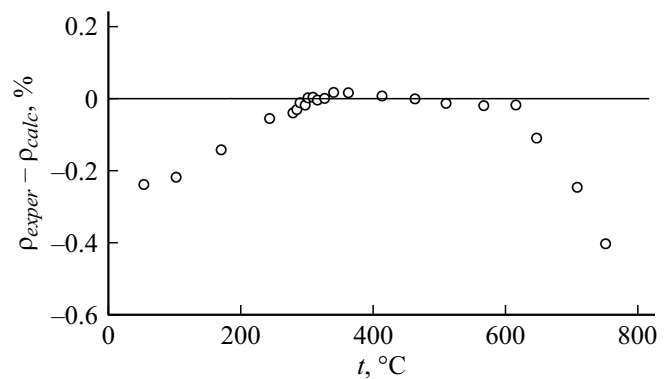


Figure 2. Pattern of anomalies of the cesium density according to [10].

and analysis of the obtained data on the density of cesium, A.S. Basin noted a considerable ($\sim 15\%$) CTE reduction in the interval from the melting point to 150°C and an increase in CTE at higher temperatures. Considering this to be an anomaly of the properties of liquid, the author did not find sufficiently strong arguments to announce the intersection of density lines in this temperature region (as it was done for gallium in [12]). The reference tables for the density of cesium in the region of 150°C [9] contain data smoothed „within possible variation“and reveal a CTE minimum on the density polytherm.

Almost ten years later, in 1979, S.N. Skovorod'ko noted the signs of anomalies on the binodal of liquid cesium in his dissertation prepared at the Institute for High Temperatures under the supervision of E.E. Shpil'rain and V.A. Fomin [10]. The method of a variable-mass pycnometer was used in this study to measure the density of liquid cesium and several alloys of alkali metals. A vial with liquid metal was placed in a meticulously temperature-controlled oven volume and was connected with a room-temperature region through a capillary. The metal in the vial and the metal reservoir were kept under pressure of inert gas. When the vial was heated, excess metal poured out through the capillary into the metal reservoir, which was plugged at the right moment, and the metal outflow was washed away after depressurization of the setup. The vial with metal was weighed before and after the experiment. With the needed corrections taken into account, these data were used to determine the metal density at the oven temperature. A total of 24 experimental points were obtained in this fairly time-consuming experiment for the density of cesium on the saturation curve in the 322–1074 K temperature interval. According to the estimates of the authors, the data error did not exceed 0.15%. The cesium anomalies on the density polytherm are represented in the discussed dissertation as three sections of experimental data $\rho(T)_{\text{exper}}$ intersecting the linear $\rho(T)_{\text{calc}}$ dependence of the cesium density from [14] (Fig. 2).

It can be seen that the slope of the fitting line changes abruptly at a temperature of ~ 600 K after the first 12 points

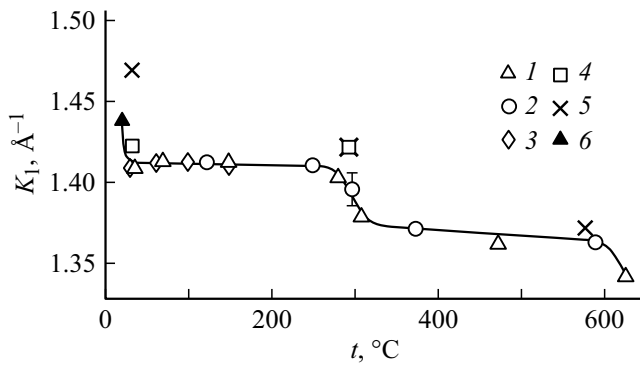


Figure 3. Temperature dependence of the position of coordinate $K_1(S_{\max})$ of the first maximum of the structural factor according to the experimental data on neutron scattering in liquid cesium [16]. The first and the second (1 and 2) experimental series and the data from other studies (3–6) are indicated.

