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Search for new superconducting compounds with a critical transition temperature T_c close to room temperature under pressure

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A new chemical composition of superconducting compounds formed on the basis of elements of the fifth group (semimetals) is proposed within the framework of the quantum Bardin-Cooper-Shriffer quantum theory of superconductivity (BCS-theory) using physical chemistry methods for analyzing equilibrium crystal structures. These compounds satisfy all the conditions for transition to the superconducting state at temperatures close to room temperature and a pressure of $\approx 10^7$ Pa.

As initial chemical elements from which superconducting compounds can be synthesized under pressure, in addition to hydrides, substances that allow the "collectivization" of electrons can be used. The most suitable substances in this sense are the elements of the fifth group of the periodic system or the so-called semimetals, which include Bi, Sb, As, graphite, etc. These elements, by their electrical properties, occupy an intermediate position between metals and semiconductors. They are characterized by a slight overlap of the valence and conduction zones, which leads, on one hand, to the fact that they remain good conductors of electricity up to absolute zero temperature, and on the other hand, they have a significantly lower carrier density compared to metals charge. Moreover, in these substances in a wide temperature range at atmospheric pressure, the stability of the solid phase is maintained and, very importantly, a partial “collectivization” of valence electrons inherent in metals is already realized in the initial state.

It is shown that, under the action of pressure $p \approx 10^7$Pa, semimetals can turn into metals characterized by a specific energy spectrum of electrons. A change in the semimetals structure and in parameters of the electronic subsystem energy spectrum is accompanied by an increase in the electron pairing constant and by the density of electronic states at the Fermi level. In turn, an increase in these parameters makes it possible to transfer semimetals to the superconducting state at temperature ≈300K.

Keywords: High-Temperature Superconductivity (HTSC), semimetals, percolation effect.

Пошук нових надпровідних з'єднань з критичною температурою переходу T_c близькою до кімнатної температури в умовах дії тиску

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В рамках квантової теорії надпровідності Бардіна-Купера-Шриффера (BCS-теорії) з використанням методів фіз-хімії аналізу рівноважних кристалічних структур пропонується новий хімічний склад надпровідних сполук, що утворюються на основі елементів п'ятої групи (напівметалів), які задовольняють всім умовам для переходу в надпровідний стан за температур, близьких до кімнатних і тиску $\approx 10^7$ Па.

В якості вихідних хімічних елементів, з яких можна синтезувати надпровідні сполуки в умовах дії тиску, крім гідридів, можна використовувати речовини, що допускають "колективізацію" електронів. Найбільш придатними речовинами в цьому сенсі є елементи п'ятої групи періодичної системи або, так звані, напівметали, до яких відносяться Bi, Sb, As, графіт і ін. Ці елементи, за своїми електричними властивостями, займають проміжне положення між металами і напівпровідниками. Для них характерним є незначне перекриття валентної зони і зони провідності, що призводить, з одного боку, до того, що вони залишаються хорошими провідниками електрики аж до абсолютного нуля температури, а з іншого боку, мають значно меншу, в порівнянні з металами, густину носіїв заряду. При цьому в цих речовинах в широкому інтервалі температур при атмосферному тиску зберігається стабільність твердої фази і, що дуже важливо, вже в початковому стані реалізується часткова "колективізація" валентних електронів, притаманна металам.

Показано, що під дією тиску $p \approx 10^7$Па напівметали можуть перетворюватися на метали, які характеризуються специфічним енергетичним спектром електронів. Зміна структури і параметрів енергетичного спектра електронної підсистеми полуметаллов супроводжується збільшенням константи спарювання електронів і щільності електронних станів на рівні Фермі. У свою чергу, збільшення зазначених параметрів обумовлює можливість переходу полуметаллов в надпровідний стан при температурі ≈300K.

Ключові слова: Високотемпературна надпровідність (ВТНП), напівметали, ефект перколяції.

