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# DIELECTRIC-TO-METAL TRANSITIONS AND SUPERCONDUCTIVITY OF NEW METALS

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Dielectric-to-metal transformations in solids under high pressure is one of more striking phenomena.

The expansion of range of pressure in experiments extends the class of the substances which undergo the dielectric-to-metal transformation at high pressure. At pressures up to 200 kbar the dielectric-to-metal transitions of some elements (Ge, Si, P, Se, Te) and compounds (InSb, InAs, AlSb, ZnS *etc.*) have been discovered.[1-3]

For the transformation to a metallic state of wider class of substances the new high pressure apparatus and methods of investigation are needed.

## 1. High Pressure Apparatus

In physical experiments we used the anvil type apparatus for megabar pressure generation. The material of anvils is the carbonado type diamond sintered at the Institute for High Pressure Physics of the USSR Academy of Sciences.[4] Now the usual form of working surfaces of anvils is either flat[5] or a concave one (for the increase of working volume). In our experiments we have used the anvils, one of which has a flat working surface, but the other is a convex one. Such a construction makes it possible to get in a small volume *near Roman* contact area the pressure which is larger than that between the flat anvils.

Theoretically the problem of generation of extremely high pressure between the two anvils was investigated by Arkhipov and Kaganova.[6] According to Ref. (6) the optimal form of anvil surface obeys the formula $Z=Ar^{\alpha}$, where $1<\alpha<2$ and is a function of material properties.

In the contact experiments, *i.e.* measurements of average contact pressures between flat

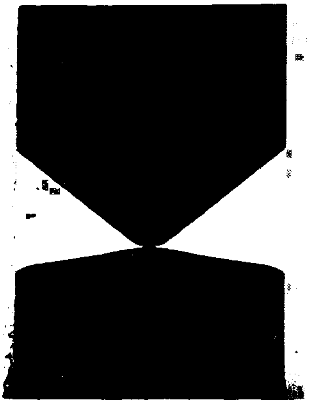

Fig. 1. X-ray photograph of "rounded cone-plane anvil" apparatus.

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and the convex anvils the pressures of megabar range were registered.[7] The attainment of the megabar range of contact pressures makes it possible to get the pressure of the same order in a small sample between the anvils.

A similar apparatus for high pressure generation was used also in Ref. (8), but the material of anvils was a natural diamond. In Ref. (8) the pressures of megabar range were also registered.

## 2. Experiment

The following procedure was used for the investigation of dielectric-to-metal transitions in solids. The sample which was a fine powder has been deposited on a flat surface of the anvil out of the acetone or ethanol suspension. The method of a sample precipitation makes it possible to get a fine but continuous and regular layer of material to be investigated.

The force was generated by hydraulic or clamp press. Resistance *versus* force measurements were registered by an X-Y recorder. The range of resistance measured was from $10^9$ Ohms(the resistance of insulation) to a few Ohms. Direct measurements of the sample resistance are difficult to make owing to smallness of the sample. Therefore the sum of sample resistance and that of the anvils was measured (carbonado diamonds are conductors of electricity).

Thus the initial value of resistance measured was $10^7$-$10^9$ Ohms, but the final corresponding to the metallic phase of the sample was usually some units or dozens Ohms.

In a number of experiments with various substances we have discovered a sharp drop of resistance similar to that seen in experiments with Ge, Si, some $A^{III}$ and $B^{V}$ compounds.[1-3]

Such a dependence in our experiments may be interpreted as various events: phase transition of the sample to a conducting state, or short circuit of the anvils, or electrical disruption of the sample.

The existence of regular layer of the sample after the unloading gives the evidence that the short circuit does not take place. To verify the electrical disruption hypothesis the following experiments were carried out: the voltage of the measuring system varied from 0.1 V to $10^{-4}$-$10^{-5}$ V, and dependences $R(F)$ did not modify. Moreover, in some experiments the anvils with the sample were loaded to the force at which in preliminary experiments the resistance became small without any voltage and then the current-voltage characteristic was measured. This characteristic appeared to be linear, which corresponds to the constant value of sample resistance beginning from the lower limit of voltage measurements $10^{-6}$ V.

The electrical disruption can be observed at the fixed force in dielectric phase of the sample at voltages 10-100 V.

