ISSN 1027-5495. Functional Materials, 28, No.3 (2021), p. 415-419.
doi:https://doi.org/10.15407/fm28.03.415

Internal photoelectric effect and possible superconductivity of group V elements (semimetals)

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Received January 21, 2021

The possibility of using the internal photoelectric effect to transfer semimetals (Bi, Sb, etc.) to a superconducting state at atmospheric pressure and room temperature is discussed. Irradiation of a semimetal with photons of a certain energy and flux power density can cause a significant change in its energy spectrum ("metallized" semimetals with "degenerate" electrons), and also the appearance of an increased fraction of optical phonons in this substance. In accordance with the microscopic theory of superconductivity in metals (BCS theory), both of these factors should determine the effective electron-phonon interaction and, as a consequence, can cause the transition of semimetals to the superconducting state. According to the estimates given in the work, the superconducting state in the near-surface semimetal layer with a thickness $\approx 10^{-6}$ m (or in film) at temperatures close to room one can be realized under conditions of their laser irradiation with a wavelength $\lambda \approx 10^{-5}$ m and pulse duration $\approx 10^{-8}$ s when power density $\approx 10^{11}$ W/m^2 is reached.

Keywords: photoelectric effect, superconductivity, semimetals.

Внутрішній фотоелектричний ефект і можлива надпровідність елементів V групи (напівметалів). *Ю.І.Бойко, В.В.Богданов, Р.В.Вовк, Б.В.Гриньов*

Обговорюється можливість використання внутрішнього фотоефекту для переводу напівметалів (Bi, Sb і ін.) до надпровідного стану за атмосферного тиску і кімнатної температури. Опромінювання напівметалу фотонами певної енергії і густини потужності потоку може зумовити значну зміну його енергетичного спектра ("металізовані" напівметали з виродженимиі електронами), а також появу в цій речовині підвищеної частки оптичних фононів. Відповідно до мікроскопічної теорії надпровідності у металах (теорії BCS), обидва зазначені чинники мають обумовити ефективну електронфононну взаємодію і, як наслідок, можуть викликати перехід напівметалів до надпровідного стану. Згідно з наведеними оцінками надпровідний стан у поверхневому шарі напівметалу товщиною $\approx 10^{-6}$ м (або у плівці) при температурах, близьких до кімнатної, може реалізуватися в умовах їх лазерного випромінювання з довжиною хвилі $\lambda \approx 10^{-5}$ м і тривалістю імпульсу $\approx 10^{-8}$ с за досягнення густини потужності $\approx 10^{11}$ Вт/м^2.

Обсуждается возможность использования внутреннего фотоэлектрического эффекта для перевода полуметаллов (Bi, Sb и др.) в сверхпроводящее состояние при атмосферном давлении и комнатной температуре. Облучение полуметалла фотонами определенной энергии и плотности мощности потока может обусловить существенное изменение его энергетического спектра ("металлизированные" полуметаллы с "вырожденными" электронами), а также появление в этом веществе повышенной доли оптических фоно-

нов. В соответствии с микроскопической теорией сверхпроводимости в металлах (теории BCS), оба указанных фактора должны обусловить эффективное электрон-фононное взаимодействие и, как следствие, могут вызвать переход полуметаллов в сверхпроводящее состояние. Согласно приведенным оценкам сверхпроводящее состояние в приповерхностном слое полуметалла толщиной $\approx 10^{-6}$ м (либо в пленке) при температурах, близких к комнатной, может реализоваться в условиях их лазерного облучения с длиной волны $\lambda \approx 10^{-5}$ м и длительностью импульса $\approx 10^{-8}$с при достижении плотности мощности $\approx 10^{11}$ Вт/м^2.

