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BIEXCITON IN Cu$_2$O CRYSTAL[1]

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With an aim at thoroughly investigating the processes of formation and decay of biexcitons and the phenomena connected with the condensation of excitons in crystals, if such phenomena exist, we have undertaken an experimental investigation of the emission spectrum of the Cu$_2$O crystal at low temperatures in liquid helium at T = 2°K, and under optical excitation (mercury lamp DRSh-500), when one can expect an accumulation, up to high concentrations, of quadrupole excitons at the level n = 1 of the yellow [1] series of Cu$_2$O.

We chose Cu$_2$O for our experiments because the excitons in this crystal have a large binding energy and make it possible to perform in greater detail and with greater discrimination the investigation which we have undertaken. In fact, while the binding energy of the indirect exciton in germanium is W_{indir}^{Ge} = 4 meV, and that of the direct one is W_{dir}^{Ge} = 1.2 meV, the binding energies W^{Cu_2O} of the "yellow" [1] and "green"[2] excitons in Cu$_2$O are larger by two orders of magnitude than in Ge, namely $W_{yel}^{Cu_2O}$ = 140 meV and $W_{gr}^{Cu_2O}$ = 200 meV. It follows therefore that the higher levels of the excitons in Cu$_2$O (n = 2, 3, 4, 5, 6...) are likewise more widely spaced in energy than, say in the case of Ge, thus affording an opportunity of performing more detailed investigations.

In an earlier paper [3], we investigated the luminescence spectrum of Cu$_2$O at T = 4.2°K.

In the Cu$_2$O emission spectrum at T = 2°K we observed, in the red part of the spectrum, a series of new smeared and relatively weak lines converning in the long-wave (red) part of the spectrum and strongly dependent on the temperature: the new lines are seen at T = 2°K and vanish at T = 4.2°K. The first term of the series, n = 2, is distinctly seen; the higher terms, n = 3, 4, 5, and 6 are not so clearly seen, because they are obscured in the spectrum by the superimposed continuous Cu$_2$O continuous luminescence band of impurity or defect origin.

The frequencies ν_n' of the lines of the new red emission series of the Cu$_2$O satisfy well the serial hydrogenlike relation

$$\nu_n' = \nu_\infty' + \frac{R'}{n^2} = 15135 + \frac{1200}{n^2} \ \text{cm}^{-1}$$ (1)

$$n = 2, 3, 4, 5, 6.$$

where the Rydberg constant R' = 1200 cm^{-1} is equal to the Rydberg constant of the "green" exciton series in the Cu$_2$O absorption [2]:

$$\nu_n = \nu_\infty - \frac{R}{n^2} = 18587 - \frac{1200}{n^2} \ \text{cm}^{-1}$$ (2)

$$n = 2, 3, 4, 5 \dots .$$

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[1]The results of this research were reported on 2 December 1969 at the Semiconductor Institute of the USSR Academy of Sciences in Leningrad, and on 28 May 1970 at the Solid State Institute to the All-union Seminar "Excitons in Crystals" in Chernogolovka (Moscow).

Table I

Frequencies ν' of the lines of the "red" series of the emission of the Cu_2O biexciton, as observed and as calculated from formula (1).

Quantum number n	Observed ν'_n, cm^{-1}	Calculated ν'_n, cm^{-1}
2	15434	15435
3	15252	15268
4	15210 *	15210
5	15183 *	15183
6	15164	15168

*The experimental values of the frequencies ν'_4 and ν'_5 were used to calculate the constants of the serial formula (1).

In Table I are compared the frequencies ν'_n of the observed lines of the "red" series of the Cu_2O emission with those calculated from formula (1). The calculated and observed frequencies agree well (with the exception of the term n = 3).

We see that the lines of the green series of exciton absorption and of the new red series in the Cu_2O emission converge in the spectrum in opposite directions, and therefore the tails of the series are oppositely directed.

On the basis of the foregoing experimental facts, we regard the spectrum observed by us (the red series) as the emission spectrum of the biexciton in the Cu_2O crystal following its recombination decay, during the course of which one exciton of the biexciton annihilates, while the other exciton, in a recombination interaction of the type of the so-called Auger process, becomes excited as a result of this energy to higher energy levels and becomes free in the excited state. This process should be manifest in the recombination radiation of the biexciton in a series of emission lines in the long-wave region of the spectrum.

As a result of such an intra-series excitation of one of the biexciton excitons there should appear in the emission psectrum of the Cu_2O emission, as can be readily understood, a hydrogen series of lines that converge in the long-wave side of the spectrum in accord with the foregoing formula (1); this is indeed observed in the experiment.

As shown by relations (1) and (2), the sum of the frequencies $(\nu_n + \nu')$

$$\nu_n + \nu'_n = \nu_\infty + \nu'_\infty = 33722 = \text{const} \tag{3}$$

is independent of the quantum number n and, as shown by Table II, this is indeed confirmed by experiment. Relation (3), together with the equality of the Rydberg constants of the green exciton series of Cu_2O [formula (2)] and of the red series of the Cu_2O biexciton

Table II

Constancy of the sum of frequencies $\nu_n + \nu'_n = \nu_\infty + \nu'_\infty = 33722$ cm^{-1} = const.

Quantum number n	Frequencies ν, in absorption, cm^{-1}	Frequencies ν', emission, cm^{-1}	Sum $(\nu_n + \nu'_n)$, cm^{-1}
2	18285	15434	33719
3	18454	15252	33706
4	18512	15210	33722
5	18539	15183	33722
6	18554	15164	33718
			Aver. (without n = 3) 33720

[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, $\Delta = 150$ cm^{-1}; this is in satisfactory agreement with the value $W_{gr}^{Cu_2O} = 93$ 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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Submitted 17 June 1970
ZhETF Pis. Red. 12, No. 2, 101 - 102 (20 July 1970)

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:

$$VN:\ T_c = 8.2°K\ [1], \qquad NbN:\ T_c = 15.6°K\ [2].$$

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, $a = 5.185$ Å, $c/a = 0.561$, $z = 3$, space group $D_{6h}^1 = $ P6/mmm), or in a structure of the WC type (TaN$_{0.8 - 0.9}$, hexagonal cell, $a = 2.925 - 2.938$ Å, $c/a = 0.983 - 0.981$, $z = 1$, 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 $a = 4.385 \pm 0.001$ Å, and a density $\rho = 15.63$ 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 $a = 2.993 \pm 0.004$ Å and $c = 2.880 \pm 0.004$