and changes again to a downward slope in the region of 900 K after another 8 points. Two factors should be noted. First, the discussed features of the experimental data remain within 0.2%, which is almost the same as the authors' estimate of their error. Second, no scatter of data around linear dependences is seen in Fig. 2 within 0.2%. This is strange for such a complex experiment. Unfortunately, we do not know how and within which boundaries did the experimental conditions vary. Therefore, the reproducibility and reliability of the obtained data cannot be verified. The first jump of derivatives $d\rho/dT$ for liquid cesium in the region of 600 K is regarded as an SPT in the dissertation. The experimental density data from [10] were later cited in [15] and represented by second-order polynomial

$$\rho = 1.747 - 0.056x - 6.2 \cdot 10^{-4}x^2 \text{ g} \cdot \text{cm}^{-3}, \quad (3)$$

where $x = T/1000$.

The deviations of experimental points from this dependence remain within 0.1% and have a wave-like nature.

It is natural to assume that the features of behavior of thermophysical properties on the isolines are associated with certain changes in the structure of matter. The structure of liquid cesium in the temperature interval of 35–650°C was studied with a neutron diffractometer at the Kurchatov Institute of Atomic Energy [16]. High-purity metal was held in a thin-walled vanadium vial. The interval of wave numbers $K = 4\pi \sin(\theta/2)/\lambda$, where $\lambda = 1.37 \text{ \AA}$ is the radiation wavelength and $\theta = 0.13\text{--}6.3 \text{ \AA}^{-1}$ is the scattering angle, was examined. Experimental data for the angular dependence of the intensity of scattering on isotherms provided an opportunity to reconstruct the values of structural factor $S(K)$ and determine the position of the first maximum $K_1(S_{\max})$ on the scale of wave numbers. The values of $K_1(t)$ decreased abruptly in the region of 230°C (Fig. 3). The authors regarded this as a confirmation of the density anomaly of liquid cesium in this temperature region. On the other hand, Fig. 3 reveals just a sharp change in the position of the first maximum $K_1(S_{\max})$ and nothing more.

Neutron diffraction studies of the changes in structure of liquid rubidium occurring at different temperatures have been conducted simultaneously at the Institute of Physics of the Latvian SSR Academy of Sciences [17,18]. The experimental procedure, the interval of wave numbers, and the temperature interval were close to those from [16]. Just as cesium at 230°C, rubidium underwent a sharp change in the position of the first maximum of structural factor $K_1(S_{\max})$ in the region of 300°C. New experimental data on the density of liquid rubidium [10] in the temperature interval of 100–750°C are presented in the figure in [17]. These data are approximated by three intersecting lines. The first intersection point is at $\sim 300 \text{ K}$. The features of behavior of the structure and density on the polytherms of liquid rubidium and cesium observed in the discussed studies are qualitatively similar.

It should be noted that neutron and X-ray diffraction studies of the structure of liquid alkali metals (specifically, cesium) in wide temperature and pressure intervals have been and are being conducted around the globe (see, e.g., [19,20]). These studies are normally focused on analyzing the properties of liquid metals in the near-critical state. At the same time, isotherms of structural factor $S(K)$ and radial distribution function $g(R)$ were plotted in a wide temperature interval (313–1873 K), e.g., in [20] based on the data on scattering of intense synchrotron γ radiation off liquid cesium. It can be seen (Fig. 4) that, e.g., the position of the first maximum $R(g_{\max})$ varies monotonically within the 313–773 K temperature interval as the density of cesium decreases from 1.82 to 1.60 $\text{g} \cdot \text{cm}^{-3}$; in a similar way to $K_1(S_{\max})$, it just decreases slightly. These observations do not confirm the presence of anomalies of behavior of the density and structure of liquid cesium and rubidium reported in the above-mentioned studies [16,17].

In the statistical theory of liquids, the relation between structural characteristics and thermophysical properties is expressed in terms of integral dependences. Various problems of this analysis are related to the difficulty of determination of the structure at small wave numbers K . In this respect, of special interest is the work of Y. Waseda [21], where the values of structural factor $S(K)$ at small wave numbers $K > 0.05 \text{ \AA}^{-1}$ in the temperature region lying 200–300°C above the melting point are given for many metals (including alkali ones).

