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A scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (RAS) was held on 21 April 1999 at the P L Kapitza Institute for Physical Problems, RAS. The following reports were presented.

(1) **Shcherbakov I A** (Institute of General Physics, RAS, Moscow) "2-µm solid-state lasers";

(2) **Pudalov V M** (P N Lebedev Physics Institute, RAS, Moscow) "The insulator-metal phase transition in two-dimensional systems";

(3) **Brazhkin V V, Voloshin R N, Lyapin A G, Popova S V** (Institute for High-Pressure Physics, RAS, Troitsk, Moscow Region) "Quasi-transitions in simple liquids under high pressures".

An abridged version of the third report is given below.

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Quasi-transitions in simple liquids under high pressures

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First-order phase transitions initiated in crystals by changes in pressure P and temperature T constitute a class of phenomena that have been thoroughly studied both experimentally and theoretically. The transitions are usually accompanied by structural transformations, although there are cases where electronic transitions are isomorphic, for example, in Ce [1]. In the P, T plane, the equilibrium of two different crystal phases is represented by a line that ends with a triple, critical, or multicritical point. When the pressure is increased isothermally, the density of the crystal phases undergoes an abrupt change upwards when the system passes through the phase transition. Structurally, this is usually accompanied by a transition to a more-closely packed atomic system [1].

Compared to crystals, liquids have been studied to a smaller degree. One phenomenon involving liquids that has been thoroughly studied is boiling, which is a first-order phase transition. The corresponding liquid–gas transition curve in the P, T plane ends at high temperatures by a critical point. But can there be first-order phase transitions between different phases of the same liquid when the pressure and temperature change? If such phase transformations occur,

Uspekhi Fizicheskikh Nauk **169** (9) 1035–1039 (1999) Translated by E Yankovsky; edited by A Radzig they are obviously accompanied by structural transformations in the liquid or by changes in the electronic states of the atoms in the melt.

At first glance the question is rhetorical, since in 'complex' melts, such as liquid crystals, first-order transitions between different phases are known to take place and have been studied rather well [2]. At the same time, it is hard to expect any sudden transitions to occur under variations of the pressure and temperature in such 'simple' melts as, say, liquid noble gases. On the other hand, the behavior of 'simple' metallic and semiconducting melts or 'reticular' liquids (water and the melt of SiO₂, to name some) under pressure *a priori* is not at all evident. Below we examine only one-component melts of chemical elements or compounds to avoid possible complications associated with stratification, decay, and chemical reactions.

Notice that studies of liquids at different temperatures and atmospheric pressure apparently yield only a limited amount of information about the behavior of melts over the entire P, T plane. In view of this the importance of highpressure studies, despite the obvious experimental difficulties, cannot be overestimated.

Our studies have shown that melts belonging to different classes of elementary substances subjected to pressure can undergo fairly abrupt changes in the structure of short-range order and in thermodynamic and transport properties. A common feature of all the transformations studied in this field so far is that the corresponding changes take place over a fairly narrow (and, possibly, finite) range of pressures and temperatures near the melting point T_m [3]. In a certain sense, one can speak of different phases of the same melt. At the same time, anomalies of the properties become fuzzy and experimentally unobservable when the temperature is increased up to $(1.3-1.7)T_m$ (see Fig. 1) [3].



Figure 1. Generalized P, T phase diagram that incorporates possible transformations in the melt (here and in the figures that follow the S regions correspond to the crystal phase, and L to the liquid phase).

The various aspects of such transformations in liquids were actively studied already in the 1960s by S Stishov (e.g., see article [4]).

In the present report we systematize the results of our investigations according to the groups of the Periodic Table to which the elements under investigation belong. Melts of elementary substances belonging to groups I and II (alkali and alkali-earth metals) and the corresponding crystals may undergo structural and 'purely' electronic transformations [5]. The behavior under pressure of a melt of Cs (Fig. 2), which belongs to this class of substances, has been studied the most [5]. Notwithstanding the apparent simplicity of the electronic transitions the alkali and alkali-earth metals have very complicated P, T phase diagrams.