The supposition that the jumps of resistance correspond to the phase transitions to the conducting state sometimes can be checked up experimentally (in the cases when these transitions are of the first order ones as for example, the dielectric-to-metal transitions in Si, Ge.[1-3] The first order phase transition does not take place at the phase equilibrium line on $P$-$T$ diagram,

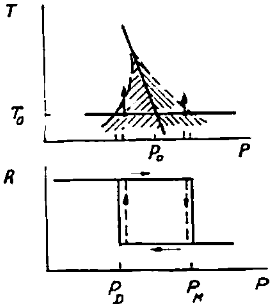


Fig. 2. The scheme of "unfreezing" of metastable phases:
a) the part of phase $P$-$T$ diagram;
b) the resistance *vs.* load curve. The dashed lines correspond to the "unfreezing" processes under heating of the sample.

but at some distance of it (supercooling, superheating, superpressing). In case the material is a dielectric one at low pressures and its high-pressure phase is the metallic one, the dielectric-to-metal transition at constant temperature takes place at some value of pressure $P_M > P_0$ and on the contrary, the transformation from metallic to dielectric phase takes place at pressure $P_D < P_0$, where $P_0$ is the equilibrium pressure. In the pressure range $(P_0, P_M)$ the dielectric modification exists as a metastable one (if this state has been developed by increasing the pressure from the stable dielectric), and *vice versa*, in the pressure range $(P_D, P_0)$ the metastable metallic modification exists. The range of the existence of metastable phase decreases with a temperature increase, the velocity of transformation from the metastable state to a stable one increases with a temperature increase. The existence of the metastable states is the cause of the hysteresis on the dependence of resistance *versus* pressure (or load applied) (Fig. 2) and hysteresis loop becomes narrower with the temperature increase.

These kinetic considerations make it possible to separate the first-order dielectric-to-metal transitions from the short circuit. In the experiment it is enough to increase the temperature when the sample is in the metastable state near the hypothetical phase transition. If the velocity of transformation increases the phenomena can be interpreted as a phase transition.

It should be noted that the "unfreezing" of the metastable phase is sufficient indication of the first-order transition, but it is not a necessary one. One can imagine such a $P$-$T$ diagram where the increase of temperature of a metastable phase leads to the same but a stable phase.

The "unfreezing" of the metastable modifications is used as a test in all our experiments on dielectric-to-metal transitions.

## 3. The Dielectric-to-metal Transitions

### 3-1. *Carbon*

In Refs. (3) and (9) was stated a supposition that at high pressures carbon should undergo the transformation from diamond into a metallic state with a structure of white tin type, similar to the behaviour of germanium and silicon under high pressure. In a shock experiment with graphite made by Alder and Christian[10] the change of the slope of the curve $P(V)$ at ~600

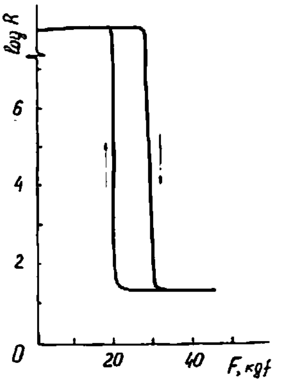


Fig. 3. The resistance *versus* load curve for diamond.

kbar was interpreted as a phase transition of diamond to a metallic phase.

In other similar experiments[11,12] such a result had not been obtained. Diamond[13] was also studied using a shock-wave loading up to pressures 6 Mbar, but in this experiment dielectric-to-metal transition had not been observed either

The theoretical evaluations give the value of transition pressure $P=1.79$ Mbar,[14] $P=1.68$ Mbar.[15]

In our experiment we have pressed the thin layer of diamond powder between carbonado anvils. On loading, a stepwise decrease in electrical resistance by several orders was observed; with release of pressure the resistance resumed its initial value (Fig. 3). The temperature dependences of resistance in dielectric state measured at successively increasing loads show that the energy gap falls as the force increases. Minimal value of $\Delta E$ measured at such conditions was 0.3 eV.

If the dielectric sample was subjected to the pressure that was insufficiently high for the dielectric-to-metal transition at room temperature, heating the sample sometimes led to the reversible transition. This fact gives the evidence that the phase equilibrium curve for carbon has a negative slope on $P$-$T$ diagram, similar to that for Ge and Si.[1-3]

The experiments on "unfreezing" of the metastable states for diamond samples give the evidence that the sharp change of the sample resistance under load is caused by a first-order phase transition to a conducting state.

