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EXCITONS AS A NEW QUANTUM SYSTEM

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Résumé.- Un exciton étant composé d'un nombre pair de fermions appartient à la classe de particules obéissant à la statistique de Bose-Einstein. On s'attend donc à l'apparition de phénomènes quantiques, liés à la statistique, dans un gaz d'excitons à densité élevée, et en particulier à l'apparition d'une condensation dans l'espace des moments d'une fraction des particules (condensation de Bose-Einstein). Dans une première partie, le concept d'exciton est rapidement introduit, les avantages d'un tel système pour l'étude des effets de statistique quantique sont évoqués ; on montre ensuite les difficultés qui empêchent l'observation d'une condensation d'Einstein d'excitons dans la plupart des cristaux. Dans une seconde partie, on présente des résultats expérimentaux qui confirment les prédictions du modèle de Bose-Einstein. Dans Cu_2O , on montre qu'un gaz d'excitons suit un comportement classique à faible densité, mais qu'il est nécessaire d'introduire une fonction de distribution des vitesses des particules très fortement dégénérée à basse température et aux densités élevées pour expliquer le spectre de recombinaison excitonique observé. Le potentiel chimique du gaz atteint des valeurs proches de zéro. Dans CuCl , les excitons sont instables par rapport à la formation de molécules (biexcitons). Il est possible de créer directement une densité élevée de biexcitons ayant un moment d'impulsion $k \approx 0$ par absorption non-linéaire d'un faisceau laser. Là encore, de fortes déviations par rapport à la statistique classique sont observées. En particulier, l'apparition d'une raie d'émission fine est attribuée à la présence d'un condensat de Bose-Einstein dans le système.

Abstract.- In a first part, a brief review of some excitonic properties is presented, with the accent put on their relevance with respect to the possibility of Bose-Einstein condensation. In a second part, recent experimental evidence is described, which supports the idea that excitonic particles may form a highly quantum fluid. In Cu_2O , the analysis of the exciton decay spectrum shows a gradual evolution of the gas from a classical regime at low densities up to a strongly degenerate one at high densities, with a chemical potential $\mu \sim 0$. In CuCl excitons are unstable against formation of molecules (biexcitons). It is possible to generate directly a high density gas of biexcitons with momentum $K \sim 0$ by giant two-photon absorption. At low excitation, the observed molecular emission is in agreement with Maxwell-Boltzmann statistics. At high densities, strong deviations occur. In particular, the appearance of a sharp emission line is attributed to the presence of a Bose-Einstein condensate of excitonic molecules.

1. Introduction. - As it is well-known an ensemble of ideal (non-interacting) particles with integer spin is expected to undergo a phase transition at sufficiently low temperature, in which a fraction of the particles condenses in momentum space into the same quantum state, of lowest energy. For a long period of time, the only system in which Einstein condensation of Bose particles (BEC) was thought to occur consisted of liquid ^4He below the λ point. Although the ideal Bose gas [1] model predicts a transition temperature close to that observed for the onset of superfluidity, serious difficulties are encountered in the physical description of this system, because of the strong particle particle interactions in the liquid, which cannot

be treated as a small perturbation, as it is assumed in the nearly ideal Bose gas model of Bogoliubov [2]

Recently there has been a strong revival of interest in the study of BEC, when it was realized that other, much more dilute systems might be experimentally accessible, in which the purely quantum statistical effects would be predominant. One such system concerns an ensemble of spin aligned hydrogen atoms, which has been predicted to remain in the gas phase even at $T = 0$. [3] Another system is given by excitonic particles in non-metallic crystals. The aim of this paper is to describe recent experimental evidence showing that excitons may indeed form a highly quantum fluid of

Bose particles. In a first part the concept of excitons is introduced, advantages and difficulties in dealing with such a system are considered. The cases of Cu_2O and CuCl are described in the second part.

The concept of exciton :

Consider an ideal crystal, with a band structure as shown in figure 1. The valence (VB) and conduction band (CB) have extrema located at the centre of the Brillouin zone, at $\underline{K} = 0$. We assume isotropic bands, with no degeneracy except for spin and a parabolic energy versus \underline{K} dependence. The crystal is kept at sufficiently low temperature, $kT \ll E_g$, so that the valence band is completely filled with electrons and the conduction band is empty.

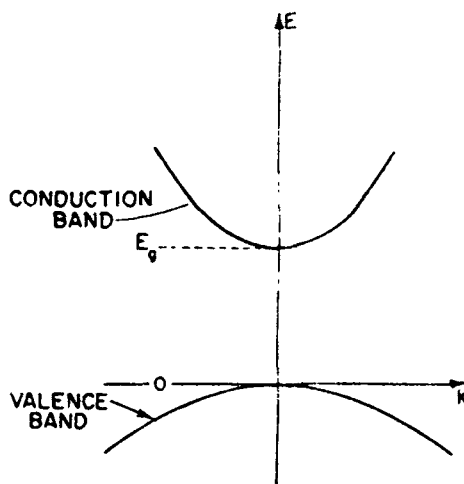


Fig. 1. - Schematic band structure of ideal crystal.

E_g is the width of the forbidden gap, at $\underline{K} = 0$.