1. Introduction

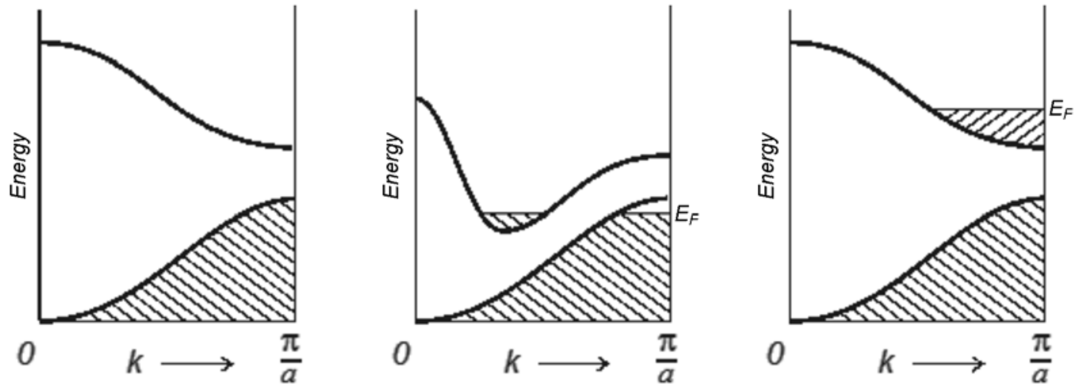
Electrical superconductivity (zero electrical resistance) of a substance is a unique physical property and therefore the study of the causes and conditions of its manifestation is very important for the development of fundamental concepts in solid state physics [1]. In addition to purely scientific significance, this property is also very important for use in modern technical devices: magnetometers, quantum interferometers, resonators, etc. [2, 3]. The main reason limiting the comprehensive and, most importantly, economically beneficial use of superconductivity for technical purposes is that it is realized at low temperatures. A record high value of the critical temperature for a transition of matter into a superconducting state, $T_c \simeq 164$ K was registered in a complex metal-oxide compound HgBaCaCuO [4]. In recent years, higher values of T_c were found when studying the electrical conductivity of compounds of some metals with hydrogen (hydrides) [5–7]. For example, in the LaH_{10} compound, the critical temperature T_c is about 250 K. This value of the critical transition temperature is more acceptable for the use of metal hydrides in practice. However, the discovery of compounds with an increased value of T_c did not fully solve the problem under discussion, since superconductivity in them is realized only under conditions of significant pressure ≥ 150 GPa.

Thus, until now, the search for new substances with an elevated temperature T_c, as well as the determination of acceptable technical conditions for the realization of superconductivity, remains an urgent task. One of the promising ways to solve this problem is to study the electrical conductivity of elements of group V of the Periodic Table (semimetals) under pressure [8, 9]. The calculated value of the pressure for achieving "metallization" of semimetals and their transition to the superconducting state is $\approx 10^{-1}$ GPa. This value is much less than the pressure required for the transition of metal hydrides to the superconducting state. However, this way also does not fully solve the described material science problem.

This paper discusses the possibility of using the internal photoelectric effect to create conditions for the transition of semimetals to the superconducting state at atmospheric pressure and room temperature. Irradiation of a semimetal with photons of a certain energy and flux power density can cause a significant change in the energy spectrum of the semimetal, as well as the appearance of an increased fraction of optical phonons in this substance. In accordance with the microscopic theory of superconductivity in metals (BCS theory), both of these factors should ensure effective electron-phonon interaction and, as a consequence, can cause the transition of semimetals to the superconducting state [10].

1.1. The physical concept of the semimetals transition to the superconducting state

Semimetals include elements of group V of the Periodic Table: Bi, Sb, etc. For concreteness, all consideration and numerical estimates will be carried out using the example of bismuth (Bi). Under normal conditions at room temperature and atmospheric pressure, the atoms of this element are characterized by an electronic configuration s^2p^3, and the solid crystalline phase of this substance in its electrical properties occupies an intermediate position between metals and semiconductors. That is why the elements of the V group are called semimetals. They are characterized by a partial overlap of the valence and conduction bands (Fig. 1). This specificity of the energy spectrum determines that, on the one hand, semimetals are good conductors of electricity, and on the other hand, they are characterized by a much lower density of charge carriers in comparison with ordinary metals. For example, at room temperature, the electron density of Bi is $n_e \simeq 10^{24}$ m^{-3}, which is $\simeq 10^5$ times less than in classical



a) b) c)

Fig. 1. Scheme of filling the allowed energy bands with electrons: a) dielectric, b) semimetal, c) metal.

metals. In addition, the conductivity of semimetals, in contrast to conventional metals, increases with increasing temperature. These features of the electrical properties make the semimetals similar to the so-called "non-degenerate" semiconductors [11]. However, under certain conditions, semimetals can "metallize", that is, the energy spectrum of these substances changes, and the nature of the filling of energy levels becomes similar to the energy spectrum of metals. At the same time, electrons "degenerate", that is, their properties obey the laws of quantum mechanics, and the energy spectrum is described by the Fermi-Dirac statistics [12]. However, it should be have in mind that metals obtained from semimetals can differ significantly in their physical properties from those of ordinary metals and, in particular, by their electrical properties: "metallized" semimetals with "degenerate" electrons can become superconductors.

