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EVIDENCE FOR EXCITONIC COMPLEX IN AgCl
AFTER UV LASER EXCITATION⁺

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In recent years the theoretical papers of Bassani et al. /1/ and Scop /2/ on band structure of silver halides have given a more detailed analysis of the electronic processes in these crystals. Simultaneously, the importance of indirect transitions (indirect absorption edge approximately at 3.2 eV) in addition to direct transitions (direct absorption edge approximately at 5.1 eV) in silver chloride has been shown. Independently, in many measurements the participation of indirect transitions to (or from) exciton states in absorption or luminescence processes /3/ was found; this fact was in AgCl crystals considerably underlined with the application of laser excitation. The results obtained in these measurements were published in our last papers /4/. On the other hand, the high densities of charge carriers and excitons produced in the crystal volume by the exciting laser pulse increase considerably the probability of the creation of different complexes, e.g. bound excitons on point or plane defects or biexcitons (excitonic molecules). Theoretical calculations of these complexes have been published by many authors /e.g. 5 a) - d)/ and many successful measurements have brought evidence for the existence of such complexes /e.g. 6 a) - d)/ in ionic crystals.

⁺) Presented at the Tenth European Congress on Molecular Spectroscopy, Liège, September 1969

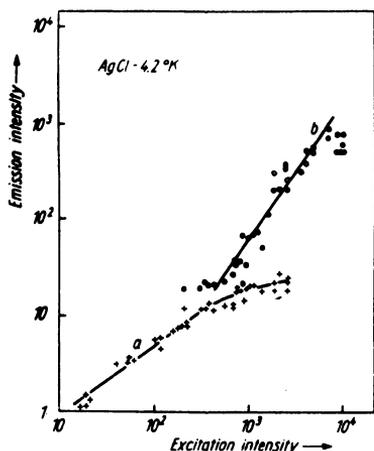


Fig. 1. Intensity dependence of the UV laser excited luminescence of AgCl at 4.2°K.

With respect to the experimental results just mentioned we have analysed our measurements on UV laser excited luminescence in AgCl crystals at very low temperatures /4/. Figure 1 (published in /4a/) shows the luminescence intensity dependence on UV laser excitation intensity ($\lambda_{\text{exc}} = 28\,810\text{ cm}^{-1}$) in AgCl crystals, measured in the luminescence maximum ($\lambda_{\text{max}} = 20\,491\text{ cm}^{-1}$) at 4.2°K. This dependence starts to be from a certain value of UV laser intensity superlinear with the slope of about 1.5, this value being approximately twice as large as the slope value at low laser excitation intensities. In Figure 2 the luminescence spectra of AgCl crystals after pulse UV laser excitation are plotted at pumped helium temperature; for comparison the luminescence spectra recorded for UV light excitation are shown in the next Figure 3. If we now summarize in a table the experimental data published in /4b/ and in this paper (the positions of luminescence maxima at different temperatures after UV light excitation - I_0 and further the maxima I_1 and I_2 recorded on luminescence curve after UV laser excitation), we can express the energy difference

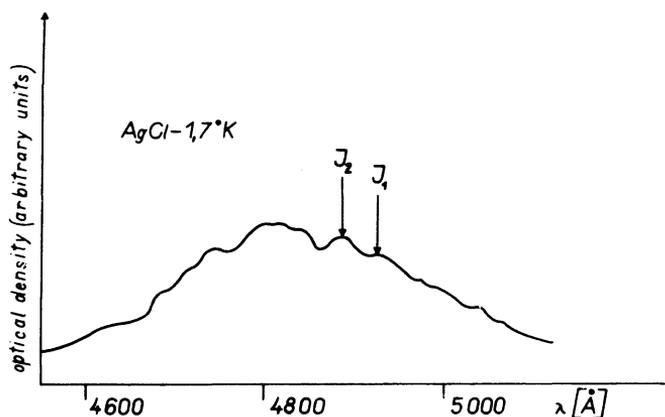


Fig. 2. Emission spectrum of AgCl at 1.7°K after UV laser excitation (photographically recorded).

