Metallic Xenon.
Conductivity or Superconductivity?

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The metallization of gases is a problem with a long history. Suspicion that the hydrogen under pressure to be metallic arose as far back as 19th century [1]. In the first half of the 20th century the metallic atomic hydrogen attract an interest as a simplest and superlight alkali metal analogy. In 1927 a simple criterion of metallization of dielectric condensates was found [2]. In 1935 the density of atomic hydrogen was calculated and the critical pressure (about 100 GPa) was evaluated. In 70th after the BCS theory was created, some ideas of non-phonon superconductivity mechanisms were advanced. It stimulated a new splash of an interest on the hydrogen metallization, especially on molecular hydrogen with two electrons with the opposite directed spins. Xenon is the only gas transformed into metal at the present time.

Thorough investigations of the xenon metallization were carried out in [4,5]. Some parameters of optical properties of xenon under pressure were obtained. At pressure larger than (107 - 130) GPa (molar volume $V_m1 \sim (11.6 - 10.7) \text{ cm}^3/\text{mol}$) appears an absorption of photons with energy below 2.7 eV. In Fig.1 (curve 1) the absorption coefficient of this type of absorption at 130 GPa is shown [4]. It is interpreted as an indirect interband absorption edge. At pressure larger than 138 GPa ($V_{m2} = 10.56\text{cm}^3/\text{mol}$) a peak of absorption at 2 eV was observed. It remains at the larger pressure, as well as the first type absorption (Fig.1, curve 2) [4]. There is no unambiguous interpretation of this absorption [4, 5]. A sharp rise of the absorption below about 1.5 eV (Fig. 1, curve 2) at the pressure larger than 142 GPa ($V_{m3} = 10.46\text{cm}^3/\text{mol}$) is regarded as an absorption of classical free-electron metal near the plasma frequency $W_p$. Existence of free electrons is a result of diminution of the energy gap under pressure [4]. According to [4]

$$W_p^{4/3} \sim (V_{m3} - V).$$

(1)
A summary absorption $b$ in the peak at 2 eV may be described by the band model relation [4]

$$b^{2/3} \sim (V_{m2} - V).$$  \hfill (2)

The main purpose of these works [4,5] was to confirm the fact of metallization but not to give its correct interpretation. Nevertheless the high accuracy of the experimental data allows to find not only some contradictions in the optical data interpretation, but also to consider some alternative mechanism of molecular bonding and metallization. In Fig 2a relations (1) and (2) are presented in a logarithmic scale. Indexes near the straight lines are the powers corresponding to these dependencies. It is clear that the more correct powers are 2 and 1. In Fig 2b relations (1) and (2) with correct powers are shown. High accuracy of the experimental data and absence of their suitable description is the cause to try to find another model of the phenomenon. The experimental relation between the plasma absorption energy and the molar volume difference from the volume at metallization is

$$0.5W_p = 3.2B(1 - V/V_{m3})^{1/2},$$  \hfill (3)

where $B = 0.48$ eV (Fig 3). Experimental data corresponds well to Eq. (3). This relation may describe the energy gap near the phase transition. Let us suppose the metallic xenon to be a superconductor. For this case $T_c \sim 0.48$ eV $\sim 5000$ K. The gap energy near transition is about 1 eV. Far of the transition gap energy is about $3.5 \cdot 0.48 = 1.68$ eV. The temperature $T$ is replaced by the volume $V$. The parameters $T$ and $V$ are equivalent in the Gibbs function. For the metallic xenon $T = \text{const}$, while for ordinary superconductors $V = \text{const}$.

Optical absorption by superconducting films has been carefully investigated [6]. A theoretical frequency dependence of a transmission curve [6] may be transformed into a frequency dependence of an absorption coefficient. In Fig.1 the dependence of the theoretical value of the absorption coefficient on the reduced photon energy $W/(3.5kT_c)$ is shown (curve 3).

One may conclude from comparision of the curves 2 and 3 that the gap energy for the experimental curve 2 is 1.4 eV and $T_c \sim 0.4$ eV. It is close to the energy gap evaluated from the plasma frequency. Increasing of the absorption in a high energy region is due to the absorption by normal electrons, as for ordinary superconductor films. For the last the hump corresponding to 2 eV peak were observed sometimes too.

The $P-V$ dependence is plotted in Fig.4 (experimental points, curve 1) [4]. The pressure dependence of the compressibility is shown by the curve 2 in arbitrary units. An approximation by two straight lines of two parts of this curve is shown as well. The possible jump in compressibility at the intersection of lines ($V_{m3} = 10.46\text{cm}^3/\text{mol}$) is neglected.