This paper discusses the "metallization" of semimetals during their irradiation with a photon flux and realization of the so-called internal photoelectric effect. As already indicated, semimetals are characterized by a specific energy spectrum structure, which consists in a partial overlap of the conduction and valence bands (Fig. 1, c). With such a structure of the energy spectrum, irradiation even with photons with low energy $\simeq (1 \div)\cdot^{-2}$ eV can be effective enough for a significant increase in the number of electrons in the conduction band [13]. When semimetals are irradiated with low-energy photons, simultaneously with an increase in the number of electrons in the conduction band, as a rule, phonon generation (relaxation process) also occurs. These phonons have a frequency that coincides in magnitude with the frequency of irradiation photons $\simeq 10^{13}$ s^{-1} (optical phonons). The frequency of these irradiation-induced phonons is an order of magnitude higher than the maximum (Debye) frequency of the irradiated substance, for example, for Bi, $\nu^{\max} \simeq 10^{12}$ s^{-1}. Consequently, first, the formation of optical phonons under irradiation causes an increase in the Debye temperature of semimetals from $\theta \simeq 10^2$ K the value $\theta \simeq 10^3$ K, because $\theta \quad \nu^{max}$. Second, the presence of optical phonons contributes to an increase in the electron pairing constant μ from the values of <1, characteristic of ordinary metals, to the values of >1. For example, according to different estimates for metallic hydrides, formation of optical phonons leads to an increase in the value of the parameter μ from $\simeq 1.5$ to $\simeq 5$. Thus, irradiation of semimetals with a photon flux can cause an increase in two important parameters characterizing the critical temperature of substance transition into a superconducting state: the Debye temperature θ and the pairing constant μ.

1.2 Quantification of the parameters of the photon flux causing the transition of semimetals to the superconducting state

To ensure the internal photoelectric effect and, accordingly, to facilitate the transition of a semimetal to a superconducting state, the following requirements for the photon flux are necessary: 1) the photon energy must exceed the optical phonon energy, i.e. $E_{phot} \geq E_{phon} \simeq 10^{-2}$ eV and 2) the densities of photons and phonons should be the same, i.e. $n_{phot} \simeq n_{phon}$.

The phonon density can be estimated using the relation:

$$n_{phon} \simeq 3T/a^3\theta. \qquad (1)$$

Here T is the temperature, a is the crystal lattice parameter of the substance, θ is the Debye temperature. Assuming $T \simeq 300$ K (room temperature), $a \simeq 2\cdot10^{-10}$ m, $\theta \simeq 100$ K, we have: $n_{phon} \simeq 10^{30}$ m^{-3}. Thus, when using photons with energy $E_{phot} \simeq 5\cdot10^{-2}$ eV, the first requirement is satisfied. In this case, the wavelength λ of the corresponding photons is $\simeq 3\cdot10^{-5}$ m. This wavelength corresponds to the lower limit of infrared radiation and, accordingly, sufficiently powerful fluxes of this radiation can be achieved using laser technology [14]. At a photon density $n_{phot} \simeq 10^{30}$ m^{-3}, a pressure arises in the irradiated substance:

$$P \simeq E_{phot}n_{phot}. \qquad (2)$$

Substituting the above numerical values E_{phot} and n_{phot}, we have $P \simeq 5$ GPa. Such a pressure value can be achieved experimentally if a laser with a flux power density $\approx 10^{11}$ W/m^2 at pulse duration $\approx 10^{-8}$ s is used [15]. The indicated pressure is sufficient to cause the "degeneracy" of conduction electrons in semimetals, that is, the transfer of electrons to the category of quantum particles with all the ensuing circumstances [9].

On the basis of the above consideration, we can draw the following conclusion: when semimetals are irradiated with photons, significant changes can occur in the energy and phonon spectrum of these substances. First, as a result of the photoelectric effect, the number of electrons in the conduction band can increase; secondly, the pressure caused by the photon flux can provide "degeneracy" of conduction electrons in semimetals, i.e., the "metallization" of semimetals; and, finally, thirdly, as a result of relaxation processes accompanying the internal photoelectric effect, optical phonons can be generated in semimetals. The factors listed above should cause the transition of semi-metals to a superconducting state during irradiation.

