Metallic Xenon, Molecular Condensates, and Superconductivity

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A possibility of explaining the light absorption observed to occur under pressure-induced xenon metallization as due to the transition to the superconducting state is analyzed. The mechanism of the van der Waals bonding is discussed.

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— Introduction. The evolution of the physical model underlying the theory of superconductivity of metals (the BCS theory) is well known. The history of investigating the possibility of metallization of molecular condensates (MC) and the onset of superconductivity in these compounds dates back much farther. In the XVIII century, it was assumed that hydrogen in the condensed state may be a metal [1]. This problem remains unsolved up to now [2]. A simple criterion of MC metallization under pressure was found in 1927 [3]. The conditions favorable for the metallization of atomic hydrogen were theoretically estimated in 1935 [4]. In 1938, the superconductivity was identified with boson condensation [5]. In 1949, theoretical and experimental investigation of the processes initiated by bringing atoms closer together were started [6]. The interest in the problem of metallic hydrogen and progress in the high static-pressure technologies have culminated in 1989 in a study by optical means of the metallization of xenon at pressures from 130 to 200 GPa [7]. The data obtained were interpreted as indicating band-gap closure induced by lattice compression. In 2000, the dc conductivity of Xe was studied up to 155 GPa [8].

— Analysis of the experimental data of Goettel et al. [9]. A reliable proof of the onset of superconductivity can be obtained only by magnetic measurements. Optical data are the least appropriate for this purpose. Nevertheless, the extremely high accuracy of the data of [10] and, at the same time, their significant deviation from band theory predictions justify an attempt at their interpretation within a different framework [11].

Figure presents the dependences of $a$, the light absorption coefficient, on photon energy $W$ in a xenon film calculated from the data of [10] for the pressures of 130 GPa (curve 1) and 200 GPa (curve 2). Curve 3 plots the coefficient $a$ calculated for superconductor films as a function of $W/(3.5kT_c)$, i.e., the ratio of photon energy to the superconducting transition temperature [12]. The right-hand part of the curves can be explained as due to absorption by normal electrons. Curves of type 3 exhibit sometimes a precursor hump, similar to curve 2 for xenon. A comparison of curves 2 and 3 permits one to estimate formally the $T_c$ point of xenon at 200 GPa as about 4000 K.

![Graph showing light absorption coefficient vs photon energy](image_url)

FIG. 1. Light absorption coefficient $a$ in xenon plotted against photon energy $W$. Pressure (GPa): (1) - 130, (2) - 200. Dashed curve: absorption coefficient of superconducting films calculated vs. $W/kT_c$, the ratio of photon to gap energy [13].

By the band model of metallization, the plasma frequency $W_p^{4/3}$ and the total absorption $b^{2/3}$ in the region of the peak should be proportional to the molar volume difference from the volume at metallization, i.e., $\sim (V_m - V)$ [10]. These dependences were used to determine $V_m = 10.7 - 10.5 cm^3/mol$ and the pressure $P_m = 130 - 140 GPa$. Figure 2 plots $W_p$ and $b$ vs. $(V_m - V)$, i.e., they are the same dependences but with other exponents. These functions approximate better the
experimental points of [10], which permits the following two conclusions:

(i) The first function can be approximated by:

\[ 0.5W_p = 3.2B(1 - V/V_m)^{1/2} \text{ for } B = 0.48eV. \]

This relation can describe the gap energy \( W_p \) in the region of a phase transition, for instance, to the superconducting state. The Gibbs function depends on the parameters \( T \) and \( V \) in the same way. In this case, \( B = T_m = T_c = 5000K \), which is close to the above estimate, and the gap energy is of the order of \( 1 \pm 1.5eV \).

(ii) The transition of xenon to the superconducting state can be described also in terms of the percolation process [14]. In this case, \( V_m \) and \( P_m \) should depend on photon energy \( W \). In Fig. 2 the data of [10] were used to plot the dependence of the absorption coefficient on xenon volume for different photon energies. The volume at which absorption appears \( (a \sim 0) \) depends on frequency. The dependence of these volumes on \( W^2 \) makes it possible to determine the onset of metallization in the case of dc measurements: \( V_{m0} = 10.26cm^3/mol \) and \( P_{m0} = 152GPa \). By the Herzfeld criterion, \( V_{m0} = 10.20cm^3/mol \) and \( P_{m0} = 154GPa \) [10]. Therefore in the dc conductivity measurements carried out in [11] up to 155GPa, the xenon metallization conditions were practically not reached, and the weak growth of the resistance with temperature is possibly due to the effect of contacts and lattice vibration anharmonicity on the total sample resistance.