The $P-V$ dependence with a break is given also in [5] without comment. Softening of the system is a result of the metallization. The touch line 3 is an extrapolation of the dielectric compressibility into the metallization region. One
may suppose the metallization not to be happened and $P-V$ curve runs along the
line 4 up to 200 GPa. At this pressure we shall "swich" a metallization transition
and find ourselves at the line 1. Volume of the system decreases by 0.12 cm$^3$/mol
and its energy changes by 0.24 eV. It means that the number of pairs is about
0.2 of the number of xenon atoms, because the energy gap is about (1–1.4) eV.
System is indeed near the phase transition. One of alternative description of the
IG atom condensates could be based on an average interatomic interaction, for
example, the Lennard-Jones potential $(6-12)$. It could lead to loss of some con-
densate properties. Because of the weakness of interatomic interactions electronic
excitations must be regarded as localized but not Bloch waves. It makes applica-
bility of band theory description of electronic properties of molecular condensates
doubtful.

The similar situation is well known in the case of small radius polarons. In
this case localizes an electron at a site much faster than spreads over the lattice.
And the electron transport is a diffusion process. It was the main difficulty in a
description of the electronic properties of TiO$_2$, treated as a narrow band material
[7]. Most of the properties of TiO$_2$ was adequate described when the small radius
polaron approach was utilized [8]. It is possible the same situation take place
for condensates of IG atoms. The most typical feature of IG condensates is the
smallness of atom size $2r_1$ relatively to equilibrium interatomic distances $2r_2$ in
condensates. For xenon $2r_1 = 1.2$ Å, while $2r_2 = 4.4$ Å. The bond energy of
condensate is about 0.13 eV. It is negligible in comparison to the first excitation
energy of atoms (10 eV).

The second very important circumstance is the coincidence of interatomic dis-
tances $2r_2$ with diameters of atoms in an excited state. Such atoms are excimer
analogies of the corresponding alcaly metals. For this case an alternative ap-
proach to a description of properties of molecular condensates is possible. These
substances have a bond of a metallic type via excited state orbitals but without
a metallic conductivity because a mean number of electrons at excited state or-
bital is $X < 1$. This situation is shown schematically in Fig. 3 (insertion). For
xenon $X = 0.038$. Most of the physical properties (condensation and adsorp-
tion energy, compressibility, metallization under pressure) may be described by ex-
pressions of the theory of simple metals with electron charge $e$ replaced by $eX$
[9]. Nevertheless such averaging in some cases is unfit also.

It is the fact that condensed xenon at normal pressure has $X = 0.038$ and
the electron concentration $n = 10^{21}$ cm$^{-3}$ what corresponds to 1/25 of the alcaly
metal electron concentration. Absence of the conductivity and the low bond
energy at high electron concentration is a result of averaging at $X < 1$. Actual
meaning of $X$ is the probability for an electron to appear on an excited state
orbital. It is a mean number of virtual excimer metallic atoms among the whole
atoms of the condensate. The conductivity is absent if $X < X_p = 0.12$ — the
percolation threshold [9].

In Fig. 3a in the lattice time scale such situation is shown. And in the elec-
tronic time scale an instantaneous electron distribution of the virtual molecular excitation gas is shown in Fig. 3b. It is obvious that electronic conductivity is possible if $X > X_p$ and the band theory description of the system is valid at $X$ much larger.

After $X$ becomes larger $X_p$ a cobweb of conducting chains or clusters of atoms in virtually excited state penetrates a whole dielectric condensate. Such conducting chains are surrounded by dielectric media in a pre-excimer state. Configuration of the conducting chains depends on the atomic wave function type. It changes permanently and statistically remaining the percolation conductivity up to appearance of the influence of the regularity of the lattice sites. At $X = 1$ condensate becomes excimer ally metal.

An intermediate situation when the nano-dispersed metal-dielectric system is realized is the most interesting one. It may be concerned with HTSC problems and various constructions discussed actively in 70th.

Properties of the condensate are determined by the excited state radius $r_2$ of atoms. It may be expressed through energy by the hydrogen-like formulae $2r_2 = e^2/(E_0 - E_1)$. Here $E_0$ - the ionization potential, $E_1 = e^2/2r_1$ — the transition energy between the ground and excited state of atom.

For the system in which the excited state radius of atoms is fixed the atomic wave functions may be expressed by the energy. Probability $X$ for an electron to appear at excited state orbital with radius $r_2$ may be obtained from the atomic wave functions of excited state

$$X(r_2) = X_1 \exp(-r_2/r_1) = X(E) = X_2 \exp(-E_1/w) = X_2 \exp(-1/g). \quad (4)$$

The pre-exponential coefficient is a relatively weak function of $r$. An average perturbation energy $w = e^2/2(r_2 - r_1)$ is the interaction energy between electrons of the ground state orbitals of the neighbouring atoms at distance $2r_2$ in condensate. For IG relation $g = w/E_1 \sim (0.30 - 0.55)$. Metallization of xenon occurs at $g = 0.75$. The main properties of condensates may be expressed through atomic spectroscopic parameters of atoms.