In this case, it is necessary to keep in mind the following important circumstance. The efficiency of the internal photoelectric effect depends significantly on the penetration depth of photons into the irradiated substance. For example, low-energy photons with a wavelength $\lambda \simeq (10^{-4} \div 10^{-5})$ m penetrate into the metal and are completely absorbed in the near-surface layer with a thickness $\approx 10^{-8}$ m. In this regard, the internal photoelectric effect is practically not realized in conventional metals. In the case of semiconductors and semimetals ("nondegenerate" semiconductors), the penetration depth of photons of the same energy can reach the value $\approx 10^{-6}$ m [16]. Thus, the described effect of the semimetal transition to a superconducting state upon irradiation with photons can be realized in a bulk sample in a layer $\leq 10^{-6}$ μm thick, or in a film of the same thickness.

1.3. Estimation of the possible critical temperature of the transition of semimetal to the superconducting state under photon irradiation

In accordance with the BCS theory, the temperature of transition to the superconducting state as a result of the electron-phonon interaction in the case of metals is described by the following relation:

$$T_c \simeq \theta\exp[-(1+\mu)/(\mu-u)]. \qquad (3)$$

Here θ is the Debye temperature, μ is the pairing constant, u is the so-called Coulomb pseudo-potential characterizing the mutual repulsion of electrons (usually $u \simeq 0.1$). In the case of weak pairing $\mu \leq 1$ (metals) and without taking into account the mutual repulsion of electrons, i.e., at $u \simeq 0$, equation (3) is transformed to the form:

$$T_c \simeq \theta\cdot\exp(-1/\mu). \qquad (4)$$

For superconducting metals and metal alloys, the Debye temperature is in the range of $\approx (100 \div 300)$ K. In accordance with formula (4), at the value of the pairing constant $\mu \simeq 0.3$, the critical temperature T_c in these substances is in the range of $\approx (1 \div 10)$ K, which is in good agreement with experimental data. In the case of strong pairing, namely, in the case of "metallized" semimetals, it can be assumed with high probability that $\mu \geq 1$. In this case, relations (3) and (4) are not applicable, and the value of T_c is described by a different relation [17]:

$$T_c \simeq 0.2 \cdot \theta \cdot \mu^{1/2}. \qquad (5)$$

In the case of substances (for example, hydrides) with optical phonons in the phonon spectrum, as already indicated, the pairing constant is in the range $\mu \simeq 1.5 \div 5$. Assuming that when irradiated with photons, "metallized" semimetals have the pairing constant $\simeq$4, and also taking into account the fact that optical phonons are generated in them and the Debye temperature increases to the value $\theta \simeq 10^3$ K, it follows from relation (5) that $T_c \simeq 400$ K. Of course, this value of the critical temperature of the transition to the superconducting state is an estimate; however, it indicates that semimetals under laser irradiation can become superconductors at temperatures close to room temperature.

2. Conclusions

Based on the presented analysis and the quantitative estimates, the following conclusions can be drawn.

Under conditions of laser irradiation with a wavelength $\lambda \approx 10^{-5}$ m and pulse duration $\approx 10^{-8}$ s when power density is reached $\approx 10^{11}$ W/m^2, as a result of the internal photoelectric effect in semimetals, the following transformations can occur: a) a semi-metal turns from a "non-degenerate" semiconductor into a metal with "degenerate" electrons in the conduction band; b) as a result of relaxation processes in semimetals under irradiation, optical phonons are generated with a frequency $\nu^{max} \simeq 10^{13}$ s^{-1}.

The appearance of a significant fraction of optical phonons in the phonon spectrum of "metallized" semimetals can cause an effective electron-phonon interaction characterized by the pairing constant $\mu > 1$.

As a result of the photoelectric effect when semi-metals are irradiated with a sufficiently powerful flux of low-energy photons ($\approx 5 \cdot 10^{-2}$ eV), a superconducting state can be realized at temperatures close to room temperature ($\approx$ 300 K) in the near-surface layer or in thin films of $\approx 10^{-6}$ m thickness.

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