Suppose light is irradiated upon such a crystal, with $\hbar\omega > E_g$, where ω is the input light frequency. There is a certain probability that a photon is absorbed in the medium, with a corresponding promotion of an electron to the conduction band. The electron in the CB interacts, via Coulomb attrac-

tion, with the (positively charged) "hole" of electrons it leaves in the VB. To describe the excitation state of the system, it is possible to write an effective two-particle Schrödinger equation, with the Coulomb term divided by ϵ_0 , the static dielectric constant of the crystal, to take into account the residual interactions of the electron-hole pair with the lattice /4/. The solutions of the Schrödinger equation are well-known from the hydrogen atom case, they lead in particular to a series of discrete resonances below the energy gap E_g , the so-called excitonic series, with energies

$$E_n = E_g - R_x/n^2 + \hbar^2 K^2/2M \quad (1)$$

n is the principal quantum number, M is the total mass $m_e + m_h$, where m_e and m_h are the effective masses of the electron and hole, R_x is the exciton Rydberg, expressed in terms of the hydrogen Rydberg by the relation $R_x = R_H/\epsilon_0^2$ (Here the reduced mass $\mu = m_e m_h / m_e + m_h$ must replace the electron mass m_0 inside R_H).

Thus, one may think of the electronic excitation states of the crystal in terms of creation of quasi-particles, the excitons, which are similar to positronium atoms if $m_e = m_h$ or resemble hydrogen atoms in the limit $m_e \ll m_h$. Excitons represent solution of the entire crystal, therefore, they can propagate freely inside the system ; hence the quadratic term in equation (1) representing the kinetic energy associated with the centre-of-mass motion of the particle. Typical values of R_x range from a few meV to several hundred meV, the exciton radius $a_x = a_0 \epsilon_0 = \hbar^2 \epsilon_0 / \mu e^2$ is of the order of a few Angströms up to a few μm .

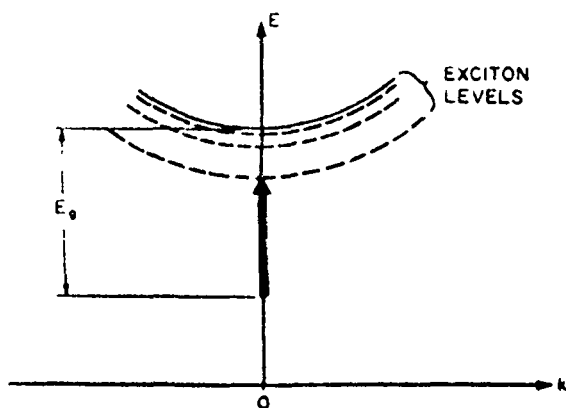


Fig. 2. - Two-particle excitation diagram of an ideal crystal.

The concept of exciton has proved to be fruitful to explain many properties of insulators or semiconductors particularly optical properties near the band edge, although a precise analysis of real situations requires a much more involved treatment, which includes the particular nature of the wave functions for the different bands. It is also a very rough approximation to assume that all residual interactions with the lattice may be expressed by a constant ϵ_0 . Nevertheless, some cases exist which come close to the simple description given above. A well-known example is Cu_2O . In fig. 3, the absorption spectrum of this compound is shown near the gap energy. As can be seen, a hydrogen-like series (the yellow excitonic series) is observed with up to 8 terms /5/. It must be stressed here that the sharp resonances do not correspond to interlevel transitions, as it is the case in atomic systems, but rather to the creation of excitons, by a transition starting from the ground state of the crystal.

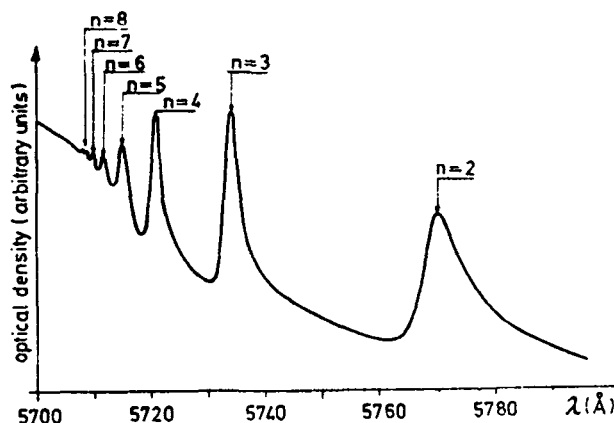


Fig. 3. - Absorption spectrum of Cu_2O near the band gap. The hydrogen-like series of lines (yellow series) correspond to the creation of *p*-like excitons.

Excitons as a Bose quantum system :

Almost twenty years ago, several authors /6/, /7/, /8/ have pointed out that excitons, consisting of an even number of fermions, should obey Bose-Einstein statistics and consequently might furnish a new system to observe BEC. It may be worthwhile mentioning several attractive characteristics in this case.

A first feature is related to the light effective mass of the particles. Typical exciton masses are of the order of the free electron mass, or even less. The ideal Bose gas model predicts a critical density n_c for condensation

$$n_c = 6,2 \cdot 10^{15} g (m/m_0)^{3/2} \cdot T^{3/2} \quad (2)$$

and thus we expect for instance $T_c \sim 100$ K for $n \sim 10^{19} \text{ cm}^{-3}$ if $m = m_0$ and g , the degeneracy factor is unity. This represents by far the highest critical temperature for BEC expected from any system.

Further, the system appears to be very simple and well suited for an experimental study.

As we have seen before, the number of particles is determined by some external means of excitation, - optical excitation is particularly convenient - and can therefore be easily varied over a very large range by changing the input intensity. The required densities seem to be fully within accessible range of presently available laser sources. For instance, assuming an exciton lifetime $\tau = 10^{-9}$ sec (in several cases it is significantly longer), an excitonic absorption coefficient $\alpha \sim 10^{4-5} \text{ cm}^{-1}$ as measured in many instances, it is sufficient to have a few Watts input power, focused on a 10^{-5} cm^2 surface to achieve the needed densities. Such requirements are obtained even with cw light sources, pulsed lasers with tunable frequency give photon fluxes higher by orders of magnitude.