![FIG. 2. Squared plasma frequency \( W_p^2 \) and total absorption coefficient \( b \) plotted vs. xenon volume \( V \) (data of [10]).](image)

(—Van der Waals bonding. In describing MCs one conventionally makes use of various kinds of averaging (for instance, by introducing the Lennard–Jones potential). This approach may result in either loosing or wrongly interpreting a number of their properties. Consider a condensate of \( Xe \) atoms \( (5s^25p^6) \). We assume the xenon atoms in a virtually excited state to have the \( (5s^25p^6s) \) configuration. In this case, \( (Xe) \) is a chemical analog of \( Cs \) \( (5s^25p^6s) \). The interatomic distances in solid \( Xe \) and in \( Cs \) are similar \((4.4 \text{ and } 4.6\text{Å})\). The hydrogenlike radius of ground-state \( Xe \), \( r_1 = e^2/2E_1 = 0.59\text{Å} \) \( (E_1 = 12.13eV \) is the ionization potential), and the excited-state radius \( r_2 = e^2/2(E_1 - E_2) = 1.88\text{Å} \) \( (E_2 = 8.3eV \) is the transition energy to the excited state). In condensates, the atomic radii increase by \( 15 - 20\% \), which yields \( r_2 = 2.2\text{Å} \). (The effect reverse to the Goldschmidt compression accompanying the removal of an atom from the condensate.) That the interatomic radii in molecular condensates are determined by the excited-state radii, i.e., by the \( (E_1 - E_2) \) energies, is well known. However, the physical interpretation of this situation may be ambiguous. The distances between ground-state atoms are large \( (r_2/r_1 = 3.7 > 1) \), and the time-averaged population of the excited-state orbitals \( X \ll 1 \). The transition probability is low, as is the exciton concentration. Therefore, as in the case of small-radius polarons, the electronic states may be considered well localized, thus permitting one to abandon the band models.

The ground-state wave functions of neighboring atoms in the xenon condensate, for instance, \( F_{5s5p} \cdot \exp (-r/5r_1) \), overlap only weakly. The prefactor is dropped, and the Bohr radius of 0.53Å is replaced by \( r_1 = 0.59\text{Å} \). The wave functions of neighboring atoms

![FIG. 3. Absorption coefficient \( \alpha \) plotted vs. xenon volume \( V \) for energies \( (eV) \): (1) - 0, (2) - 1.0, (3) - 1.7, (4) - 2.0, (5) - 2.7 (data of [10]). The onset of metallization depends on the light frequency. Curve (6): dependence of the volume at metallization on squared photon energy \( W^2 \).](image)
coupled by van der Waals bonding are not correlated (unlike the covalent bonding). Therefore the probability for two electrons of neighboring atoms to occupy simultaneously the same point \( r \), to become excited, and to transfer to the excited-state orbitals can be written as:

\[
X \sim \exp \left( -\frac{2r}{5r_1} \right) \exp \left( -\frac{2r_2 - r}{5r_1} \right) = \exp \left( -\frac{4r_2}{5r_1} \right),
\]

\[
X \sim \exp \left( -0.8\frac{E_1}{w} \right) \quad \text{for} \quad w = \frac{e^2}{2r_2}.
\]

This relation may be regarded as the probability to overcome a barrier \( 0.8E_1 \) when acted upon by a random perturbation of average energy \( w \). The energy of an atomic transition to the excited state \( E_2 \) (\( \sim 0.7E_1 \) for Xe) is close to \( 0.8E_1 \). Therefore it appears natural to treat the probability \( X \sim \exp (-E_2/w) \) as the time-averaged fraction of excited atoms in the condensate, and \((1 - X)\), as the fraction of the ground-state atoms. Such a condensate is a statistical mixture of ground- and excited-state atoms at lattice sites. The excitations being pairwise, this gives rise to the formation of virtual \((Xe)_2\) molecules in the singlet state, which determine both the mean lattice bonding energy and the equilibrium distances, because ground-state atoms are bound by attractive forces only. The existence of the virtual \((Xe)_2\) molecules was deduced from optical data [14]. This scheme of atomic bonding can be described by a periodic alternation of the bonding type ("resonance").