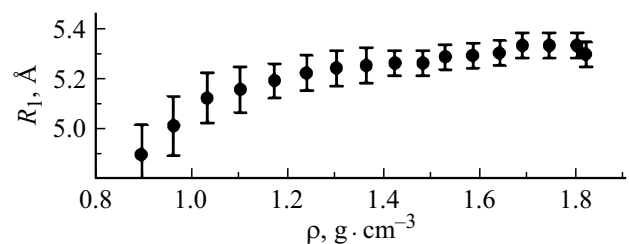


Figure 4. Dependence of the position of the first maximum R_1 of the radial distribution function on the density of liquid cesium according to [20].

The reports [9,10,16–18] of a possible SPT in liquid cesium on the saturation curve have aroused the interest of many research groups. Specifically, this formed the basis for a long-lasting cooperation between researchers investigating the properties of liquid metals at the Joint Institute for High Temperatures of the Russian Academy of Sciences and their colleagues from the Molecular Physics Department of the Moscow State University. By that time, the Department was actively involved in research into the thermophysical properties of solid and liquid metals with the use of methods of cyclic heating of conductors (supervised by professor L.P. Filippov) [22], and the heat capacity of liquid cesium was measured in a wide temperature range [23]. In addition, the thermodynamic properties of dielectric liquids (water, hydrocarbons) were measured at the Department with the use of the thermoelastic effect based on the Thomson relation [24] for characterizing the process of isentropic compression of the medium

$$\gamma = (\partial T / \partial p)_s = T \alpha_p / (\rho c_p), \quad (4)$$

where γ is the adiabatic thermal pressure coefficient (ATPC), s is entropy, α_p is the isobaric coefficient of thermal expansion, and c_p is the specific isobaric heat capacity. An experimental setup, which was intended to verify or refute the presence of an SPT in liquid cesium in the region of ~ 590 K based on the concept of cyclic adiabatic thermoelastic influence on matter, was constructed at the Department. At the same time, if one analyzes the structure of the Thomson relation, it becomes apparent that specific features (anomalies) of behavior of CTE and the heat capacity (see Fig. 1 for sulfur) may compensate each other exactly in the region of an SPT. However, practical experience in experiments at specific facilities is of importance here.

The key characteristics of the experimental setup constructed at the Department for investigating the thermoelastic effect in liquid cesium are detailed in [25]. This setup implements the scheme of comparative measurements of the temperature response under simultaneous quasi-adiabatic compression of the metal and the reference liquid (*n*-hexane). The substance under study is introduced into a metal vessel with a capillary 3 mm in diameter at the bottom. A chromel/alumel (CA) thermocouple 0.2 mm in diameter is welded to the lid on the inside. A hydraulic generator produces pulsed hydraulic pressure varying periodically from ~ 1 MPa to zero with a frequency of ~ 3 Hz. The measured hydraulic pressure is imparted via a silphon on the working medium. According to the estimates based on Thomson relation (4), this pressure pulse should induce a temperature response of 0.2–0.7 K in liquid cesium in the 400–700 K interval. The corresponding voltage at the CA thermocouple ($U = 10$ – $20 \mu\text{V}$) is readily detected by modern high-sensitivity equipment. In essence, this version of an ATPC experiment comes down to measuring the U_{Cs}/U_{Stand} ratio of cesium and the reference

liquid and introducing the necessary corrections. In the course of operation of this setup, the fixing arrangements for thermocouples were refined, the procedure for correcting the results for nonadiabaticity was developed, and other improvements were made [23]. The results of a certain stage of these studies were reported in [26,27]. Specifically, experimental values of U_{Cs}/U_{Stand} , the corrections for nonadiabaticity, and coefficients $\gamma = (\partial T / \partial p)_s$ were tabulated for the temperature interval of 403–605 K in [26]. Somewhat surprisingly, this and other studies published by the same authors lack the data on the quality of metal before and after the experiment, the procedure of filling of the setup, and the analysis for gaseous impurities in cesium. The dependences of $U_{Cs}(T)/U_{Stand}(T_0)$ for two series were plotted in [26] based on tabulated data. A jump in values in the region of 590 K and a change in the monotonic run of the curve are apparent (Fig. 5).