### 3-2. *Boron nitride*

The possibility of dielectric-to-metal transition for BN was discussed in the work by Bundy and Wentorf[16] and the transition pressure evaluated in Ref. (16) is 400-700 kbar. Van Vechten[15] gave a higher value $P=2110$ kbar.

In some experiments[17] boron nitrde was investigated by the shock-wave methods, but dielectric-to-metal transition was not observed.

Our experiments were carried out with the samples of different modifications of BN: cubic, hexagonal, wurtzite. From the data of resistance-load dependence measurements and experiments on "unfreezing" of metastable states one can conclude that the boron nitride undergoes also the transition to a metallic state under load.

### 3-3. *Oxides and fluorites.*

The problem of dielectric-to-metal transitions in oxides is closely connected with a problem of earth's structure.

Silica $SiO_2$ was investigated in a number of experiments by a shock-loading methods,[18,19] but in Refs. (8) and (19) metallic phase of $SiO_2$ was not discovered. Kawai and Nishiyama[20] using split-sphere apparatus have registered the sharp decrease of $SiO_2$ resistance under high pressure. In our experiments[21] the $SiO_2$ samples also undergo the phase transition to a state with a high conductivity. It should be noted that in a recent work[22] with a magnetic implosion technique, phase transition into a state with density ~10 g/cm$^3$ at the pressure $1.25 \pm 0.15$ Mbar was observed, but the conductivity of the sample in Ref. (22) was not measured.

Magnesium oxide MgO was investigated in Ref. (23) by Kawai and Nishiyama, and the phase transition into a conductive state was discovered. Our experiments give also the evidence on the existence of this transition.

Aluminium oxide $Al_2O_3$ is of a great interest owing to the high pressure measurement method using "ruby" scale.[24]

Phase transition of $Al_2O_3$ in shock-wave experiments has not been obtained.[25] Our experiments with the sample of $Al_2O_3$ show the sharp drop of resistance under pressure which is characteristic of dielectric-to-metal transition. The "unfreezing" of metastable states of $Al_2O_3$ gives also the evidence of phase transition. The destruction of the metastable state has been observed at the external heating as well as at heating by means of the current putting through the sample.

In Fig. 4 the current-voltage curve of system (anvils + sample) is shown. The rise of the current through the sample leads to the local heating of metastable sample and to the transition into the stable state.

Fluorites $CaF_2$, $SrF_2$, $BaF_2$ have been investigated earlier in the experiments with static high pressures[26,27] as well as at shock-wave conditions,[28] but the metallic conductivity of these substances has not been discovered.

Our experiments[29] show that under high pressure the fluorites $CaF_2$, $SrF_2$, $BaF_2$ undergo

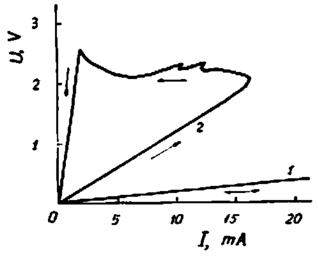


Fig. 4. Voltage-current characteristic of $Al_2O_3$ sample. The curve 1 corresponds to the constant value of resistance $R=20$ Ohm load applied $F=80$ kgf, the initial value of resistance at $F=12$ kgf (curve 2) $R=1$ 23 Ohm, but the final $R=1300$ Ohm.

a phase transition into a metallic state.

### 3-4. *Sodium chloride*

The use of sodium chloride in a number of experiments as the pressure gauge makes it very interesting to observe the phase transitions of NaCl. From one of the theoretical evaluations the pressure of the dielecetric-to-metal transition in NaCl is 1.35 Mbar.[30] In shock-wave experiments at megabar pressures this transition has not been observed.[31] Our experiments with NaCl show the reversible sharp drop of resistance under pressure as well as a set of phenomena of metastable phases "unfreezing".

### 3-5. *Sulphur*

Molecular crystals also exibit the dielectric-to-metal transitions under high pressures. Such phenomena have been discovered in phosphorus, selenium, and iodine. Sulphur has been studied in a set of experiments.[32-36] Slykhouse and Drickamer[32] evaluated the pressure of dielectric-to-metal transition $P\sim400-500$ kbar. Experimentally David and Hamann[33] at $P\simeq230$ kbar and $T\sim1000-1500$K have observed the decrease of resistance. In our work[34] a smooth decrease of sulphur resistance with pressure increase was observed, as well as in subsequent works by Chhabildas and Ruoff[35] and Dunn and Bundy.[36]