The fact that excitons have a finite lifetime - the excited electron has a given probability to fall back into its hole, emitting a photon in the process - may also offer an interesting feature : the emitted radiation gives direct information upon the condensate, in contrast to the case of liquid ^4He , where access to the fraction of the condensate, of infinite lifetime, is difficult and indirect.

One may also point out to the very large variety of crystal parameters encountered in real systems, leading to a wealth of different situations : excitons may have mass ratios $\sigma = m_e/m_h$ ranging from $\sigma \sim 0$ to $\sigma \sim 1$, anisotropic effective mass is a commonly used concept in solid state physics, the total angular momentum of the excitons may have values $J = 0, J = 1$, etc..., raising the possibility of interesting phases for the condensate (excitonic ferromagnetism?).

Finally the dynamical aspect of the problem should be mentioned. Excitons, being neutral entities, do not carry any current in their displacement. However, they transport considerable internal energy, of the order of the energy gap, which can reach several eV per particle. If an exciton condensate takes place at $k \neq 0$, it will correspond to a superconductor with a lossless transport over large distances of an important energy current /9/.

The description so far is somewhat idyllic. The present state of the experimental situation shows very little evidence of quantum statistics, a sign that serious difficulties are at hand. In fact, a number of prerequisites must be met in order to reach the desired exciton densities ; as will be shown these requirements are not satisfied in most studied inorganic crystals.

A first difficulty concerns the finite lifetime of the particles. Clearly, in order to define such concepts as temperature or chemical potential of the gas, it is necessary to have a particle lifetime much longer than a characteristic relaxation time necessary to achieve thermodynamical equilibrium. If a pair of hot carriers is generated, by absorption of a photon with $h\omega > E_g$, it will quickly form a bound state and relax down to the lowest, $n = 1$ exciton band, by interaction with the lattice. This relaxation will occur on a very fast timescale, of the order of picoseconds, as long as the excess energy of the pair ΔE , with respect to the bottom of the $n = 1$ exciton band exceeds $h\omega_0$, the energy of an optical phonon of the crystal /10/. By contrast, if $\Delta E < h\omega_0$, the further relaxation involves interaction with acoustic phonons. Here, each scattering event dissipates much less energy, due to the low frequency of acoustic phonons further; the

accessible exciton density of states and the exciton-acoustic phonon matrix element tend to zero as the exciton momentum diminishes $/10/$. As a result, the relaxation is much longer, in the nanosecond range.

The measured exciton lifetimes do not correspond to radiative lifetimes in most situations, but are limited by the presence of residual impurities, which act as very efficient recombination centers, leading to values in the subnanosecond range. Even in very pure crystals, radiative exciton recombinations are expected to occur within nanoseconds if the interband optical transition is dipole allowed at $\underline{k} = 0$, so that a large category of systems appears to be excluded from the start.

The situation is not quite so bad, if one considers an ensemble of excitons, because another thermalization mechanism is available, from particle-particle collisions. A simple classical collision model shows that at densities $n \sim 10^{17} \text{ cm}^{-3}$ and $T \sim 10\text{K}$ a quasi-thermodynamical equilibrium is reached within $\sim 10^{-11}$ sec, so that an effective temperature for the electronic system may be defined. However there is a price to pay ; the electronic system is only weakly coupled to the lattice through interaction with acoustic phonons, so that it is not possible to reach arbitrarily low exciton temperature by cooling the crystal itself $/11/$.

Another difficulty relates to the exciton-photon interaction. In fig. 4a), the excitation diagram of the $n = 1$ exciton is shown, together with the dispersion curve of light in the medium. If a coupling between both systems is turned on, no level crossing can occur, instead the true eigenmodes of the system are described in terms of mixed exciton-photon modes, called polaritons $/12/$. The dispersion curve of a polariton is shown

in fig. 4b. At low $\underline{k} \sim \omega c$, the polariton is essentially a photon, at large \underline{k} it is exciton-like, with an intermediate region where the excitation wave in the medium has both electromagnetic and mechanical polarization character. Note the presence of a longitudinal polarization mode (longitudinal exciton with a dipole moment parallel to \underline{k} , which consequently does not interact with a purely transverse mode - the photon) ; there is a complete analogy with polar optical phonons.

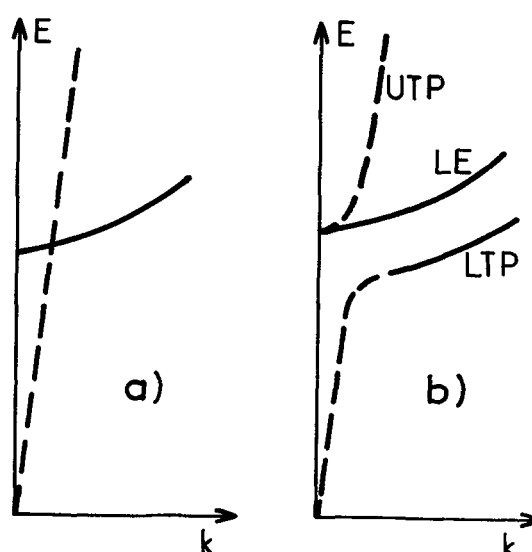


Fig. 4 -

- a) exciton and photon dispersion curves, in absence of interaction.
 b) with interaction ; LE = longitudinal exciton, UTP(LTP) = upper (lower) transverse polariton.