As the interatomic interaction is a pair one it leads to the possibility of the H$_2$-like molecule Xe$_2$ creation. Such virtual excimer molecules Xe$_2$ has a bond energy of about 1 eV. It is about 2.2/0.529 less the bond energy of H$_2$ molecule (4.37 eV). Lowering of the excitation process energy by 1 eV may facilitates generation of virtual molecular electron pairs and their participation in both the bonding of condensate and the conductivity at the metallization. Energies of the same order have appeared in a discussion of the metallic xenon properties.

The conclusion is that the energy band theory either is not applicable for a description of the metallic xenon properties or it must be more carefully worked up.

At the above consideration the condensation of xenon atoms is a result of atoms interaction with participation of virtual excitations with concentration $X$.,
The conductivity arises at \( V_m \) corresponding to transition over the percolation threshold \( X_p(W) = 0.12 \), which might depend on the light frequency. Fig. 5 on the base of data [4] shows dependencies of the absorption coefficient (the electron concentration) at frequencies 1, 1.7, 2, 2.7 eV on the difference \( V_m - V \). It is clear, that the lower pressure (more \( V_m \)), the more light frequency. The straight line a is the dependence of \( 1 - V/V_m \sim (X_p - X) \) on \( W^2 \). The experimental data \( V_m \) correspond well to this dependence. To a zero frequency corresponds \( V_{m0} = 10.28 \text{ cm}^3/\text{mol} \), which is nearer to 10.2 cm\(^3\)/mol [2], than \( V_m = 10.7 \text{ cm}^3/\text{mol} \) [4] obtained at nonzero frequency. Up to \( V_{m3} = 10.46 \text{ cm}^3/\text{mol} \) light is absorbed by normal electrons of metallic chains \( (W_p \sim 10 \text{ eV}) \). But the mean concentration \( n \sim (X - X_p) \sim (1 - V/V_m) \) (4). A peak at 2 eV might be a "precursor" of the superconductivity, which arises at the pressure higher than 142 GPa. The phase transition occurs (the condensation of the virtual molecular type excitations with zero momentum and spin). The absorption typical for superconductive metallic films below the metal plasma frequency appears. A compressibility of the system (energy capacity) increases at this point. Energy gap (1 - 1.4) eV at 200 GPa corresponds to a number of pairs about 0.2 number of atoms. Of course, all the problems that arise in discussion concerning metallic xenon properties cannot be solved without direct experiments on magnetism. From the other side these experiments would be interesting taking into account the existence of some virtual structures inside dielectric condensates of IG atoms. May be they are simulate to some materials and interactions discussed earlier in connection with the HTSC problem and sometimes mentioned in search of adequate description of the contemporary HTSC.
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Figure 1: The frequency dependence of the absorption coefficient $a$ \cite{4} (1) at pressure 130 GPa; (2) at pressure 200 GPa; (3) the calculated absorption coefficient $\ln t$ of superconducting films dependence on the relative photon energy $W/kT$ \cite{6}. 
Figure 2: a — the logarithmic dependencies of $W_p$ (eV) on $V/V_{m3}$ and of the absorption $b$ (arb. units) at 2 eV on $V/V_{m2}$ [4]. The numbers at straight lines are powers in expressions (1) and (2); $b$ — the volume dependence of $W_{p2}$ (eV) and $b$ (arb units). The numbers at straight lines are powers in expressions (1) and (2). Square points are $V_{m2} = 10.56 \text{ cm}^3 /\text{mol}$ and $V_{m3} = 1046 \text{ cm}^3 /\text{mol}$. 
Figure 3: The volume dependence of $W_p$ (eV) at $A = 0.48$ eV. The points are the experimental data at 200 GPa [4]. Insertions - a — the average electron density $eX$ distribution at excited state orbitals in a lattice relaxation time scale; b — The instantaneous (momentary) distribution of electrons at $X$ lattice sites of condensate in the electron relaxation time scale.
Figure 4: The pressure dependence of the volume $V$ for xenon. 1 — the points are the experimental data [4]; 2 — the compressibility $k$. The straight lines are approximation; 3 — the compressibility of the dielectric phase extrapolated into the metallic phase region; 4 — the $P - V$ dependence at the compressibility corresponding to the dielectric phase. Arrows show the hypothetic transition into the metallic phase from the curve 4 to the curve 1 at 200 GPa.
Figure 5: The dependence of the light absorption coefficient on the Xe volume [4] at the frequencies 1, 1.7, 2, 2.7 eV (the numbers at the straight lines). a — the dependence of the critical volumes $V_m$ (the points) on the squared light frequency.