Many crystals of elements of groups III - V do not have a close-packed structure and are semiconductors or semimetals. A transition to more compact and isotropic structures occurs when pressure is applied to the crystals and to the corresponding melts. The appropriate anomalies associated with the influence of pressure have been found and studied in experiments or by the molecular dynamics method in melts of gallium, carbon, bismuth, phosphorus, antimony, and arsenic [3].

One of the main features of crystal phases of the elements of group VI is the presence of a semiconductor – metal phase transitions at high pressures, which are accompanied by dramatic structural changes and substantial volume anomalies. Similar transformations are also observed in melts of



Figure 2. (a) *P*, *T* phase diagram of cesium. The points marked by \circ , \bullet , and \blacksquare correspond to different short-range order structure. The transformation 'bands' in the melt are depicted schematically. (b) Experimental pressure curves of the electrical resistivity of cesium melt and the jump in volume on melting.



Figure 3. (a) *P*, *T* phase diagram of selenium with allowance for a transformation in the melt. SI and SII match with semiconducting and metal crystalline Se, and LI and LII match with semiconducting and metallic liquid Se. The points marked by \circ correspond to anomalies in electrical conductivity; the \blacktriangle correspond to thermal anomalies in differential thermal analysis, and the \blacksquare correspond to volume anomalies in thermobaric analysis. (b) Pair correlation function found from the data of Tsuji et al. for a selenium melt at different pressures. This shape of function suggests that pressure initiates an essential transformation of the short-range order structure.

elements of group VI, such as S, Se, Te (Fig. 3) [3, 6]. Here a variation of conductivity by three to four orders of magnitude and corresponding considerable variations in volume are observed over a temperature interval $\Delta T \approx 50$ K and a pressure interval $\Delta P \approx 5$ kbar near $T_{\rm m}$. When $T > 1.5T_{\rm m}$, the electronic-structure and volume variations are gradual. In all these cases, the pressure of metallization of melts near the melting point is much lower than the pressure of metallization of the corresponding crystals at room temperature.

Of all the elements of group VII the one studied most extensively under pressure in both crystalline and liquid phases is I₂ [3]. Building up pressure, the metallization of iodine and transition to an atomic structure is detected in both crystal and melt [3]. Molecular hydrogen H₂ can also be conditionally assigned to group VII. The problem of hydrogen metallization under pressure is a burning issue in the physics of recent decades [7]. So far no insulator-metal transition in crystalline hydrogen has been discovered with pressures as high as 3.4 Mbar [8]. At the same time, the metallization of liquid hydrogen has recently been observed in shock-wave experiments, but it has still to be established whether this transition is accompanied by structural changes and volume anomalies. As for elements of group VI, the metallization of melts of I_2 and H_2 occurs under pressures that are much lower than those at which the metallization of the corresponding crystals takes place [3].

Not only elementary melts but also melts of a number of compounds, especially of such 'reticular' liquids as H2O and SiO₂, are of profound interest when the behavior of compounds under pressure is studied. It must be noted that the results of investigations of the behavior under pressure of the SiO₂ melt, as well as of other silicate melts, are important to many geophysical problems [10]. Under a pressure $P \approx 6$ GPa, the SiO₂ melt undergoes a transition to a denser liquid modification, marked by a peak in the melting curve [11]. As for studies of the behavior of water over a broad range of pressures and temperatures, these have been conducted for many centuries. Under atmospheric pressure, water exhibits a number of intriguing anomalies, the bestknown of which is the maximum of density at 4°C, and the minimum in heat capacity at 37 °C. All the extraordinary properties of water can be explained if we assume that there occurs an abrupt phase transition under pressure in supercooled water. In this case, the anomaly in the compressibility of water at -40 °C corresponds exactly to the supercritical region for this transition. Indirect experimental evidence of such a transition has recently been obtained by Mishima and Stanley [12].

The existence of volume anomalies in melts near the melting curve makes it possible to explain the 'exotic' types of phase diagrams and melting curves [3, 4].