The polariton effect has drastic consequences upon the possibility of achieving BEC of excitons : as we follow a hot exciton relaxing down its kinetic energy band, it will acquire more and more photon character as it loses kinetic energy, until it eventually leaks out of the crystal in the form of radiation. The crystal does not form a container for the stored excitation, the number of excitons is not conserved and condensation is not possible. It is therefore essential to consider systems in which the coupling to the electromagnetic field represents

only a small perturbation, which can be safely ignored.

Other requirements refer to an ensemble of excitons :

There is an upper limit to the density of excitons which can be reached, due to the fact that they are not ideal Bose particles, but consist of fermions. If the average distance between particles becomes comparable to the exciton radius, then a dissociation of the particles into their constituents is expected (Mott dissociation), since there is no reason for preferential pairing of a given electron with a particular hole. This collapse into a two-component plasma occurs in the density range $na_0^3 \sim 1$. It is useful to compare the density at which Mott dissociation occurs with the density for Bose-Einstein condensation. It can be expressed in the following form /8/, which gives a measure of the deviation from ideality at the critical density n_c :

$$a_x / r_c = 0.62 \cdot (M/\mu)^{1/2} \cdot (kT/R_x)^{1/2} \quad (3)$$

where $4\pi r_c^3/3$ is the volume associated with each particle at n_c .

Thus from (3) it appears necessary to consider excitons with as large a binding energy as possible.

Finally, a last criterion concerns the form of exciton-exciton interactions. In the weakly interacting Bose gas model of Bogoliubov, it is assumed that the pair potential is repulsive. Otherwise the system is unstable against the formation of new elementary excitations in the system with a lower energy per electron-hole pair. There is no general answer to the problem of the exciton-exciton potential. Instead the particular band structure must be analysed in each case. There are presently two well established examples of formation of new elementary

excitations at increasing exciton densities. One case is the liquefaction of excitons, first recognized by Keldysh/13/. Calculations/14//15/ show and experiments confirm/16//17/ that it may be energetically favourable for the system to separate into a low density gas phase of excitons, coexisting with regions of a high density phase of a degenerate plasma of electrons and holes. This effect is favoured by complex band structures such as indirect gap and anisotropic effective masses, but should not occur in the ideal crystal of fig 1./18/. The most reliable experimental evidence for the existence of e-h drops is found in Ge, Si, AgBr, GaP, SiC, all indirect band gap structures.

The second case refers to the formation of excitonic molecules. In fig 5., the binding energy of a molecule (biexciton) expressed in units of R_x is shown in function of $\sigma = m_e/m_h$, the ratio of masses of the constituents, as calculated by a variational method in a two-band model/19/. It predicts that molecule formation should always occur ; however there is still some uncertainty for the value in the limit $\sigma = 1$ due to the lack of experimental evidence of the positronium molecule. A biexciton belongs to the class obeying Bose-Einstein statistics so that a gas of these particles may also undergo BEC. This system is less advantageous than excitons in some respects, since here the mass is larger and the binding energy smaller, thus increasing n_c and lowering the limit for Mott dissociation. On the other hand, an excitonic molecule formed with dipole-active excitons has a quadrupole moment, so that it does not suffer the complications due to the polariton effect. Also a high density gas of biexcitons in a crystal with simple band gap structure is not expected to form a dielectric liquid, because of the large zero-

point motion of the particles : applying the quantum theorem of corresponding states, one finds, for biexcitons with mass $m = 4 m_0$ and assuming an intermolecular potential similar to that of H_2 , a value of the quantum parameter much higher than the critical one for liquefaction /20/.

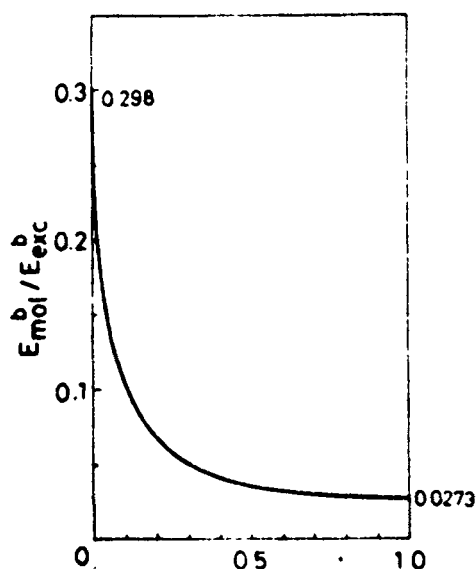


Fig. 5. - Binding energy of excitonic molecule expressed in exciton Rydberg units, in function of $\sigma = m_e / m_h$ (after Akimoto and Hanamura).

Experimental results

Cu₂O : It is a fortunate set of circumstances that the criteria for BEC of excitons presented in the previous paragraph are fulfilled in Cu₂O. The band structure of cuprous oxide is schematically shown in fig. 6. Both bands have positive parity at $\underline{k} = 0$ (the crystal belongs to the O_h group, cubic with an inversion center so that parity is a good quantum number). The energy dependence of the bands is parabolic with nearly equal effective masses $\sigma = m_e / m_h$ /21/ and $M = m_e + m_h = 3 m_0$ /22/.

