

[formula (1)], shows that the Cu_2O biexciton, which produces the emission spectrum observed by us, consists of identical "green" excitons and was thus a "green" biexciton.

The biexciton emission spectrum observed by us enables us to determine the binding energy Δ of the green biexciton, $\Delta = 150 \text{ cm}^{-1}$; this is in satisfactory agreement with the value $W_{\text{gr}}^{\text{Cu}_2\text{O}} = 93 \text{ cm}^{-1}$ obtained by us for the green biexciton from theoretical estimates based on [4].

The sharp temperature dependence of the Cu_2O emission spectrum observed by us and described here makes it possible to attribute this spectrum to the bound state of the excitons, the biexciton, and not to phenomena that can be observed in exciton collisions without formation of stable bound states.

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CRYSTAL STRUCTURE AND SUPERCONDUCTING PROPERTIES OF TANTALUM NITRIDE OBTAINED AT HIGH PRESSURES

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Among the nitrides of the transition metals of group V (vanadium, niobium, tantalum), only tantalum nitride, as is well known, exhibits no superconducting transition down to 1.2°K [1], whereas the nitrides of vanadium and niobium have high critical points near compositions corresponding to stoichiometric mononitrides:

$$\text{VN: } T_c = 8.2^\circ\text{K [1]}, \quad \text{NbN: } T_c = 15.6^\circ\text{K [2]}.$$

The most probable reason for such a behavior of these nitrides is the difference in their crystal structures: VN and NbN crystallize in a type-NaCl structure, whereas TaN crystallizes under ordinary conditions, depending on the composition, either in a structure of the CoSn type (TaN, hexagonal cell, $a = 5.185 \text{ \AA}$, $c/a = 0.561$, $z = 3$, space group $D_{6h}^1 = P6/mmm$), or in a structure of the WC type ($\text{TaN}_{0.8-0.9}$, hexagonal cell, $a = 2.925 - 2.938 \text{ \AA}$, $c/a = 0.983 - 0.981$, $z = 1$, space group $D_{3h}^1 = P6m2$) [3]. The influence of the crystal structure on the superconducting properties and the appearance of high critical points just in structures that crystallize in type-NaCl structures is well known in the case of carbides of transition metals [4].

We have investigated the possibility of crystallizing tantalum nitride in a structure of the NaCl type at high pressures and temperatures. The initial product employed was tantalum nitride of stoichiometric composition, which crystallizes, as already mentioned, in a structure of the CoSn type.

To carry out the experiments at high pressures (from 30 to 100 kbar), graphite or tantalum containers were used and served also as heaters.

In the entire indicated pressure range, at a temperature close to 1800°C, we obtained a new nitride phase with a structure of the NaCl type, with a unit-cell parameter $a = 4.385 \pm 0.001 \text{ \AA}$, and a density $\rho = 15.63 \text{ g/cm}^3$ as determined by x-ray diffraction. When the experiments were performed in a tantalum container, the new phase was observed in most cases in a mixture with tantalum nitride having a composition Ta_2N , produces as a result of the reaction between the mononitride and the metallic tantalum of the container. The X-ray diffraction data agree fully with results on the synthesis of a nitride having this composition at normal pressure [3, 5, 6].

At lower temperatures (from 1800 to 500°C) we observed a tantalum-nitride phase with structure of the WC type, with unit-cell parameters $a = 2.993 \pm 0.004 \text{ \AA}$ and $c = 2.880 \pm 0.004$

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A. A structure of this type, as indicated above, is produced under ordinary conditions only upon crystallization of non-stoichiometric tantalum nitride $TaN_{0.8-0.9}$. This fact, and also the values of the obtained unit-cell parameters, points to the possible violation of the stoichiometry of tantalum mononitride under the aforementioned temperature and pressure conditions.

Heating of tantalum nitride, which has a structure of NaCl type, for four hours at $1200^{\circ}C$ in a vacuum not worse than 10^{-5} mm Hg causes a complete transition to the phase with the WC structure.

Measurements of the critical temperature of the obtained samples was performed by a magnetic method down to $4.2^{\circ}K$. The phase with the NaCl structure has an average critical temperature of transition into the superconducting state of $6.5^{\circ}K$, and for most samples the width of the transition is about $1.0^{\circ}K$. The phase with the WC structure has no transition to the superconducting state down to $4.2^{\circ}K$. Nor was a superconducting transition observed in Ta_2N down to this temperature, in agreement with the data of [1].

Thus, the use of high pressure makes it possible to obtain a new phase of tantalum nitride with superconducting properties. We note that the phase synthesized under the aforementioned pressure and temperature conditions has a lower critical temperature than tantalum carbide, whereas for niobium nitrides and carbides obtained in the usual manner the ratio of the critical temperatures is reversed. One cannot exclude the possibility that this circumstance is connected with the aforementioned possible violation of the stoichiometric composition; such a deviation from stoichiometry should lead, as is well known from the published data, to a lowering of the superconducting transition temperature.

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OBSERVATION OF "ANDREEV" REFLECTION OF ELECTRONS FROM THE BOUNDARY BETWEEN A NORMAL AND SUPERCONDUCTING PHASE, USING THE RADIO-FREQUENCY SIZE EFFECT

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As shown by Andreev [1], reflection of excitations (electrons, holes) coming from the normal (n) phase to the boundary with the superconducting (s) phase is accompanied by reversal of the signs of the velocity vector, mass, and charge of the excitations, and the probability of reflection is equal to unity for quasiparticles with energy lower than the width of the gap in the spectrum of the superconductor.

Measurements of the integral characteristics of the intermediate state, namely the thermal conductivity [2], the specific heat [3], and the electric conductivity [4], confirm the validity of Andreev's theory. However, a more direct observation of the phenomenon of electron reflection from the n-s boundary is also possible. In measurements of the surface impedance of an n-layer that borders on one side with vacuum and on the other side with the s-phase, in the case when the electrons have a large mean free path, the reflection of the electrons from the n-s boundary and their return to the skin layer should exert an influence on the value of the surface impedance and should lead to the occurrence of radio-frequency size effects (RSE) of a new type.

In our experiment (see Fig. 1), the n-layer was deposited on the internal surface of a hollow cylindrical sample 5 under the influence of a magnetic field of a current I flowing through conductor 2. A single-crystal sample of diameter 12 mm, length 15 mm, and with an aperture having a radius $r = 3.10$ mm was cast from tin 99.9999% pure in a glass tube with an