Bose-Einstein Condensation Picture of Superconductivity in Ag$_2$(Ag$_3$Pb$_2$H$_2$O$_6$), Na$_{0.05}$WO$_3$ and Na$_{0.041}$NH$_3$ composites. (Dilute metals).

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Traditionally, when one describes the crystallographic structure of oxides, the oxygen ion radius $r_{O^2–}$ is assumed to be approximately equal to 1.4 Å. The oxygen ions occupy in this case 80–90% of the crystal volume. Metal atoms are considered then as ions playing a role of donors with rather small radius of (0.5−0.8) Å. However, the atomic packing picture and, therefore, physical properties such as electric conductivity and superconductivity of oxides will be essentially different, if we assume $r_{O^2–} \sim 0.56$ Å. Such magnitude of the radius is known from the quantum mechanics calculations. According to this picture, 80−90% of the crystal volume is occupied by the metal atom orbitals with radius (1.3−1.9) Å, while the oxygen ions play a role of acceptors, which reduce occupancy of these orbitals ("indirect" dilution of the metal). A "direct" dilution of metals takes place in stoichiometric matrices. When $r_{O^2–}$ 0.56 Å, channels with diameter 3.6 present in the hexagonal matrix Ag$_3$Pb$_2$H$_2$O$_6$ directed along the "c" axis. The channels are filled by chains of the Ag$_2$ molecules with atomic diameter of 2.6 Å and the molecule concentration $n_B = 25.6 \times 10^{20}$ cm$^{-3}$. The Bose-Einstein condensation (BEC) temperature $T_{c,B} \sim 400$ K is calculated for the electron effective mass value $m^* = 7.5m_e$, where $m_e$ is the isolated electron mass. Three-dimensional networks of Na$_2$ chains form in Na solutions in NH$_3$ and WO$_3$ as well (respectively, with $n_B = 4.71 \times 10^{20}$ cm$^{-3}$; $T_{c} \sim 180$ K; $m_e = 5.0m_e$ and $n_B = 4.74 \times 10^{20}$ cm$^{-3}$; $T_{c} \sim 91$ K; $m^* = 10m_e$). Close magnitudes of the Ag$_2$ and Na$_2$ chains parameters respectively in NH$_3$ and WO$_3$ favors the opinion that all these structures have a composite structure and similar mechanisms of the high temperature superconductivity.

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A conductivity of Ag$_2$(Ag$_3$Pb$_2$H$_2$O$_6$), significantly higher than conductivity of pure Ag in the temperature range of 300−500 K was observed in [1]. As high as this the conductivity magnitude is possible only if at least a part of the sample volume is in the superconducting state. However, the quasi one-dimensional nature of this crystal makes confirmation of the superconducting state by means of magnetic measurements rather difficult. If one will use, instead of the traditional value of 1.4 Å, the value of 0.56 Å for the O$^2–$ ion radius, which was obtained in result of quantum mechanical calculations, the concept the crystal structure, packing of atoms, conductivity and superconductivity of the oxide will change essentially and they will appear to be similar to properties of the nano-composites Na$_{0.05}$WO$_3$ and Na$_{0.041}$NH$_3$.

Packing of atoms in the Ag$_2$(Ag$_3$Pb$_2$H$_2$O$_6$) compound according to the X-ray analysis data [1] is depicted in Fig. a. Pb atoms have an intermediate valence, which equals 3.5 in the present case (Pb$^{3+}$−Pb$^{4+}$). The following values of radii were used: $r_{Ag^0} \sim 0.56$ Å, $r_{Ag^1} = 1.30$ Å, $r_{Pb^2} = 1.65$ Å, which are near to the related metal atomic radius values. The Ag$_2$ molecule concentration $n_B = 25.6 \times 10^{20}$ cm$^{-3}$. A view along the "c"-axis onto one atomic layer is presented in Fig. a.