As a consequence of the positive parity

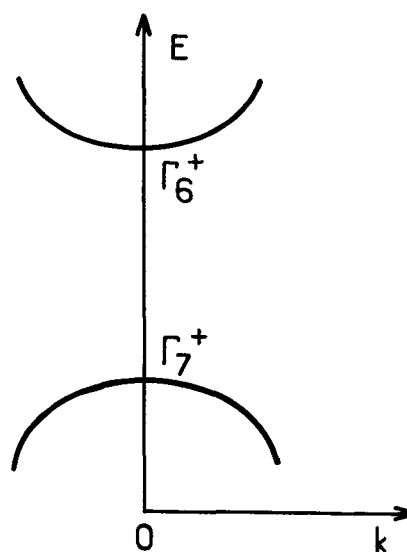


Fig. 6. - Schematic band structure of Cu₂O (after Elliott)

of the bands, the direct optical creation of an exciton with S-like symmetry is forbidden in dipole approximation at $\underline{k} = 0$. The yellow series starting with the $n = 2$ term shown in fig. 2 corresponds to the creation of p-like excitons, a transition process weakly allowed in dipole approximation /4/. The $n = 1$ term of the yellow series can be seen, as a very weak optical quadrupole transition, see fig. 7.

There is negligible polariton effect in this case due to the small exciton-photon coupling. The creation (or annihilation) of a S-like exciton may also occur with the cooperation of a parity and momentum conserving optical phonon of negative parity. This process is the origin of the two absorption edges seen in fig. 7. The low energy shoulder corresponds to the creation of the $n = 1$ yellow exciton with simultaneous absorption of a phonon of symmetry Γ_{12}^- - it disappears at very low temperature where the phonon population is negligible - the higher energy shoulder corresponds to the creation of a Γ_{12}^- phonon and an $n = 1$ exciton /5/.

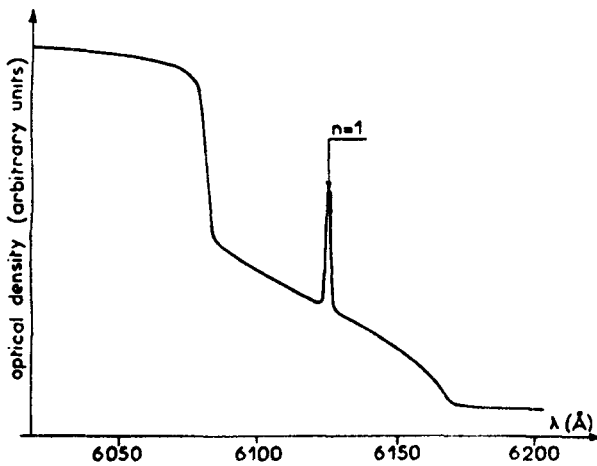


Fig. 7. - Absorption spectrum of Cu_2O near the $n = 1$ exciton of the yellow series at $T = 77$ K. (after Nikitine)

The exciton Rydberg deduced from the absorption data is large $R_x = 0.149$ eV. Applying the criterion for Mott dissociation, it means that densities in excess of 10^{20} cm^{-3} should be attainable. Further, the simple band structure with only two fold degeneracy of both valence and conduction band prevents liquefaction of the excitons. The value $\sigma = 0.73$ minimizes the attractive part of the exciton-exciton potential. Interband electron-hole exchange interaction leads to a splitting of the $n = 1$ exciton state into a triply degenerate Γ_{25}^+ orthoexciton (at 16403 cm^{-1} for $T = 2\text{K}$) and a lower lying paraexciton Γ_2^+ at $16307 \text{ cm}^{-1} \text{ cm}^{-1} / 23$. Inclusion of this electron-hole exchange interaction in the calculation of the binding energy for the molecule has been performed by Bassani et Rovere and leads to the conclusion that the biexciton is not bound /24/.

The lifetime of the excitons in Cu_2O has been recently measured in high purity single crystals of natural growth /25/. It was found that the lower lying paraexciton has a long lifetime $\tau_p \simeq 10^{-5}$ sec. This value still does not correspond to the true radiative lifetime which should

be in excess of seconds, but is limited by non-radiative processes. The direct radiative decay of the paraexciton is forbidden to all orders - it corresponds to a transition :

$$J = 0 - J = 0$$

The only possible luminescence channel here is by simultaneous emission of a Γ_2^- phonon, which gives rise to a very weak emission line.

The orthoexciton lifetime τ_o is strongly temperature dependent. At low $T \lesssim 2$ K it is of the order 30 ns. With increasing T , τ_o first decreases then increases to values in the μsec range. This behaviour is explained by a temperature dependent ortho-para transfer rate : the ortho-para coupling increases with T , thereby reducing the orthoexciton lifetime in the range $T < 20$ K. In the regime $kT \gtrsim \Delta E$ where $\Delta E = 96 \text{ cm}^{-1}$ is the ortho-para splitting energy, thermal activation from the paraexciton band leads to the observed long lifetime. $\tau_o \sim 10^{-6}$ sec /25/.

The radiative recombination of the $n = 1$ excitons provides a very convenient measure of the velocity distribution of the particles. Indeed, consider the radiative decay of orthoexcitons, which occurs predominantly through simultaneous emission of a photon and a Γ_{12}^- optical phonon, the reverse process of that responsible for the shoulder in fig. 7.

Since the involved phonon is non-polar the exciton-phonon interaction occurs via the deformation potential and is therefore independent of the phonon wave vector q . /26/. As a consequence, the lineshape of the recombination is expressed in the following form /27/ :

$$I(h\omega) = \rho(E) f(E) \quad (4)$$

where $\rho(E) = c.E^{1/2}$ is the exciton density of states, and $f(E)$ is the distribution function

which takes the well known form for bosons :

$$1/f(E) = \exp[E - \mu]/kT - 1$$

where μ is the chemical potential of the gas.