It is unclear why more detailed data for this temperature region were not presented. However, having discussed these experimental data on ATPC, the authors note that „the observed anomalies of thermophysical properties of cesium share similarities with a second-order phase transition.“In another study [27], the authors once again review all the available arguments (specifics of the temperature dependences of density [10] and viscosity of liquid cesium, experimental data on the structural changes [16–18], and above all, the ATPC measurement results (Fig. 5)) and proclaim the signs of an SPT in the region of 590 K.

The inset in Fig. 5 presents a fragment of experimental data on the speed of sound in liquid cesium on the $u(T)$ saturation curve and on isobars up to 600 bar [28]. The temperature dependences of these data provide little indication of the nonregular behavior of ATPC in the region of 590 K reported in [26,27] and thus do not confirm the presence of an alleged SPT.

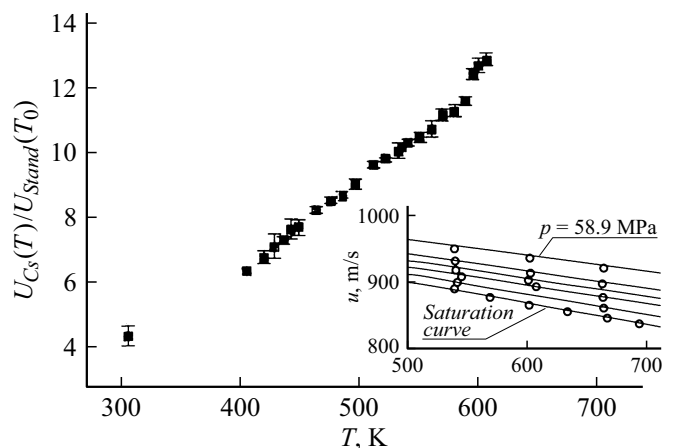


Figure 5. Experimental data on ATPC [26] and the speed of sound in liquid cesium [28].

2. Calculation studies with signs of anomalies in liquid cesium

M.H. Ghatee and M. Bahadori (Shiraz University, Iran) have analyzed the properties of liquid cesium on the saturation curve and under pressure up to 600 bar using the method of linearized isotherms

$$[(Z - 1)V^2]_T = C + BV,$$

where $Z = pV/(RT)$ is the compressibility factor, p is pressure, R is the gas constant, and B and C are coefficients related to parameters $m-n$ of the Lennard-Jones potential function, potential well depth ε , and collision diameter σ [29,30]. Using tabulated experimental data on the density of liquid cesium from [28] in the temperature interval of 400–1900 K with a pitch of 100 K, the authors estimated the values of coefficients $B(T)$ and $C(T)$ on isotherms and plotted the $\varepsilon(T)$ and $\sigma(T)$ dependences. Two regions of nonmonotonic behavior are seen in the $\varepsilon(T)$ plot. The first one is in the region of 1350 K, which is regarded by the authors as the onset of the metal–nonmetal transition in liquid cesium. The second one (weakly pronounced) is at 600 K and is attributed to the alleged SPT discussed in [16,17,26,27]. Naturally, this result obtained through complex calculations is worthy of note. However, with an isotherm pitch of 100 K, one needs to be very careful in associating an SPT with the nonmonotonicity of $\varepsilon(T)$ in [28].

Research groups from Ekaterinburg (Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences), Chelyabinsk (South Ural State University), and Izhevsk (Udmurt Federal Research Center of the Ural Branch of the Russian Academy of Sciences) work on modeling the structure and properties of liquid metals and alloys (topologically disordered systems). Liquid alkali metals feature prominently in these studies: they are convenient test objects with a simpler (compared to transition metals) electron system and experimental data on their properties available up to critical temperatures for substantial variations of density on the saturation curve. These calculations are specific in the extensive use of methods of topological analysis of structures with Voronoi polyhedra and Delaunay simplexes. Various issues of methodology and details of such calculations are discussed, e.g., in [31]. The characteristic simulated pattern of variation of the structure of liquid cesium on the saturation curve is presented in Fig. 6 [32].