Darkened circles stand for Ag atoms forming molecular chains with the interatomic distance of 3 Å, which having the diameter 2.6 Å, the molecular chains are well isolated from the Ag$_3$Pb$_2$H$_2$O$_6$ matrix. Interphase space of such scale ($h \sim 0.5$ Å−1.0 Å) was experimentally observed in the metal-zeolite systems [7]. A view onto the (a-c) face of the unit cell is shown in Fig.b. A lattice of the Ag$_2$ quasi one-dimensional chains forms an anisotropic 3D medium ("gossamer" type, see Fig.c.)

BEC occurs in the ideal Bose gas, when the de Broglie wavelength satisfies the relation

$$\lambda_B = \frac{2.612/n_B}{h} = \frac{2}{2\pi M kT_c B^{1/2}},$$

or

$$T_{c,B} = 3.31 (h/2\pi)^2 n_B^{2/3}/M.$$  

Assuming that BEC occurs in the array of the Ag$_2$ chains at $T_{c,B} \sim 400$ K, we can estimate the electron effective mass in chains $M/2 = m^*$:

1) For $n_B = 24.6 \times 10^{20}$ cm$^{-3}$ and estimated $T_c \sim 400$ K [1], we obtain $M = 2m^* = 15m_e$, or $m^* = 7.5m_e$.

2) It is seen from Fig.c. that overlapping of the electron pairs of the Ag$_2$ molecules is stronger along the chains, than between ones. However, $T_c$ is determined by the distance between the molecule centers (X), which equals $\sim 6$ Å $\sim \lambda_B/1.38$ Å $\sim 7.4$ Å.

3) Anisotropy of the molecular pairs seemingly shows itself in anisotropy of the superconducting state of the quasi one-dimensional superconductor.

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Ag$_2$(Ag$_3$Pb$_2$H$_2$O$_6$).

Arguments in favor of forming of the 3D network of Na$_2$ molecule chains in the insulating matrix of Na$_{0.05}$WO$_3$ [3] and Na$_{0.041}$NH$_3$ [4] (irregular "cobweb") are presented below.

Concentration of the Na$_2$ molecules is also known. It equals $4.71 \times 10^{20}$m$^{-3}$ in Na$_{0.041}$NH$_3$(T$_{c,B} \sim 180$K) [4], and $4.74 \times 10^{20}$m$^{-3}$ in Na$_{0.05}$WO$_3$(T$_{c,B}$ 91K) [3]. Assuming that BEC takes place, we conclude that the electron effective mass magnitudes in Na$_2$ chains in these nano-composites (respectively, $5m_e$ and $10m_e$) are near to $m^*$ value in Ag$_2$ chains ($7.5m_e$). Distinction of the mass values can be a result of the interatomic distance $D$ in these pairs can be considered as an evidence in favor of these nano-composites (respectively, 5 and 35 at 300K) and Ag$_2$Pb$_2$H$_2$O$_6$.

Not only closeness of the effective mass values in all of these materials, but a nature of the binding energy $\Delta$ of these pairs can be considered as an evidence in favor of the chain structure for Na$_2$ molecules in Na$_{0.041}$NH$_3$ and Na$_{0.05}$WO$_3$ as well. The molecular chains can be one of the steps of the phase separation process in the composites (atoms - molecules - chains - clusters...).

The BEC transition temperature $T_c$ for the molecular chain structure can be estimated from the energetic consideration. If the atomic chain with the binding energy $Q$ is stretched (by the matrix, for instance) up to the interatomic distance $D_1$, and subsequently atoms comprising the chain pair off forming diatomic molecules with the interatomic distance $D_2$, the binding energy of the diatomic molecules reads

$$\Delta \sim (D_1 - D_2)Q/D_2 \sim T_{c,B}.$$ 

This relation is very good satisfied for a variety of fullerides [3].

1) In the case of Ag$_2$(Ag$_3$Pb$_2$H$_2$O$_6$) all parameters are known: $Q = 2.85eV; D_1 = 3.2\,\AA; D_2 = 3.0\,\AA$; therefore, $\Delta = 0.187\,eV$. From the relation $\Delta \sim 5.5kT_{c,B}$ [3] it follows that $T_c = 395\,K$, which is very near to the estimates in [11].

