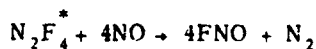


The reaction between N_2F_4 and NO is initiated by the interaction of the vibrationally-excited molecules of N_2F_4 with NO:



($\Delta H_p = -149.2$ kcal/mole for N_2F_4 in the ground state). The reaction takes place in the irradiated zone of the cell. The flash covers the entire volume of the reactor.

Excited products are produced during the course of the chemical reactions. The presence of intense luminescence gives ground for carrying out experiments aimed at detecting inverted populations of the products in laser-chemical reactions and at observing lasing effects.

Irradiation of N_2F_4 , BCl_3 , SF_6 , PF_5 , and SiH_4 has shown that all substances with the exception of silane do not dissociate at intensities lower than ~ 40 W and pressures lower than 200 Torr. This gives grounds for assuming that the investigated reactions (with the possible exception of reactions with silanes) begin not with a stage of dissociation of the vibrationally-excited molecules, but with an exothermal-reaction stage (for example, the reaction for the system $N_2F_4 - NO$).

A comparison has revealed an appreciable difference between laser-chemical and thermal reactions. Thus, when mixtures of N_2F_4 with NO and of N_2F_4 with N_2O are heated, only decomposition of N_2F_4 takes place, viz., $3N_2F_4 = 4NF_3 + N_2$, and there is no reaction with NO or N_2O . This can be attributed to the fact that the vibrationally-excited molecules produced upon absorption of the IR radiation have chemical properties different from those of the molecules in the ground state.

- [1] N.G. Basov, E.P. Markin, A.N. Oraevskii, and A.V. Pankratov, Dokl. Akad. Nauk SSSR 198, No. 5 (1971) [Sov. Phys.-Dokl. 16, No. 6 (1971)].
[2] S.W. Mayer, M.A. Kwok, R.W.F. Cross, and D.J. Spenser, Appl. Phys. Lett. 17, 516 (1970).

BIEXCITON IN Cu_2O CRYSTAL

O.I. L'vov and P.P. Pavinskii

Leningrad State University

Submitted 21 June 1971

ZhETF Pis. Red. 14, No. 2, 253 - 256 (20 August 1971)

An anomalous hydrogen-like series, converging not to the short-wave region of the spectrum, as usual, but to the long-wave region, was recently observed [1] in the luminescence spectrum of the crystal Cu_2O . The series was interpreted as the emission spectrum of a biexciton that becomes converted into an exciton of the green series (see the review [2]). The anomalous sequence of lines in the new series is due to the fact that the initial level in the emission of the quantum is the electronic excited state of the lattice (biexciton) with an excitation energy 33720 cm^{-1} , which is approximately double the excitation energy of the main electrons of the yellow or green series.

A variant of the biexciton structure is also proposed in [1]. On the basis of the presented experimental information, the authors conclude that the biexciton in Cu_2O consists of two identical excitons of the green series with the frequency sum exceeding the level indicated above by 150 cm^{-1} . The latter quantity is interpreted as the binding energy of the biexciton relative to its dissociation.

We note that from the point of view of agreement with the experimental data [1, 2] the proposed model has three major shortcomings: a) The model does not explain the very strong temperature dependence of the observed spectrum of the new emission line, i.e., the fact that the lines appear at 2°K and vanish already at 4°K. The proposed binding energy 150 cm⁻¹ should not lead to such a strong change of the intensity in an interval of only two degrees Kelvin. b) A system of two excitons of identical symmetry does not admit, in slow collisions, of an optical transition to a final exciton state in the dipole approximation. As shown in [3], the probability of such a transition is equal to zero. c) The "green exciton" line n = 1 has not been observed in the radiation even at extremely low temperatures. This shows that the accumulation necessary to produce a noticeable biexciton concentration in the crystal by collisions does not take place.

We wish to propose here another model that takes into account both the energy considerations and the aforementioned conditions under which biexciton emission is possible. An analysis of the energy spectrum of exciton absorption of light and Cu₂O (yellow and green series) permits the choice of two exciton states, the total energy of which is close to 32720 cm⁻¹. One of these states is the long-lived quadrupole exciton n = 1 of the yellow series. The concentration of these excitons, even at not very low temperatures, can be so large that a direct radiative transition from the state n = 1 to the ground state of the crystal is observed in spite of the small oscillator strength. It is most probable that the second exciton participating in the formation of the biexciton is the exciton n = 2 of the same yellow series.

The sum of the excitation energies of the excitons n = 1 and n = 2 of the yellow series is 33733.3 cm⁻¹ at T = 4.2°K and 33738.1 cm⁻¹ at T = 1.3°K. If we take the biexciton level to be the experimental value 33720 cm⁻¹, then the binding energy is 13.3 cm⁻¹ at 4.2°K and 18.1 cm⁻¹ at 1.3°K. Linear interpolation between these two values yields a value $\Delta E = 16.9 \text{ cm}^{-1}$ for T = 2°K.