Three zones are indicated in Fig. 6: dense liquid (I), transition zone (II), and loose liquid (III). Clear boundaries between these zones are drawn: I–II 590 K, $1.6 \text{ g}\cdot\text{cm}^{-3}$, II–III 930 K, $1.46 \text{ g}\cdot\text{cm}^{-3}$. The first boundary is associated with the SPT temperature (Fig. 5), and the phase transition itself is regarded as an established fact [26,27]. D.K. Belashchenko has published a series of papers focused on the modeling of properties of liquid metals in a wide temperature and pressure interval. Experimental data on

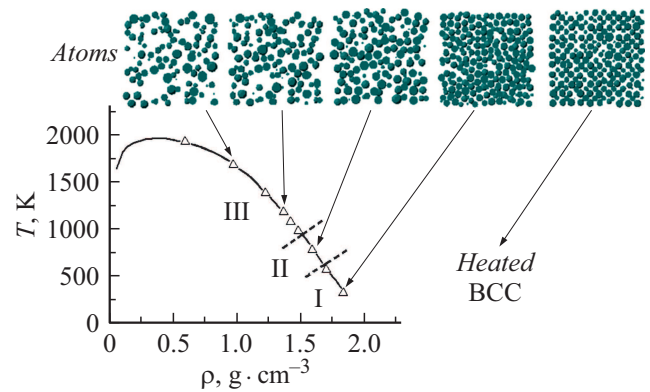


Figure 6. Structural fragments of liquid cesium and tentative boundaries of zones [32].

the structure, steady-state compression, and shock waves were used as the initial ones for the reconstruction of potentials. In recent years, the author has consistently used the embedded atom model (with the effect of environment added to the traditional pairwise potential) for the interaction potential [33]. As for liquid cesium, D.K. Belashchenko has tackled the issue of its polymorphism at a pressure of ~ 4 GPa and a temperature of 220°C in his paper „Structural Transitions in Liquid Cesium“ [34]. It was written in response to a 2005 paper [35] where experimental data on the scattering of X-rays in cesium at the above temperature and pressure were presented. Analyzing the variation of the structural factor and the radial distribution function on the isotherm with pressure, the authors of [35] reported an abrupt reduction in volume (up to 17%) and an FPT in the region of 4 GPa. It should be noted that only calculated density data were used in this study. Set against the backdrop of other studies into the polymorphism of liquid disordered systems, this result for a relatively simple system was of fundamental importance and provided an indirect confirmation of the possibility of emergence of an SPT in cesium at atmospheric pressure (see above). Drawing on years of expertise in handling such experimental data and on the results of his own calculations, D.K. Belashchenko noted in his analysis of [35] that the results of these diffraction studies may be incorrect due to the erroneous determination of volume and coordination numbers in liquid cesium. The conclusion was that „no indications of structural transitions are observed.“ Four years passed. No signs of an FPT in liquid cesium in the considered parameter range were found in a new experimental study [36] that focused on the absorption of X-rays instead of their scattering.

Structural and phase transformations in disordered systems are one of the areas of focus of the Institute for High Pressure Physics (IHPP) of the Russian Academy of Sciences. In 2018, Yu.D. Fomin and his colleagues from IHPP have published the results of computer molecular dynamics (MD) simulations of thermodynamic properties of liquid cesium at moderate pressures to probe the alleged polymorphism in the region of 590 K [37]. MD simulations

were performed in an NpT ensemble (isothermal–isobaric ensemble) for an array of 3456 particles. The embedded atom potential from [34] was used. Arrays of pVT data and the values of enthalpy on isobars in the interval of 300–1200 K were calculated. Differentiating them, the authors determined the values of CTE, heat capacity C_P , and ATPC (4). The calculated coefficients agree qualitatively with experimental data up to 900 K. The plots reveal slight perturbations of monotonicity of the behavior of CTE and heat capacity, which are reflected automatically in the behavior of ATPC, in the region of 600 K. In view of the authors, the results of their calculations do not corroborate the assertion regarding the presence of a polymorphic liquid–liquid transition [26,27], but the reasons for the occurrence of „noise“ on polytherms of physical properties in the region of 600 K require further study. The latter part is hard to disagree with.