2) The unit cell of Na$_{0.05}$WO$_3$ has an orthorhombic symmetry ($a = 3.67 \times 2\,\AA; b = 3.73\,\AA; c = 3.85\,\AA$) [11]. Since the Na atoms diameter $d_2 = 3.71\,\AA < 3.85\,\AA = D_1$, the Na$_2$ molecules are directed along the c-axis. We have $\Delta = 0.043eV$ and $T_c = 88.8K$ for $Q = 1.17eV$ that is almost in conformity with experimental results (91K) [3].

3) The Na solution in NH$_3$ is metastable and superconductivity with $T_c \sim 180K$ was observed (using the Meissner effect) only a few times from 200 attempts [3]. Forming of Na$_2$ molecules means beginning of the phase separation. The Na atomic volume in NH$_3$ is known to be larger, than in the metal [4]. The interatomic distance increase in molecules is related to a decrease of the binding energy for the metal bonding. The binding energy of the isolated Sn$_2$ molecules equals $\sim 0.35Q$ [11, 12, 13]. Therefore, $T_c \sim 180K$ for $d_2 = 3.71\,\AA$ could be related to the distance $D_2 \sim 4\,\AA$.

The most reliable calculations can be done, to be sure only for Ag$_2$(Ag$_3$Pb$_2$H$_2$O$_6$). They are only qualitative in other cases, but the scale of magnitudes seems to be reasonable. A quantitative relation between $\Delta$ and $T_{c,B}$ can be found from the simple consideration as well. Tuning of the molecular electronic pairs can lead to their BEC. But increase of $n_B$ leads to the drop of the electron pair binding energy $\Delta$ and at some value of $n_B$ it is energetically favorable for electrons to pass into the Fermi state (metal) or into the insulator state. Equating the electron energy density in a metal and in the Bose condensate we have:

$$E_F* \sim 2.87(h/2\pi)^2n_B^{5/3}/m^* \sim \Delta n_{c-B}/2,$$

That gives the estimate for the BEC - BCS crossover: $\Delta \sim 5.5kT_{c,B}$ [3]. Besides,

$$\lambda_B = (2.612/n_B)^{1/3} = h/(2\pi M kT_{c,B})^{1/2} = h/(2m^*6.28kT_{c,B})^{1/2} \sim h/(2m^*\Delta)^{1/2};\ m^* = M/2$$

or

$$\lambda_F = (2.612/n_B)^{1/3} \sim h/(2m^*\Delta)^{1/2}$$

(the single electron tunneling condition). Conclusions:

Similarity of parameters of Ag$_2$ and Na$_2$ chains in essentially distinct matrices Ag$_3$Pb$_2$H$_2$O$_6$, WO$_3$ and NH$_3$ indicates the chain composite structure of these materials and likeness of the phase transition mechanisms (BEC mechanism of the high temperature superconductivity). There exists a 3D network of the Me$_2$ chains in the form of "gossamer" or "cobweb" structures with circular closed loops [14, 15] demonstrating superconductivity of the BEC type.

We can formulate the material requirements for development of promising for practice new superconductors.

1) Essential three-dimensionality of high temperature superconductors is necessary.

2) High magnitude of $\Delta$ is good (for instance, Na can be substituted by Li, Ag or divalent atoms).

3) Maximum concentration of Me$_2$ molecules or of other particles with electron pairs is desirable.

Approaching of such magnitudes of the parameters can be a major physical-chemical and methodical challenge. The Na$_{0.25}$WO$_3$ system, for example, is located at the margin of the structure transition into the stoichiometric compound (tungsten bronze) Me - WO$_{3-n}$-1 with the electrons in the Fermi state. There are a lot of matrices having nano-size voids (zeolites, for instance), which can be used for developing of such nano-composites. Chains or "gas" of particles with electron pairs can be stabilized by the matrix near the threshold of the insulator - superconductor transition.

Similar problems can be encountered in consideration of stoichiometric compounds like YBaCuO. But in this case the situation is not so clear since the effective density of electron pairs is determined by occupation of the metal atoms orbitals: "diluted" metals [3].
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