### 3-6. *Hydrogen*

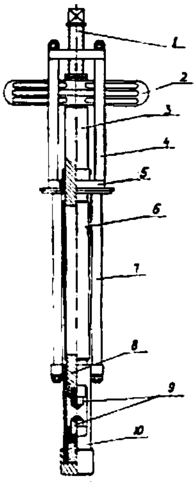
The problem of metallic hydrogen attracts the attention for a set of reasons. The atom of hydrogen is the simplest one and the exact calculation may be made. The solid consisting of hydrogen atoms is therefore convenient for the theoretical calculations. To the present time the theoretical calculations of the equation of state of hydrogen have been made by many authors, as well as the evaluation of pressure of dielectric-to-metal transition.[37-44]

The pressure of this transformation by estimations[37-42] is in the limits of 0.25-10 Mbar. Experimental examination of these calculations is of great significance for the right understanding of many-body problem.

The metallic hydrogen is of considerable interest as a material which has perhaps the temperature of superconducting transition. The authors of Refs. (43) and (44) predict the value of $T_c$ for hydrogen from 50K to 200K and the critical magnetic field intensity $10^4$ Oe.

Moreover, metallic hydrogen should be a fuel with a high heat value.

To the present time hydrogen was investigated at megabar pressures by shock-wave methods. In Ref. (45) hydrogen with density about 2 g/cm$^3$ was obtained at pressures 8 Mbar by the magnetic implosion technique. An analogous method was used in Ref. (46). The resistivity of hydrogen measured in Ref. (46) was less than 0.04 Ohm cm, but the temperature in shock experiments is usually about $10^3$-$10^4$K, and it makes it difficult to measure the resistivity and to register the dielectric-to-metal transition. Therefore the results of great interest should be obtained in the experiments with the static pressures of megabar range.



1—screw
2—spring of dynamometer
3—rod
4—column
5—cap of the cryostat
6—thin-walled tube
7—thin-walled tubular columns
8—piston
9—anvils
10—cylinder

Fig. 5. The scheme of low-temperature press.

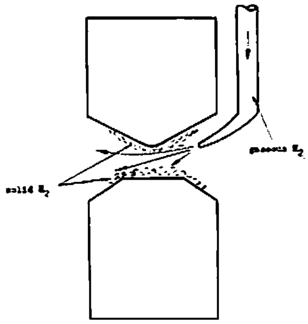


Fig. 6. The scheme of hydrogen sample preparation.

Now there are three scientific groups where the hydrogen is investigated at static megabar pressures.

The group of the Institute for High Pressure Physics of the USSR Academy of Sciences published the results of observation of dielectric-to-metal transition in hydrogen[47] at static pressures 1 Mbar.

Group of Osaka University[48] has also observed the transition of hydrogen into a metallic state. These experiments were made using the split-sphere apparatus.

Mao and Bell[49] from Geophysical Laboratory of Carnegie Institute used the anvils made of natural diamonds. They have investigated the hydrogen at room temperature in pressure range 600-700 kbar. The metallic hydrogen had not been observed by them.

Our experiments with hydrogen were carried out using the installation, the main part of which is the low-temperature press (Fig. 5). The carbonado anvils were deposited in a lower part cooled by liquid helium. Hydrogen was transmitted to the anvils through a heated capillary and condensed on its surfaces as a thin layer (Fig. 6).

Solid hydrogen is a plastic medium, and therefore it was not clear whether it would be a success to keep the hydrogen sample between the anvils under a load. For the elucidation of the problem of plastic medium running out from the clearance between anvils the experiments were carried out with the $H_2O$ ice which is also the plastic solid.

The water vapors condensed on the anvils surfaces at low temperature and the loading of anvils was sufficiently high but insufficient for the dielectric-to-metal transition. At room temperature the anvils with the layer of ice were kept for several hours. After keeping the sample for 1-2 hours no change of resistance was noticed. This fact shows that the velocity of ice running out from the high-pressure region is small enough.