Conclusion

Twenty years have passed since the publication of seminal papers [26,27] where the anomaly of properties of liquid cesium at atmospheric pressure „resembling a second-order phase transition“ was discussed. New experimental data in favor of this hypothesis have not been presented since then.

X-ray absorption studies of the density of liquid metals and alloys in a wide temperature range, which were initiated by A.S. Basin at the Institute of Thermophysics of the Siberian Branch of the Academy of Sciences [9,12,13], are continuing now. In 2020, a research group from the Institute of Thermophysics have published a paper focused on the density of a liquid Cs–Bi alloy at temperatures up to 1000 K. Data for liquid cesium were also presented in this study [38]. High-purity metal was held in a thin-walled steel container. Temperature was measured with a CA thermocouple. Detailed information regarding the experiments and estimates of errors of experimental data are provided in papers published by the group. We had an opportunity to analyze more thoroughly the experimental data for cesium on heating and cooling in the 500–700 K interval. The results of density measurements in reverse directions of temperature variation agree within 0.2–0.3%. Crucially, the deviations of experimental data from the fitting dependence at each stage are random in nature, and no section of systematic deviations revealing a certain anomaly in the behavior of density could be identified (see table).

Analyzing these data, we find no grounds to isolate two intersecting sections of the density polytherm in the considered temperature range (as it was done in [10], see Fig. 2) and thus confirm the occurrence of an SPT.

In the meantime, new studies into the thermoelastic effect in liquid cesium have been conducted at the Faculty of Physics of Moscow State University in the temperature interval of 320–620 K [39]. The experimental procedure was refined somewhat compared to that in [26,27]. Experiments

were conducted in short series. The authors did not detect an expected ATPC jump in the region of 590 K in their analysis of experimental data, but noted an enhanced scatter of data in the 550–600 K interval.

Thus, new experimental data on the structure [20] and density [38] of liquid cesium and the results of computer simulations [37] of its properties at atmospheric pressure in the region of 590 K do not verify the alleged polymorphism in the form of an SPT that was reported in [10,26,27].

Apparently, an SPT is unlikely to occur on the thermodynamic surface of liquid metals. At the same time, the presence of various anomalies in the form of extrema on isolines of parameters is entirely possible. For example, the maximum of sound speed u_{\max} was recorded experimentally for liquid cesium on the 500 K isotherm at a pressure of ~ 2 GPa [40]. The aim is to plot the $(p, T)_u$ line in a wide interval of parameters (as was done for the density maxima of water in normal and metastable states [41]).

It should be noted that the authors of all studies into the properties of liquid cesium in wide interval of parameters refer explicitly or inexplicitly to the works on compressibility and the constitutional diagram of the solid phase. It is known that cesium at room temperature undergoes a sequence of transitions under compression: the structural BCC–FCC transition in the region of 21 kbar is followed by the electron $5s$ – $5d$ transition at a pressure of ~ 42 kbar [42,43]. That said, when considering the structural and electron properties on the binodal of the liquid phase of cesium, we operate in a different region of densities of the packing factor of atoms and the structure of the electron subsystem.

The issue of polymorphism of substances in liquid state remains topical, which is reflected, e.g., in a new comprehensive review on the subject [44] detailing the results of experimental and theoretical studies into phase transitions in single-component liquid and amorphous media (with most of them updated to 2019). New and unique experimental data on the constitutional T – p diagram of sulfur [45] were analyzed in [44]. This diagram includes the SPT curve and its intersection with the liquid/solid equilibrium line. At higher pressures, the FPT curve of two polymer liquids ending with a critical point at 1100–1200 K and 2.1–2.2 GPa was measured experimentally. This is the second (after supercooled water) critical point in the liquid phase.

Acknowledgments

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Conflict of interest

The authors declare that they have no conflict of interest.

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