If the \((Xe)_2\) molecule is considered as hydrogenlike, its binding energy should be \( \sim 1eV \). The average energy per Xe atom in the condensate \( \sim 0.13eV \). Therefore \( X \sim 0.13/1 \sim \exp (-4r_2/5r_1) \). In (metallized) \(\text{Xe}, r_{2m} = 1.47\AA \) (\( r_2 = 2.2\AA \)) and, hence, \( X_m \sim 0.35 \), which yields for the binding energy about \( 0.35\times(2.2/1.47) = 0.5eV \). There are many MCs with binding energies close to this value with no pressure applied altogether (see below).

A pair of electrons in a \((Xe)_2\) molecule may be considered as a boson, or as a Cooper pair two lattice constants in size and with a binding energy of \( \sim 1eV \). Under compression, this energy increases \((2.2/1.47)\) times to reach \(1.5eV\). This figure is close to the above estimates of the gap energy when treating metallic Xe as a superconductor.

MCs present apparently the only possibility of following continuously the process of boson condensation at equilibrium and of realizing consecutive transitions from an excitonic insulator to a superconductor and to a Fermi metal, where the average fermion energy exceeds the average boson energy of the system for \( P > P_m [10, 17] \). When forced close together, stable \( Cs_2 \) molecules or \( Ba \) atoms will immediately transfer to a Fermi metal by passing through the unstable superconducting phase (the Mott transition), the situation occurring, for instance, when a metal is "diluted" by an insulator [13, 17]. Steady-state \( H_2 \) molecules brought into proximity produce virtual \((H_2)_2\) molecules, and it is the latter that account for the properties of condensed hydrogen.

Compression of Xe increases the concentration of \((Xe)_2\) molecules, and they form chains and clusters, between which the electron tunneling sets in. This may account for the frequency dependence of absorption in the pretransitional pressure region [10, Fig. 3]. The possibility of existence, prior to Bose condensation, of such chains ("cycles"), which nucleate through attraction between particles, was conjectured from theoretical considerations [18].

The possibility of attaining superconductivity under compression can be studied using MCs with complex molecules which do not possess magnetic moments. Ground-state molecules with magnetic moments act as magnetic impurities with a concentration \( \sim (1 - X) \), thus reducing dramatically \( T_c \). This situation is realized, for instance, in \(\text{O}_2\) at metallization, where \( T_c = 0.6K [14] \).

Figure 4 plots the entropy of evaporation \( S \) as a function of binding energy for MCs and metals. The energies of about \(0.4eV\) for the most typical MCs and \(0.6eV\) for \(\text{Hg} \) (metals) bound an empty region. When "forced" into metallization, the binding energy of \( Xe \) \( \sim 0.5eV \) falls into this instability region separating the insulators from metals [15, 17]. In the case of complex molecules, the pressures may be lower, but there is a danger of their pressure-induced fracture or “chemical” metallization.

\[ \begin{array}{c}
\text{insul.} \\
\text{s/c ?} \\
\text{metal}
\end{array} \]

**FIG. 4**. Dependence of the entropy of evaporation \( S \) on binding energy \( E_b \) for a number of molecular condensates and metals: (1) - \( Ne \), (2) - \( Ar \), (3) - \( Kr \), (4) - \( Xe \), (5) - \( CF_2\text{Cl}_2 \), (6) - \( C\text{Cl}_4 \), (7) - \( CsH_2\text{Cl} \), (8) - \( H_2\text{O} \), (10) - \( Hg \). Dashed line (9) specifies the binding energy estimate for metallic xenon.
The concentration of virtual molecules can probably be increased, and stable superconductors obtained, without applying pressure at all. When an MC is brought in contact with a metal, adsorption forces transfer adsorbed molecules to the excimer state (the catalytic effect [20]). The fullerides \((\text{Me}_3)\text{C}_{60}\) belong possibly to such systems. In the closely-packed array of the \(\text{C}_{60}\) spheres \(\sim 10\,\text{Å}\) in diameter, there are three voids per sphere, which contain one metal atom each. Superconductivity sets in with \(T_c\) of up to \(\sim 40\,\text{K}\) [21]. In complex molecules, virtual excitations are created apparently in their composite parts. It is such systems (clathrates), in which at least one of the components is a molecular condensate, that are of practical interest. Considered from this standpoint, in conventional HTSCs the system is stabilized by “chemical” bonds, and the “low” \(T_c\) temperatures are determined by magnetic atoms.

—\textit{Conclusions.} The properties of metallized xenon may thus far be a manifestation of superconductivity with \(T_c > 300\,\text{K}\).

Molecular condensates are systems in which the Bose condensate state (intermediate between the insulator and the metal) may be detected; this state is unstable in atomic systems bound through stationary states (the Mott transition).

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