Поиск новых сверхпроводящих соединений с критической температурой перехода T_c близкой к комнатной температуре в условиях действия давления

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В рамках квантовой теории сверхпроводимости Бардина-Купера-Шриффера (BCS-теории) с использованием методов физ-химии анализа равновесных кристаллических структур предлагается новый химический состав сверхпроводящих соединений, образующихся на основе элементов пятой группы (полуметаллов), который удовлетворяет всем условиям для перехода в сверхпроводящее состояние при температурах, близких к комнатным и давлении $\approx 10^7$ Па.

В качестве исходных химических элементов, из которых можно синтезировать сверхпроводящие соединения в условиях действия давления, кроме гидридов, можно использовать вещества, допускающие "коллективизацию" электронов. Наиболее подходящими веществами в этом смысле являются элементы пятой группы периодической системы или, так называемые, полуметаллы, к которым относятся Bi, Sb, As, графит и др. Эти элементы, по своим электрическим свойствам, занимают промежуточное положение между металлами и полупроводниками. Для них характерным является незначительное перекрытие валентной зоны и зоны проводимости, что приводит, с одной стороны, к тому, что они остаются хорошими проводниками электричества вплоть до абсолютного нуля температуры, а с другой стороны, обладают значительно меньшей, по сравнению с металлами, плотностью носителей заряда. При этом в этих веществах в широком интервале температур при атмосферном давлении сохраняется стабильность твердой фазы и, что очень важно, уже в исходном состоянии реализуется частичная "коллективизация" валентных электронов, присущая металлам.

Показано, что под действием давления $p \approx 10^7$Па полуметаллы могут превращаться в металлы, характеризующиеся специфическим энергетическим спектром электронов. Изменение структуры и параметров энергетического спектра электронной подсистемы полуметаллов сопровождается увеличением константы спаривания электронов и плотности электронных состояний на уровне Ферми. В свою очередь, увеличение указанных параметров обусловливает возможность перехода полуметаллов в сверхпроводящее состояние при температуре $\approx$300К.

Ключевые слова: Высокотемпературная сверхпроводимость (ВТСП), полуметаллы, эффект перколяции.

Introduction

The problem of synthesis of new polycomponent compounds with zero electrical resistance (superconductivity) at room temperatures ($\approx$ 300 K), arose immediately after the discovery of the so-called high-temperature metal-oxide superconductors, characterized by a transition temperature $77\,K \le T_c \le 164\,K$ [1, 2]. However, in the future, despite the efforts of a great number of researchers, it was not possible to find new compounds that would have a higher temperature T_c for a long time.

An important successful breakthrough in this situation, which served as the beginning of a new stage in the search for superconducting compounds with an elevated transition temperature, was the discovery of superconductivity in hydrogen compounds (hydrides) [3 - 5]. At the same time, it turned out that a prerequisite for the transition of hydrides to the superconducting state at $T_c \ge 200$ K is the need for very high pressure. So, for example, it was found that the LaH10 compound becomes a superconductor at a temperature of $T_c \approx 250$ K under pressure $P \approx 170$ GPa [4, 5]. In this case, with a decrease in pressure, the stability of this compound is violated and its superconductivity is vanish.

The need to apply such a high pressure for the transition of hydrogen compounds to the superconducting state is primarily associated with the process of “collectivization” (association) of valence electrons, which is realized in these compounds under pressure. The “collectivization" of electrons leads to an increase in the density of states in the energy spectrum, which contributes to the phonon pairing of electrons, that is, the appearance of quantum particles - bosons that carry an electric charge without resistance [6]. In addition to the “collectivization” of electrons process under the pressure, the formation of a specific crystal structure is very important for the hydrogen compounds superconductivity (clathrate-like structure), for which the presence of a direction with the smallest possible distance between the nearest neighboring atoms is characteristic. This circumstance, as well as the minimum mass of hydrogen atoms contributes to the formation of high-frequency phonons, which, in turn, leads to an increase in the binding energy in bosons. Both of the above reasons determine the stability of hydrogen compounds and their transition to the superconducting state at a higher temperature than is observed in metal-oxide superconductors. Herewith, as already indicated, this is realized only under pressure $P \ge 10^2$ GPa.

The need to apply so much pressure practically eliminates the use of these compounds for technological purposes. In this regard, the synthesis of new superconducting compounds, which are characterized by a rather high transition temperature $T_c \approx 300$ K, has become very urgent. However, it is very important that this transition is realized under the action of a significantly lower pressure.