The change of resistance was not either noticed at the warming of the anvils to the

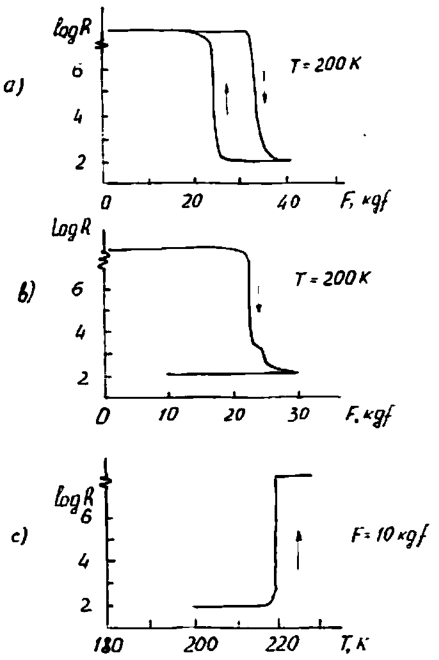


Fig. 7. The dielectric-to-metal transition in $H_2O$ sample and the "unfreezing" of metastable metallic phase.

temperature of 100°C. The subsequent loading of the anvils leads to the decrease of the resistance on several orders. The reality of phase transition in $H_2O$ ice was verified by the "unfreezing" (Fig. 7). It should be noted that the dielectric-to-metal transition of $H_2O$ was later discovered by Kawai.[50]

The experiments with hydrogen were started also from the observation of running out from the clearance between the anvils.

For this purpose the solid hydrogen placed between the anvils at 4.2K kept there under load a long time.

First the resistance of the sample was so high as to correspond to a dielectric phase, but several hours later the short circuit was registered. If the anvils were loaded without hydrogen the conductivity appeared at a negligible load.

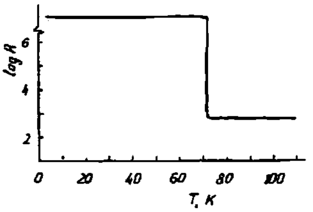


Fig. 8. The resistance *versus* temperature curve at the running up of hydrogen at the heating.

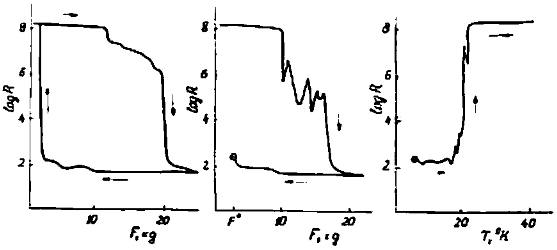


Fig. 9. Dielectric-to-metal transition of hydrogen sample and "unfreezing" of metastable metallic phase.

Warming the anvils with the hydrogen sample with a velocity about 1 K/min the conductivity appeared at temperatures 70-100 K only (Fig. 8). These experiments show that the hydrogen can be kept in a high-pressure apparatus consisting of flat and convex anvils during the time which is enough for the experiments to carry out.

Figure 9 shows the resistance of hydrogen sample *versus* load applied. The preparation of metastable metallic phase and its "unfreezing" is shown in Figs. 9 b and c.

## 4. The Sequence of Dielectric-to-Metal Transformations by Increasing of Pressures

The values of phase transformation pressures were not measured in our experiments, but we made an attempt to determine the sequence of such transformation at room temperature.

One of the simple methods of the localization of some phenomenon at the pressure axis is the direct comparison of its pressure with the pressures of the phase transitions of other substances even if the exact values of these pressures are not known.

Experiments were carried out with the samples which were binary mixtures of dielectric particles. Under pressure enough for the dielectric-to-metal transition in one of the components the sample becomes the medium heterogeneous on conductivity. In the heterogeneous samples of finite size the conductivity is the function of conducting component concentration, as it can be seen from the theory of the percolation.[51,52]

In our experiment metal appears firstly in a small region because of pressure inhomogeneity, and the conducting particles do not form the closed circuit between the anvils, and conductivity is absent.

The increasing of the force applied increases a pressure as well as the volume where $P>P_1$ ($P_1$ is the pressure of dielectric-to-metal transition in the first component of mixture).

At some value of the force applied the conducting particles form the conductive cluster between the anvils and the first jump of resistivity is registered. The further increasing of the applied force makes this cluster greater, and conductivity slowly decreases. At pressure

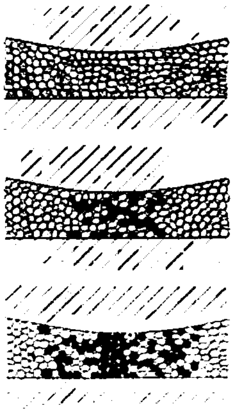


Fig. 10. Binary mixture of dielectric powders at the loading $F_1<F_2<F_3$:
a) at small value of load applied $F_1$ all the particles are dielectric ones;
b) at $F_2$ some particles of the first component became metallic ones (black particles);
c) at $F_3$ all the particles in a small volume are metallic ones.