Since the lifetime of the state with binding energy ΔE relative to thermal decay is determined mainly by the factor $\exp[\Delta E/kT]$, we arrive at the conclusion that the lifetime of the biexciton (n = 1 and n = 2 of the yellow series) relative to thermal decay at T = 2°K is approximately 3000 times longer than at T = 4.2°K. This agrees with the observations, i.e., with the fact that the series appears only at 2°K [1]. We see therefore that the observed temperature dependence indicates a very low binding energy of the biexciton in the Cu₂O crystal, lower by approximately one order of magnitude than the value expected on the basis of a theory such as Sharma's [4], wherein the biexciton is regarded as a system of four light quasiparticles, similar to the bipostronium. As shown by Schmidt [5], the binding energy of excitons and biexcitons depends strongly on the polarizing action of the light particles on the crystal lattice. Correct allowance for the polarization should lead to an appreciable lowering of the biexciton binding energy.

One of the evidences favoring the biexciton mechanism of the luminescence of the new series might be the establishment of a dependence of the luminescence quantum yield on the intensity I of the exciting radiation. It is natural to assume that the luminescence intensity is proportional to the stationary concentration of the biexcitons N_b

$$N_b = A \tau N_1 N_2, \quad (1)$$

where τ is the biexciton lifetime, N_1 and N_2 the stationary concentrations of the excitons n = 1 and n = 2 of the yellow series, and A is the constant of the biexciton production reaction.

We have assumed above that the concentration of the excitons n = 1 is high. It is therefore necessary to take into account in the kinetic equation

for N_1 both the monomolecular reaction with the characteristic time τ_1 and the bimolecular reaction with constant γ_1 . For N_2 we confine ourselves to the monomolecular reaction with lifetime τ_2 . Under these assumptions, the concentrations N_1 and N_2 are readily expressed in terms of the aforementioned coefficients. Using the formulas of [6], we obtain the following expression for the dependence of N_b on I :

$$N_b = \frac{A a_2 r r_2}{2\gamma_1 r_1} (\sqrt{1 + 4a_1 \gamma_1 r_1^2 I} - 1) I. \quad (2)$$

The coefficients a_1 in the kinetic equation determine the rate of excitation of the excitons of type 1.

At low light intensities I , when the radicand in (2) is close to unity, we obtain a quadratic dependence of N_b on I . With increasing I , this dependence goes over into the relation

$$N_b = \text{const } I^{3/2}. \quad (3)$$

As shown in [7], the intensity of the luminescence of the biexciton in CuCl at low power of the exciting radiation is proportional to the square of the light intensity. At high excitation intensities, the growth of the luminescence quantum yield decreases. The data of [7] for the CuCl crystal agree with the dependence of the luminescence on the light intensity predicted by formula (2).

- [1] E.F. Gross and F.I. Kreingol'd, ZhETF Pis. Red. 12, 98 (1970) [JETP Lett. 12, 68 (1970)].
- [2] E.F. Gross, Usp. Fiz. Nauk 63, 575 (1957).
- [3] F. Culic, Czechosl. Phys. J. 3, 16, 194 (1966).
- [4] R. Sharma, Phys. Rev. 170, 770; 171, 36 (1968).
- [5] P.P. Schmidt, J. Phys. C. (Solid State Physics), Ser. 2, 2, 785 (1969).
- [6] O.I. L'vov and P.P. Pavinskii, Vestnik, Leningrad State Univ. No. 22, 23 (1962).
- [7] A. Mysyrowicz, J.B. Grun, R. Levy, A. Bivas, and S. Nikitine, Phys. Lett. 26A, 12, 615 (1968).

CONCERNING MAGNETIC BREAKDOWN IN BERYLLIUM

N.E. Alekseevskii, P. Djir¹⁾, and V.I. Nizhankovskii
 Institute of Physics Problems, USSR Academy of Sciences
 Submitted 16 July 1971
 ZhETF Pis. Red. 14, No. 4, 256 - 260 (20 August 1971)

Magnetic breakdown in beryllium observed back in 1963 [1], has been the subject of relatively many investigations. As is well known, breakdown causes giant oscillations to appear on the magnetoresistance curves of beryllium, if the field is parallel to the hexagonal axis [2]. A study of the nature of these oscillations is of considerable interest, since it yields additional information on the dynamics of electrons in the metal.

We have investigated the temperature dependence of the magnetoresistance-oscillation amplitudes in a wide temperature interval, using beryllium samples with $\rho(300^\circ\text{K})/\rho(4.2^\circ\text{K}) \sim 150$. The measurements were performed in the field of a superconducting solenoid. In a number of cases, permendur concentrators were

¹⁾Delhi University, India.