In this paper, we propose a new chemical composition of superconducting compounds formed on the basis of elements of the fifth group (semimetals), which, according to the authors, can satisfy the specified requirements.

2. Substantiation of the possibility of using elements of the fifth group (semimetals) for the synthesis of superconducting compounds under pressure

Experimental studies of the superconductivity of substances containing hydrogen (hydrides), as well as the considerations described in the previous section regarding the role of the valence electrons "collectivization" in the formation of hydrogen compounds, indicate that the stability boundary and superconductivity of these compounds are shifted toward lower pressures if we move up the periodic table. In this regard, the idea arose that as the initial chemical elements from which superconducting compounds can be synthesized under pressure, in addition to hydrides, you can use other substances that assume the "collectivization" of electrons.

The most suitable substances in this sense are the elements of the fifth group of the periodic system or the so-called semimetals, which include Bi, Sb, As, graphite and others [7, 8]. These elements, in their electrical properties, occupy an intermediate position between metals and semiconductors. They are characterized by a slight overlap of the valence and conduction zones, which leads, on the one hand, to the fact that they remain good conductors of electricity right up to the absolute zero temperature, and on the other hand, they have much lower charge carrier density than metals. For example, at atmospheric pressure and room temperature in bismuth (Bi), the electron density is $n \approx 10^{24}\,\mathrm{m}^{-3}$, and in antimony (Sb) $n \approx 10^{25}\,\mathrm{m}^{-3}$ [9]. In addition, the electrical conductivity of semimetals increases with temperature.

These features of the electrical properties of semimetals make them close to semiconductors. Moreover, in these substances in a wide temperature range at atmospheric pressure, the stability of the solid phase is maintained and, very importantly, already in the initial state, partial "collectivization" of valence electrons inherent in metals is realized.

Let us estimate the pressure value under the influence of which complete "collectivization" of electrons in semimetals can be achieved, i.e., the pressure at which the semimetal – metal transition can occur. For the sake of concreteness, we will carry out further discussion and evaluations in relation to semimetals Bi and Sb.

In the general case, the pressure P, under the action of which the process of "collectivization" of electrons in a solid crystalline substance is realized, is described using the following relation

$$P \approx 0{,}1 \cdot h^2 n / m r^2. \qquad (1)$$

Here h is the Planck constant, m is the mass of the electron, r is the size of the potential "well" characterizing the localization of valence electrons in the initial state before they are united, n is the density of "collectivized" electrons, that is, the number of charge carriers contained in a unit volume of the formed substance [10]. In the physical sense, for a multi-electron atom, r is the radius of the orbit of the valence electron, i.e. $r \approx (1-5)a$, where a is the Bohr radius of the hydrogen atom $a \approx 0{,}5 \cdot 10^{-10}$ m. Specifically for atoms Bi $r \approx 1{,}8 \cdot 10^{-10}$ m, and for Sb $r \approx 1{,}6 \cdot 10^{-10}$ m [9]. Substituting the numerical values of the constants h, m and the corresponding values of n and r in formula (1), we have for Bi and Sb $P \approx 10^6$ Pa = 10 bar (bismuth) and $P \approx 10^7$ Pa = 100 bar (antimony). This pressure range is much easier to technically implement and therefore, at this pressure, the experimental verification of a possible transition to the superconducting state of compounds formed on the basis of semimetals is simplified significantly, and also makes it easier to use these compounds in practice.

We emphasize that the "collectivization" of electrons is only one of the necessary conditions for the superconductivity of matter display. Another important condition for the realization of the superconducting state is the formation of a special phonon spectrum, characterized by the presence of high frequency phonons (see part 1).

We show that this condition can also be satisfied, if, for the manifestation of superconductivity under pressure, solid solutions based on semimetals are used (e.g., compound $Bi_{1-x}Sb_x$; here x is a parameter characterizing the stoichiometric composition of the compound).