Summing up the experimental data, we can conclude that the question posed at the beginning of our report about phase transitions in 'simple' liquids, actually amounts to two questions. First, how is one to describe the observed anomalies in the physical properties and changes in the short-range order structure that occur within a narrow range of pressures and temperatures? Second, can 'real' firstorder phase transitions of zero width occur in 'simple' melts?

One of the first attempts to describe the smooth transitions in Cs and Te melts was the work of Rapoport, in which a melt was interpreted as a regular solution of liquids of two types (see the literature cited in Ref. [3]). The 'fuzziness' of the transformations emerges in a natural manner due to the entropy of mixing of two 'different' liquids. Rapoport's model fails to provide any microscopic description of the transitions since actually, of course, there is no difference in the structural states of the atoms of the same melt. However, this model can easily be modified if we account for the presence of nanoregions with a definite short-range order in the melt. In this case, instead of 'distinct' atoms we deal with the possible states of clusters with different short-range order. These clusters (or, to put this another way, the regions of existence of structural correlations in the liquid) usually encompass several coordination spheres, i.e. several tens or hundreds of atoms. In comparison to Rapoport's model, the width of the respective transformations decreases N-fold due in reality to the decrease in the entropy of mixing in the cluster system, where N is the number of atoms in the above regions. Here, the width of the transformation in temperature amounts to $\Delta T \approx T/N$, and in pressure to $\Delta P \approx T/\Delta VN$, where ΔV is the difference in the atomic volumes in the nanoregions with different short-range order [3]. As in the case of crystals, the loose and anisotropic packing of atoms in the nanoregions of the liquid can exist due to the substantial contribution of noncentral forces and three-body interaction. Under pressure, the contribution of the pairwise central

interaction increases, which leads to the emergence of close and isotropic atomic packings. As the temperature is increased, the size of nanoregions with a definite short-range order becomes smaller and there occurs a transition to a melt of quasi-gas type with chaotic close packing of the atoms, which explains the presence of critical regions for the transformations [3].

The temperature spreading of the transitions in melts can be estimated by elementary reasoning if the energy kT of thermal fluctuations is referred to a nanoregion consisting of N atoms [3]. This reasoning makes it possible to understand why phase transitions in small particles consisting of N atoms must also be 'spread' over the temperature by $\Delta T \approx T/N$ [3, 13]. Thus, the question of the nature of phase transitions in melts unexpectedly becomes very close to the problem of phase transitions in systems with a finite number of particles (clusters or nanopowders).

In describing such transformations, certain problems emerge with the use of standard terminology. For instance, it goes without saying that the melting of a small particle consisting of several hundred atoms is, from the viewpoint of changes in the aggregate state, a normal phase transition. But according to Ehrenfest's classification, this is not a first-order phase transition since the thermodynamic properties change smoothly instead of abruptly. There is still a lot of work to do in describing the phase transitions in systems with a finite number of particles, i.e. in the absence of passage to the thermodynamic limit $N \rightarrow \infty$. We believe that a meaningful description of such transitions as well as transformations in liquids requires new terminology, a fact reflected in the title of the present report.

We note once more that although a liquid, like a crystal, can be interpreted as a system consisting of an infinite number of particles, the regions of existence of structural correlations in melts, i.e. regions in which the concept of the order parameter determining the phase transition is valid, incorporate a finite, small number of particles. The reasoning about phase transitions in small particles and in liquids refers to equal extent to all disordered systems, such as amorphous solids, spin and quadrupole glasses, etc., for which the metastable nature and nonergodicity are complicating factors [14].