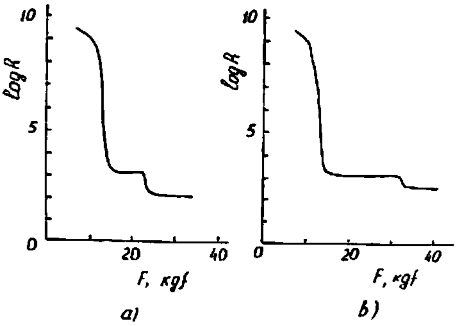


Fig. 11. Dielectric-to-metal transition in binary mixstures $CaF_2+Al_2O_3$. The ratio of component is:
a) 10: 1.
b) 2: 1 (by weight)

$P_{II}$(pressure of second component dilelectric-to-metal transition) the resistance shows a second jump because of the region of the sample where all the particles are conducting is springing up. The increasing of the force after the second jump is accompanied by a slow decrease of the resistance that corresponds to an increase of the region where all the particles are conducting.

The $R(F)$ curves at pressure decrease are the same as those at pressure increase, but a certain hysteresis takes place here.

Values of the resistance jumps in the R(F) curves are the functions of the concentrations of the mixture components.

The value of resistance after the first jump at pressure increase is determined by the conducting particles circuit configuration, which closes the contact between the anvils, or, in percolation theory terms, by cluster topology.

Variety of the concentrations changes the value of this resistance. If the concentration of substance 1 increases the resistance after the first jump decreases and quite the reverse, the decreasing of the concentration of substance 1 leads to the increasing of this resistance value.

Thus by varying the mixture concentration one can determine from the resistance measurements under pressure the sequence of dielectric-to-metal transformation in the components of binary mixture. Figure 11 shows the $R(F)$ dependences for binary mixture of $CaF_2$ and $Al_2O_3$ powders. The concentration of the components in the first case is 10:1 (by weight).

The second curve shows the change of the values of resistance jumps with $CaF_2$ concentration decrease. As it can be seen from Fig. 11, the decrease of $CaF_2$ concentration leads to a second jump decrease, hence, the pressure of dielectric-to-metal transition in $CaF_2$ is greater than for $Al_2O_3$, *i.e.* $P_{CaF_2}>P_{Al_2O_3}$.

We carried out the experiments with binary mixtures whose components were silicon, gallium phosphide, silica, sodium chloride, magnesium oxide, and fluorites. Using these methods the sequence of dielectric-to-metal transitions in various substances was determined. At room temperature the following sequence of pressures of dielectric-to-metal transitions occurs:

$$P_{Si}<P_{GaP}<P_{NaCl}<P_{BaF_2}<P_{SrF_2}<P_{Al_2O_3}<P_{CaF_2}<P_{BN}<P_{C}<P_{SiO_2}<P_{MgO}$$

## 5. The Superconductivity of Substances Transformed into Metals at High Pressures

The superconductivity at low temperatures is one of the more interesting and widespread properties of metals. According to the hypothesis[53] all the metals, except the magnetically ordered ones, are the superconductors at the low enough temperatures. Inasmuch as the modern opinion is that all the substances at high pressure become metals, the logical continuation of this hypothesis is the assumption that all the substances at low temperatures and high pressures are superconductors.

At high pressures the superconductivity was discovered in a set of substances, for example Te, Se, Ge, Si *etc.*[54-60]

The investigations of the substances which become metals at high pressures are of great interest owing to the necessity to systematize the physical properties of various substances under high pressure as well as in connection of the search of new high-temperature superconductors.

For the superconductivity investigations at high pressure we used the low-temperature installation employed earlier for a search of dielectric-to-metal transitions in hydrogen and other gaseous and liquid substances at normal conditions (Fig. 5). The experiments with a superconducting magnet were carried out using a slightly modified installation (Fig. 12) which allowed the heating of the sample at constant temperature of superconducting magnet.

The search of a superconductivity was made by traditional method of conductivity measurements. The resistance was measured by the usual potentiometric way. The current and potential wires were connected to the metallic sets of carbonado anvils. The change of measured resistance in such experiments at superconducting transition was registered usually on the background of residual resistance of some dozens Ohm.