This law is very well obeyed over a large temperature range, at least up to $T = 120$ K, if a classical Maxwell-Boltzmann distribution for the particles is introduced in formula 4 with T given by the lattice temperature /25/. Here the excitation of the system occurs through optical pumping with a cw laser of low intensity, tuned within the phonon-assisted absorption band of the $n = 1$ orthoexciton so that a low density of particles is present. If the generated exciton density is increased, with the crystal kept at 1.6K, by increasing the input intensity, a gradual change of the emission lineshape is observed, which cannot be reproduced any more by assuming classical statistics, fig. 8

On the other hand, by introducing the correct distribution function valid for a degenerate Bose system D. Hulin, A. Mysyrowicz and C. Benoit à la Guillaume find a good agreement between experiment and theoretical lineshape see fig. 8 /28/. From a best fit at different excitation intensities, they extract values of μ and T . A temperature increase of the exciton system is observed with a law $\Delta T = C I_0^{1/2}$. It indicates that the exciton gas is heated by the excess energy furnished to the system in the pumping process and does not reach complete thermal equilibrium with the lattice during the particle lifetime as discussed in paragraph 2. Knowing μ and T it is also possible to deduce a particle density, by integration of 4 ; only fundamental constants are required as well as the total mass of the particle, $M = 3 m_0$ which is well-known from resonant Raman measurement /22/. A good agreement is found between densities obtained in this way and those evaluated from the experimental conditions. The density of particles is found to

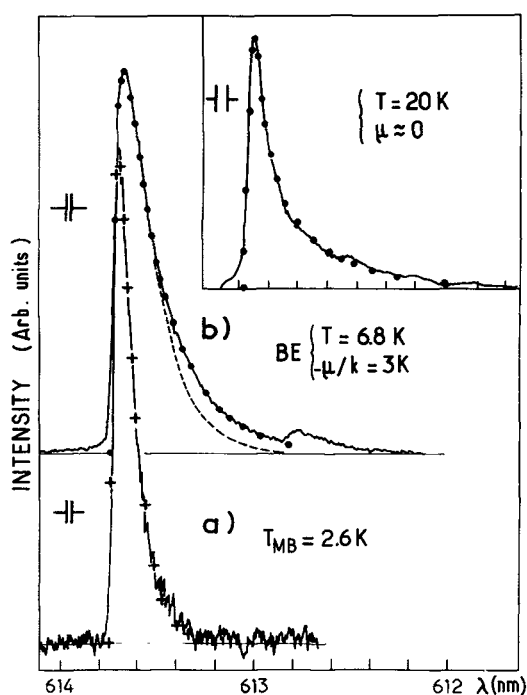


Fig. 8. - Lineshape of phonon-assisted decay of the Γ_5^+ exciton in Cu_2O immersed in He at 1.6K.

- a) low intensity Ar^{++} cw excitation
 b) same as a) except for an increase of excitation by factor 14.

inset : pulsed dye laser excitation.

Crosses give a best fit with Maxwell function; circles with a Bose function with parameters as shown.

follow a linear law dependence upon input light intensity over at least two orders of magnitudes $10^{16} - 10^{18} \text{ cm}^{-3}$, indicating that there is no substantial increase of the volume of the exciton gas at high densities, a fact expected from particles with weak interactions.

In fig. 9 the extracted orthoexciton densities obtained with cw and pulsed excitation is shown in function of the exciton temperature, together with the variation of the critical density for Bose-Einstein condensation of the ideal gas. As can be seen, the substantial heating of the gas makes it difficult to reach n_c . Nevertheless, a highly

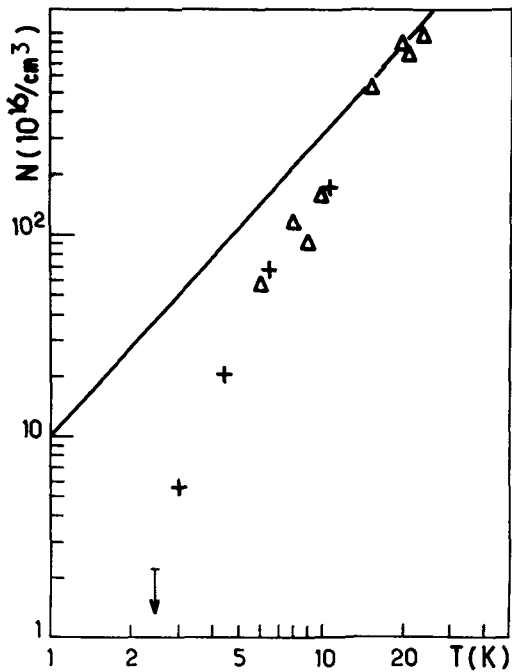


Fig. 9. - Densities of orthoexcitons obtained with different excitation conditions, as deduced from a lineshape analysis. The straight line gives the critical density for BEC in the ideal Bose gas.

degenerate system, well described in the framework of the ideal Bose gas is obtained, with a value of the chemical potential close to zero at $T = 20K$.

There are many aspects of the problem of quantum statistics of excitons in Cu_2O which need further exploration. In particular, the question whether it is possible to reach densities well beyond n_c requires more experimental work. In this respect, the precise mechanism responsible for the temperature increase of the electronic system is important and must be elucidated in detail.

Another problem concerns the population of paraexcitons which should in principle reach even higher densities than those reported here for orthoexciton, since the most important decay channel for orthoexciton is due to ortho-para conversion. Experimental work along these lines is in progress.