The above ideas provide a key to the answer to the second question: can 'real' first-order phase transitions with a zero width occur in liquids? Landau and Zel'dovich [15] were first to point out the possibility of first-order semiconductormetal phase transitions occurring in liquids. Later the same problem was actively elaborated by Mituś and Patashinskiĭ [16], and Stishov [17] put forward interesting ideas in this field. Obviously, first-order phase transitions in liquids initiated by changes in pressure and temperature are determined by the order parameter characterizing the entire system of atoms. The most obvious realization of such an order parameter is a region of structural correlations that extends over the entire volume occupied by the melt. Another possibility is a situation in which the states of all atoms in the momentum space are correlated. This situation is realized in quantum liquids. In cluster models of melts, the long-range correlations in the coordinate or momentum space can be attained by introducing an interaction between clusters (regions in which there is short-range order). When the temperature is so high that it becomes comparable to the cluster-cluster interaction energy, long-range correlations disappear, i.e. the curve of a 'real' first-order phase transition in a liquid must end, at high temperature, with a critical point [3]. However, at temperatures below the vitrifying point, the above reasoning loses all meaning, since phase transitions in a frozen, glassy state are determined primarily by kinetic properties rather than thermodynamic factors [14]. Consequently, 'real' first-order phase transitions in melts can be observed only when the temperature of the corresponding critical point is higher than the vitrifying point, viz. $T_{\rm cr} > T_{\rm g}$. Here, in the interval from $T_{\rm cr}$ to $T_{\rm g}$, the liquid makes up a totally correlated system.

Liquid crystals demonstrate the possibility of long-range translational structural correlations being present in melts [2], with $T_{\rm cr} > T_{\rm m} > T_{\rm g}$. Less-evident correlations may also exist — for instance, long-range orientational order may set in a supercooled van der Waals liquid [18]. During recent years it has been discovered both by analytical methods that lean upon simplified interatomic potentials [18] and by molecular-dynamics methods that use more realistic potentials [20, 21] that first-order phase transitions can exist in model liquids. At the same time, it is difficult to think of model liquids as being 'simple,' since usually fairly exotic noncentral potentials were employed.

The above examples show that one of the conditions that must be met if we want a first-order phase transition to be realized in liquids is that there must be a strong anisotropy or energy hierarchy in the structure-forming part of the interaction potential. Typical examples are as follows: strong orientational anisotropy (geometric anisotropy, as in the case of liquid crystals), strong three-particle (multiparticle) interaction leading to substantial angular correlations, the presence of a hierarchy in the interactions between different types of atoms in molecular liquids, etc. The presence of a



Figure 4. Hypothetical phase diagram of water placed against the *P*, *T* phase diagram of ice. Under positive pressures, the region of transfrmation between two forms of water (LI and LII) goes over into the curve of the first-order phase transition of supercooled water, beginning with the critical point *K*. Below the vitrifying point T_g , this curve in turn transforms to the line of conditional equilibrium between amorphous phases of ice (lda and hda).

'weaker' structure-forming interaction determines the melting of the system, while the 'stronger' interaction ensures the existence of an order parameter (i.e. correlations) that characterizes the entire system. For instance, melting involves the translational degrees of freedom, while angular correlations are retained in the liquid phase. Notice that systems with a hierarchy of structure-forming interactions may also exhibit other remarkable properties, such as superionic conductivity, which is related to the melting of the sublattice for one of the ionic components in the crystal.

Lately serious attempts have been made to describe a possible phase transition in supercooled water [21-24]. Various model calculations yield different positions of the P, T curve relating to the transformation in water and of the corresponding critical point [22-24]. Nevertheless, it has probably been established without any doubt that $T_{\rm g} < T_{\rm cr} < T_{\rm m}$ for water, i.e. there exists a temperature range within which supercooled water undergoes a 'real' first-order phase transition under pressure variations (Fig. 4). It is unclear what other fairly 'simple' liquids can undergo a first-order phase transition provided $T_{\rm cr} > T_{\rm g}$. Another intriguing question is: are there other examples of first-order phase transitions in 'simple' melts for which $T_{\rm cr} > T_{\rm m}$, i.e. the 'true' first-order phase transition takes place in the liquid's stability region in the P, T diagram? One cannot exclude the possibility that the observed anomalies in Te and Se melts subjected to pressure are examples of such transitions [3, 6, 25].

In the years to come, further experimental and theoretical investigations into the problems raised in this report will be among the most urgent in the physics of phase transitions and disordered media.

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