To identify the changes of resistance observed in the experiments with superconducting transitions the dependences of $T_c$ *versus* current flowing through the sample were measured and current-voltage characteristics were obtained, as well as the investigations of $T_c$ dependences

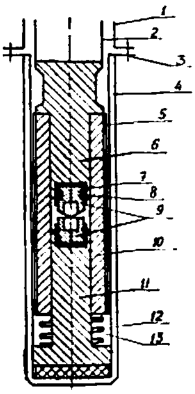


Fig. 12. The scheme of low-temperature installation.
1—external tube;
2—internal tube;
3—flange with packing made of indium;
4—vacuum jacket;
5—winding of the heater;
6—upper rod;
7—insulator;
8—resistance thermometer;
9—anvils;
10—sleeve;
11—lower rod;
12—backward spring;
13—thermal exchange gas (He).

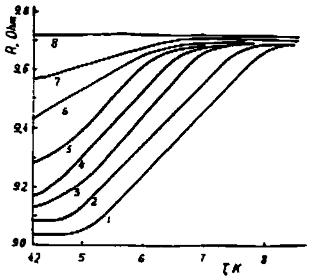


Fig. 13. The superconducting transition in silicon at various values of intensity of magnetic field:
1—H=0; 2—H=1.2 kOe;
3—H=2.3 kOe; 4—H=3.5 kOe;
5—H=4.7 kOe; 6—H=7.0 kOe;
7—H=11.8 kOe; 8—H=23.5 kOe.
Measuring current is 100 mkA.

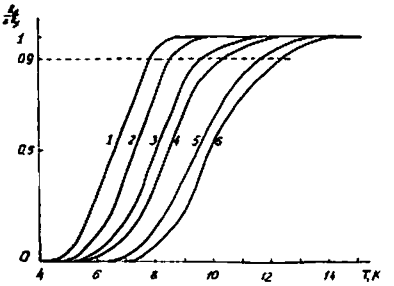


Fig. 14. The superconducting transition in silicon at various values of load applied:
1—$F$=80 kgf; 2—$F$=45 kgf;
3—$F$=10 kgf; 4—$F$=6 kgf;
5—$F$=2 kgf; 6—$F$=0.5 kgf.

*versus* magnetic field intension were carried out.

The investigations of superconducting properties of germanium and silicon in the metallic state carried out by Wittig[55] were repeated by us for the testing of the possibilities of methodics and apparatus. The dependences of resistance *versus* temperature for Ge and Si at pressures near to the pressure of phase transitions proved to be similar to that published by Wittig.[55] These measurements show that in spite of small sizes of the sample the superconductivity of these samples can be clearly observed. Figure 13 shows the dependences of the resistance of Si *versus* temperature at the pressure near that of dielectric-to-metal transition at various intensities of magnetic field. As it can be seen from Fig. 13 the critical temperature of superconducting transition at zero magnetic field is $T_c = 6.7$ K, which is in a good agreement with Wittig's results[55]. The critical intensity of magnetic field at 4.2 K proved to be about 20 kOe.

It is interesting to note that on pressure decreasing $T_c$ of silicon increases. The maximal value of $T_c$ registered in our experiments at pressure decrease is 13 K (Fig. 14).[61]

## 5-1. *Gallium phosphide*

The observation of a dielectric-to-metal transition in gallium phosphide was reported in Ref. (62). According to the data of Ref. (25) the transition pressure is 220 kbar, which was for a long time the limit of attainable pressures. The superconductivity at so high pressures earlier has not hitherto been investigated. In some $A^{III}$ and $B^{V}$ compounds the superconductivity was observed earlier but at lower pressures (*e.g.* GaAs,[57] AlSb[63]).

The measurements of GaP resistance at low temperature show the characteristic behaviour of $R(T)$ curve (Fig. 15). The critical temperature of GaP is the function on a current and pressure applied. The load decrease leads to $T_c$ increase. The maximal value of critical temperature of superconducting transition measured in our experiments is 6.6±0.1K.

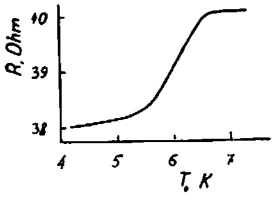


Fig. 15. The superconducting transition in gallium phosphide.

Later the superconductivity of GaP was observed by Wittig *et al.*[64] The temperature of superconducting transition in GaP at pressure near that of dielectric-to-metal transition is about 4 K.