$\Delta\nu = I_0 - I_2$ for corresponding temperatures; the average value of $\overline{\Delta\nu}$ in the temperature range used is equal to $\overline{\Delta\nu} = 145 \text{ cm}^{-1}$.

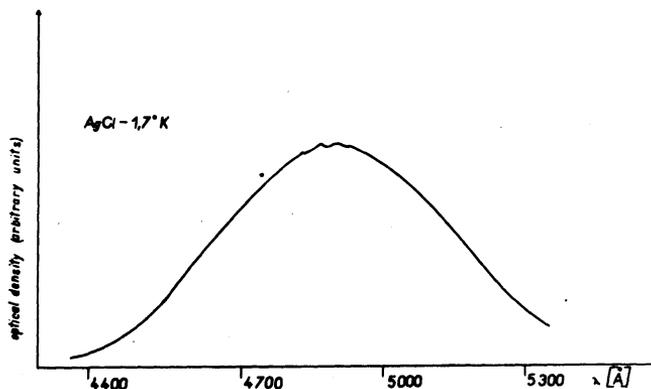


Fig. 3. Emission spectrum of AgCl at 1.7°K after UV light excitation (recorded by PM 56 AUP).

Table 1

| Temperature (°K) | I_0 -emission band maximum after UV light excitation, ($\lambda_{exc} = 27\,322 \text{ cm}^{-1}$) | UV laser excitation ($\lambda_{exc} = 28\,812 \text{ cm}^{-1}$) | | $\Delta\nu = I_2 - I_1$ (cm^{-1}) |
|---------------------|--|--|--|---|
| | | Emis. band I_1 (cm^{-1}) | Emis. band I_2 (cm^{-1}) | |
| 77 | 20704 | 20636 | 20812 | 108 |
| 4 | 20358 | | 20513 | 155 |
| 1.7 | 20317 | 20288 | 20488 | 171 |

The position of the maximum I_1 is near to the position of the luminescence maximum after UV light excitation I_0 , the origin of which has been explained /7/ as radiative recombination of bound exciton on cation vacancy. As the measurement of intensity dependence (see Fig. 1) was recorded in the vicinity of the I_2 maximum, it seems to us very probable that the measured superlinear intensity dependence corresponds to the energy of dissociation of an exciton molecule as in the case of CdS crystals /6c/. In silver chloride the effective mass ratio $m_e^*/m_h^* \approx 0.12$ and so one can expect that the dissociation energy of excitonic molecule will be

close to the binding energy of exciton on a donor. According to /6a/ the energy of photon which originates with free exciton during biexciton dissociation changes to a great extent with the value of dielectric constant used. In our case it comprises energy values between 65 cm^{-1} (for $\epsilon_{\text{stat}} = 9.5$) and 356 cm^{-1} (for $\epsilon_{\infty} = 4.04$); the most probable value in our opinion will be the value calculated with dielectric constant including Haken's correction /8/. For this case we obtain the value of 126.5 cm^{-1} ($\epsilon_{\text{H}} = 6.8$) which is quite close to the observed energy difference $\overline{\Delta\nu} = 145 \text{ cm}^{-1}$. On the other hand, utilising the results of Wehner /5d/, from his graphical dependence of binding energy of excitonic molecule on effective mass ratio we can determine the ratio W/E_0 (where W is binding energy of biexciton and E_0 represents binding energy of free exciton) for AgCl. Extrapolating the published curve for $m_e^*/m_h^* \simeq 0.12$ we obtain for W the value of 132 cm^{-1} which is also close to the observed value. Regarding first the good agreement between the calculated and measured values of binding (=dissociation) energy for excitonic molecule and further the superlinear luminescence intensity dependence measured in the vicinity of I_2 , we can conclude that the observed emission band I_2 in AgCl crystals originates in excitonic molecule dissociation.

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