CuCl : The band structure of $CuCl$ is very similar to that of Cu_2O , except for two features : there is no parity assignment to the bands (the crystal,

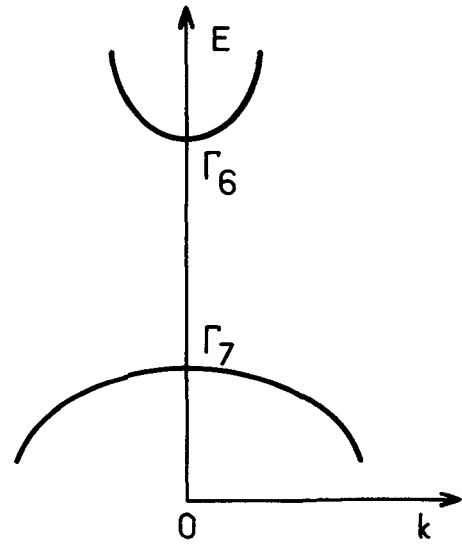


Fig. 10. - Schematic band structure of $CuCl$.

although with cubic structure, has no inversion centre) and the mass ratio $\sigma = m_e/m_h$ is smaller, of the order 0.2 or less /29/.

The linear absorption spectrum of $CuCl$ below the band gap shows very strong lines, corresponding to the creation of excitons with S-like symmetry /5/. The oscillator strength for the transition to the $n = 1$ line is $f \sim 10^{-3}$, six orders of magnitude higher than for the quadrupole line of Cu_2O shown in fig. 7. A description of this resonance in terms of polariton is necessary and has been successful in explaining many of its characteristics. Thus, there is at least one good reason to prevent BEC of excitons here. Another reason is the formation of excitonic molecules occurring at high exciton densities, which is favoured by the heavy hole effective mass. If the crystal is irradiated with intense light of frequency corresponding to interband transition above the gap, a new emission, located below the $n = 1$ free exciton becomes apparent, with a quadratic intensity dependence upon input excitation. This new emission has been attributed to the presence of excitonic molecules, which decay by emitting photons, restituting free excitons in the process /30/. The decay time τ is of the order 10^{-9} - 10^{-10} sec and the dissociation energy of the mole-

cule is $B = 27$ meV, a rather large value comparable to the binding energy of excitons in many II-VI compounds. There has been a considerable amount of work devoted to the study of biexcitons in CuCl.

In particular, it is possible to observe the absorption line corresponding to the direct creation of excitonic molecules from the crystal ground state, via a two-photon process. As shown by Hanamura /31/ this should occur with a giant cross-section for two reasons : first, because of the proximity of the exciton to the energy of the incident photons acting as a nearly resonant intermediate state ; secondly, because of the particular type of transition, in which two electrons, separated by a distance of the order of the biexciton radius $a_{XX} \simeq 10 \text{ \AA}$ are simultaneously promoted to the conduction band. This prediction has been confirmed experimentally /32/, with measured cross-sections 4-5 orders of magnitude higher than typical values for allowed two-photon interband transitions in semiconductors, making it possible to obtain biexciton densities in excess of 10^{19} cm^{-3} with input light intensities in the megawatt range /33/.

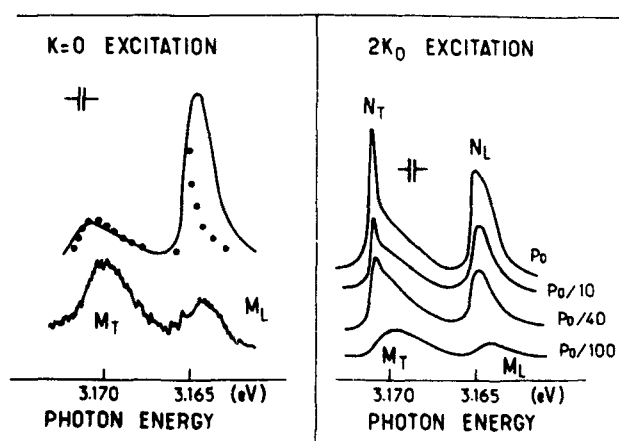


Fig. 11. - Biexciton emission spectrum of CuCl thin films held at 4K. Left curves are obtained by two-photon excitation with two counterpropagating laser beams ; Right curves with a single beam.

Black circles result from a calculated lineshape assuming an ideal Bose gas with chemical potential $\mu=0$

Fig. 11 shows the subsequent molecular recombination spectrum, obtained in thin polycrystalline films of high purity, held at $T = 4$ K, with two different excitation geometries /34/.

On the left of fig. 11, two laser beams of same frequency ω (with $2\hbar\omega = E_{XX}$, where $E_{XX} = 2E_X - B$ is the internal energy of the biexciton), but opposite propagation directions are used. Each beam is right (or left) circularly polarized, so that biexciton production by non-linear self attenuation of each beam alone is forbidden by selection rules ; on the other hand, creation of a biexciton by removal of one photon from each beam is possible, with the resulting excitonic molecule at $\underline{K}_{XX} = 0$ because of momentum conservation.

On the right side of figure 11, the excitation is performed with a single linearly polarized beam, with a corresponding creation of molecules at $\underline{K}_{XX} = 2 \underline{K}_0$ where \underline{K}_0 is the input photon wave vector.

If the input light intensity is sufficiently low, the resulting luminescence is identical in both cases, (bottom curves). It means that the system has lost all memory of the particular excitation mechanism, due to the presence of an efficient thermalization process /35/. The observed spectrum is readily explained by assuming a classical distribution of the decaying molecules inside their kinetic energy band ; since the dispersion curve of the biexciton $\hbar^2 \underline{K}_{XX}^2 / 2 M_{XX}$ (where $M_{XX} = 2 M_X$, the exciton mass) is half that of the exciton, the lineshape corresponds to an inverted Maxwell-Boltzmann function, with a doublet structure because the final state reached in the transi-

tion is either a two-fold degenerate transverse exciton (M_T line) or a longitudinal exciton (M_L line) /36/ ; an effective temperature for the particles $T_{eff} \simeq 15 - 25K$ is found. In this temperature range, only a small fraction of the molecules are distributed near $\underline{k}_{xx} = 0$, that the polariton aspect of the final exciton does not affect M_T lineshape significantly.