### 5-2. *Xenon*

The problem of dielectric-to-metal transition in xenon was considered in Refs. (65-68). The theoretical evaluations of the transition pressure by Brust[66] give the value of pressure in limits 1-5 Mbar. According to evaluations by Ross[67,68] the pressure of dielectric-to-metal transition is ~700 kbar. Nelson and Ruoff[69] observed the dielectric-to-metal transition in xenon at pressure 330 kbar. The apparatus used in Ref. (69) the "diamond indentor-diamond anvil" technique that is similar to the technique developed at the Institute for High Pressure Physics of the USSR Academy of Sciences.[71]

We have also observed the dielectric-to-metal transition in xenon. At low temperatures was discovered the superconducting transition of metallic xenon[70] (Fig. 16). The temperature of superconducting transition depends on the load applied and the maximal value of $T_c$ registered in experiment with load decrease is $6.8 \pm 0.1$ K. The dependence of superconducting transition temperature $T_c$ *versus* a current flowing through the sample at 4.2 K for Xe is shown in Fig. 17.

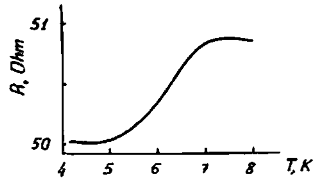


Fig. 16. The superconducting transition in xenon.

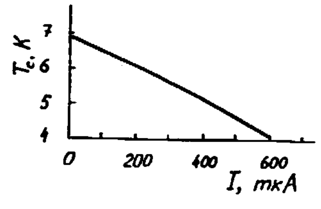


Fig. 17. Critical temperature of superconducting transition in xenon *versus* current intensity.

### 5-3. *Sulphur*

The search of a superconductivity of sulphur was stimulated by the fact that the superconductivity of metallic modifications of selenium and tellurium had been observed.[54,55]

The superconductivity of metallic sulphur was discovered in Refs. (71-73). The dependence of resistance *versus* temperature is shown in Fig. 18. The maximal value of superconducting transition temperature in sulphur registered in our experiments is 9.7 K.

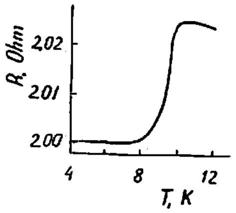


Fig. 18. The superconducting transition in sulphur.

### 5-4. *Sodium chloride*

As it was shown in our experiments[34] sodiumchloride NaCl undergoes the phase transition into a metallic state under high pressure. The superconductivity of metallic phase of NaCl was discovered in Ref. (74). Figure 19 shows the dependence of resistance of NaCl sample *versus* temperature at various intensities of magnetic field.

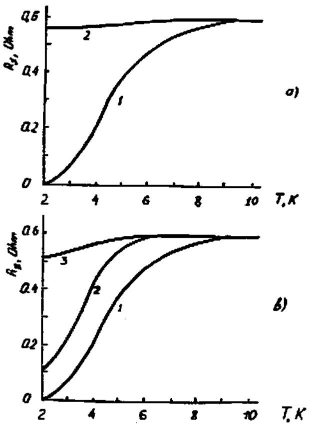


Fig. 19. The superconducting transition in NaCl sample at various values of current intensity:
a) 1–I=100 mkA; 2–$I$=500 mkA; and various values of magnetic field intensity
b) $I$=100 mkA; 1–$H$=0; 2–$H$=12 kOe; 3–$H$= 24 kOe.

## 6. Summary

This short review is devoted to the consideration of the main steps of dielectric-to-metal transitions investigations at high pressures and the search of a superconductivity of new metals. The difference between our apparatus and traditional ones is that the "sample" in our experiments is the small part of the substance investigated *i. e.* the high pressure is generated only in a small volume of substance. The linear dimensions of this "sample" is usually 0.1-0.001 mm. but the small size of the "sample" proved not to be an obstacle for the observation of polymorphic transformations and even for the superconductivity investigations. The apparatus is applicable to the investigations at very high pressures of liquid and gaseous substances at normal conditions, which at low temperatures become solids and then are subjected to very high pressure. Using this apparatus and methods described above we have observed the dielectric-to-metal transitions in a set of substances (diamond, boron nitride, fluorites, silica, aluminium oxide, magnesium oxide, sodium chloride, hydrogen, water, xenon *etc.*) and have discovered the superconductivity of some of these substances (gallium phosphide, sulphur, xenon, and sodium chloride).

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