3. Substantiation of the possibility of using semimetals solutions for the synthesis of a compound characterized by a phonon spectrum containing high-frequency phonons

In addition to the features of electrons "collectivization" process described above, semimetals also have other specific properties, which are very important for the formation of a superconducting compound based on them. So, for example, the elements Bi and Sb are characterized by a very small difference in atomic radii (≈ 7,5 %) and therefore, the replacement of these atoms by one another in the crystal lattice during the formation of solutions (two-component compounds) is not associated with a noticeable lattice deformation. Therefore, Bi and Sb form a continuous series of solid solutions, and the phase diagram has the form of a cigar [12]. Investigation of compounds based on this pair of elements ($Bi_{1-x}Sb_x$) by varying the stoichiometry parameter x, it was shown that jump-like changes in such physical properties as electrical conductivity, heat capacity, thermal conductivity, etc. [13]. The close relationship between the changes occurring with the indicated physical properties and the stoichiometric composition of the compound indicates that an abnormally strong electron-phonon interaction is realized in the substance under discussionThis is due to the formation of high-frequency phonons in solid solutions of Bi and Sb elements, which, as already mentioned, should also contribute to the transition of this compound to the superconducting state under certain conditions (temperature and pressure).

Let us pay attention to some more features of Bi and Sb elements, as well as solid solutions based on them. The Bi and Sb atoms separately crystallize into a rhombohedral lattice of the α-A_S type ($R\bar{3}\bar{2}/m$ spatial group). Atoms in the crystal lattice of this symmetry type are located in two parallel planes so that an atom located in one plane has three nearest neighbors located in another plane. Such a specific spatial arrangement of atoms in the substance set its crystal lattice closer to the type of an ordinary face-centered “pseudo-cubic” lattice. This type of crystal lattice in the $Bi_{1-x}Sb_x$ compound remains unchanged upon variation of the parameter x, however, it is accompanied by a significant decrease in the lattice parameters a and c for certain values of the parameter x [13, 14].

The indicated features of a change in the crystal lattice parameters with variations in the stoichiometric composition of the $Bi_{1-x}Sb_x$ are associated with the special nature of its formation (percolation effect) [15]. In this case, when the stoichiometry parameter x changes during the formation of the solution, the following significant changes in the crystal lattice occur: a) for small values of the parameter $x \le 0.05$, clusters (complexes of atoms) arise, the structure of which differs significantly from the structure of the main substance, b) with an increase in x, a superstructure is formed with a long-range ordered distribution of heterogeneous atoms in the structure of the base substance. These structural changes are naturally accompanied by a change in the phonon spectrum of the substance, including the formation of high frequency phonons. This circumstance should contribute to the possible transition of the $Bi_{1-x}Sb_x$ compound to the superconducting state.

Finally, a change in the energy spectrum of the electrons of these compounds can also play an important role for the possible display of superconducting properties in solid solutions based on semimetals under pressure, also observed upon variation of the x parameter. Detailed studies of the dependences of the electrical conductivity σ (x), thermoelectric properties (Seebeck coefficient S (x)), and the galvanomagnetic properties of the $Bi_{1-x}Sb_x$ compound indicate that when the values of the parameter x are varied, the semimetal – metal, semimetal – semiconductor transformations are observed [14].

Conclusions.

Based on the analysis, we can conclude that alloys based on semimetals, in particular alloys of Bi and Sb elements, can be transferred to a state with a high degree of “collectivization” of valence electrons by applying a pressure of $\approx 10^2$ bar. "Collectivization" of valence electrons is one of the necessary conditions for the display of multicomponent compounds superconductivity.

Due to the specific nature of the process of formation of a solid solution based on these elements at critical values of the parameter $x \ge x_c$ (x_c percolation threshold) a crystalline structure can be formed, characterized by the presence of high-frequency phonons, which, in turn, should facilitate the phonon pairing of electrons and, accordingly, the transition of this compound to the superconducting state. x_c percolation thresholds for solutions $Bi_{1-x}Sb_x$ are ≈ 0,25 (Bi base element) and ≈ 0,6 (Sb base element).

The increase in electron pairing energy due to the formation of high-frequency phonons in solutions of semimetals, should also lead to an increase in the critical transition temperature T_c up to room temperature.

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