The spectra observed at higher input intensities differ considerably from the shape corresponding to a classical statistical distribution of the excitonic molecules ; they have been interpreted as an evidence for the occurrence of a Bose-Einstein of the biexcitons, with the condensate either at $\underline{k}_{xx} = 0$ (left side of fig. 11) or at $\underline{k}_{xx} = 2\underline{k}_0$ (right side of fig. 11 and fig. 13) /34/.

In order to discuss the luminescence spectrum expected from a condensate of biexcitons near $\underline{k}_{xx} = 0$, the polariton curve of the exciton resonance must be examined in details since it is precisely in the region of \underline{k} space where it shows a strong dispersion that the transition will now terminate : in fact, the decay process is better described in term of fission of the molecules in two polaritons, with both momentum and energy conservation law simultaneously satisfied. Figure 12, shows the polariton dispersion curve in CuCl, as determined experimentally /37/. The wavevector diagram corresponding to three different geometrical configurations, with respect to an initial biexciton wavevector $\underline{k}_{xx} = 2\underline{k}_0$ is shown in fig. 12,

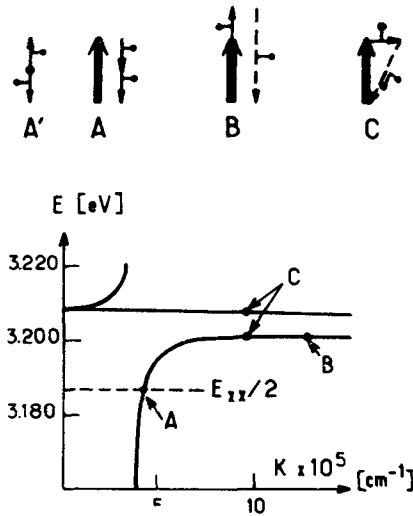


Fig. 12. - Polariton dispersion of the $n = 1$ exciton in CuCl. Points A, B, C correspond to the final state reached in the decay of a molecule having initial momentum $2\underline{k}_0$ in a forward (A), backwards (B) and non-collinear (C) detection geometry.

together with the corresponding points on the energy diagram. For instance, in the backwards geometry (case B), the two fission fragments consist of an exciton-like polariton with wavevector $3\underline{k}_0$ and a photon-like polariton $-\underline{k}_0$, which is detected outside the crystal as radiation at a frequency corresponding to the high energy edge of the M_T band. Like wise, in a forward detection geometry (A), two equal photon like polaritons with wavevector $-\underline{k}_0$ are generated, which cannot be distinguished externally from the incoming photons used for the excitation of the system. Note that in the collinear detection geometries A and B, the decay process creating a photon and a longitudinal exciton is forbidden, because selection rules dictate that the final products must have parallel dipole moments. By contrast in a non collinear geometry, case C, one may convince oneself that a transition towards the longitu-

dinal exciton branch is possible, but only if the external photon has its polarization vector lying in the plane containing \underline{K}_{XX} and \underline{K}_0 .

Similar considerations show that the only possible radiative decay channel of a biexciton $\underline{K}_{XX} = 0$ is by emission of two counterpropagating photon-like polaritons (case A') which again cannot be distinguished energetically from the incident photons used for the excitation.

Thus, the features observed in fig. 11 and 13 may be consistently explained by the presence of a condensate of biexcitons, the radiative decay of which gives rise to the sharp line N_T observed at high densities. Further support for this interpretation is given by the presence of a threshold for the appearance of N_T , which is temperature dependent in the manner shown in the inset of fig. 13.

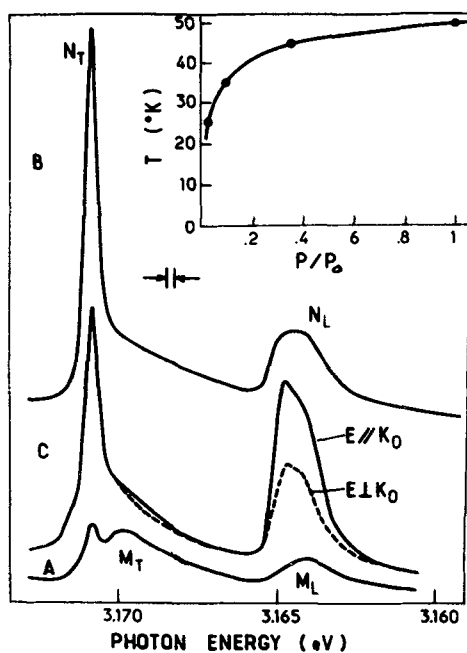


Fig. 13. - Luminescence of a high density of biexcitons in CuCl created at $2\underline{K}_0$ for different detection geometries (see fig. 11). Inset shows the temperature threshold for appearance of narrow N_T line with laser intensity P/P_0 .

However, a model of non-interacting particles is insufficient in several respects. First, in the ideal Bose gas, condensation is only expected to occur at $\underline{K} = 0$. Also, it does not reproduce adequately the luminescence spectrum obtained with $\underline{K}_{XX} = 0$ excitation (see fig. 11 upper left). The assumption of partial depletion of the condensate due to repulsive interactions would lead to a better agreement for line M_L , but no quantitative analysis has been performed so far. In this respect, Chase et al /33/ have observed a broadening of the biexciton resonance at high densities, which they attribute to collisions amongst the particles. A cage model, characteristic of a dense, liquid-like fluid, must be introduced in order to explain the observed behaviour /33/.

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