

the temperature at which localization is apparent is inversely proportional to $A^{1/2}$, or the diameter of the wire. For reasonable values of the parameters this makes Aq^2 greater than unity, but not large, so a one-dimensional-phonon behavior sets in at a slightly lower temperature. When electron-electron scattering predominates τ_{ph} in Eq. (6) should be replaced by τ_{ee} as given in Eq. (8), and then the temperature is inversely proportional to A . Below this temperature the electrons are free to diffuse over the distance L , but can then go no further until a phonon or another electron causes a transition to a new wave packet of states. In this temperature range the resistance will increase as T^{-2} , whether the transitions are caused by electrons or one-dimensional phonons. Finally we may be concerned with temperatures so low that $k_B T$ is of the order of the spacing between overlapping localized states, and below such temperatures we should describe the conduction as activated hopping between localized states; in one dimension⁸ the resistance for this process increases exponentially with T^{-1} .

If we consider a system with a cross-sectional area of $2.5 \times 10^{-15} \text{ m}^2$, an impurity mean free path of $0.5 \times 10^{-9} \text{ m}$, and $k_F = 1.2 \times 10^{10} \text{ m}^{-1}$, then the length of localized states given by Eq. (4) is about 0.012 mm. With $\Gamma = 1$ equal to 0.01 and the sound

velocity c equal to 4000 m/s, the condition (6) is satisfied at about 1.7 K, while if τ_{ph} is replaced by τ_{ee} the condition is satisfied at about 1.2 K. In this example the electron-electron scattering is slightly more important, and so the T^{-2} increase in resistance should occur below about 1.2 K. The energy spacing between overlapping localized states is of order $5 \times 10^{-5} k_B$ under these conditions, so that the exponentially rising resistance should be observed in the region of 50 μK .

I am particularly grateful to Dr. E. M. Forgan and Professor W. F. Vinen for pointing out the importance of the condition $q\lambda < 1$ and of the electron-electron interaction.

¹N. F. Mott and W. D. Twose, *Adv. Phys.* **10**, 107 (1961).

²K. Ishii, *Prog. Theor. Phys., Suppl.* **53**, 77 (1973).

³D. J. Thouless, *J. Phys. C* **6**, L49 (1973).

⁴G. Yuval, *Phys. Lett.* **53A**, 136 (1975).

⁵J. T. Edwards and D. J. Thouless, *J. Phys. C* **5**, 807 (1972).

⁶D. C. Licciardello and D. J. Thouless, *Phys. Rev. Lett.* **35**, 1475 (1975), and *J. Phys. C* **8**, 4157 (1975).

⁷C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971), 4th Ed., p. 283.

⁸J. Kurkijärvi, *Phys. Rev. B* **8**, 922 (1973).

Electron-Hole Liquid and Biexciton Pocket in AgBr

D. Hulin, A. Mysyrowicz, M. Combescot, I. Pelant,^(a) and C. Benoît à la Guillaume
Group de Physique des Solides de l'École Normale Supérieure, Université Paris VII,
Tour 23, 75005 Paris, France

(Received 30 June 1977)

A new emission band in AgBr is attributed to electron-hole-liquid recombination. Excitonic molecules appears only at higher excitation and temperature, corresponding to a limited region of the (T, n) plane called biexciton pocket.

The occurrence of a liquid phase of degenerate electron-hole plasma (EHL) is now well established in Ge,¹ Si,¹ and GaP.² The properties of the liquid are in good agreement with theory, provided the detailed band parameters of these semiconductors (in particular their indirect-band-transition structure) is properly taken into account. Recently, it has been shown by Keldysh and Silin,³ and Beni and Rice,⁴ that the interaction between free carriers and the lattice in polar materials increases the stability of EHL, and makes it possible to observe it even in direct-gap compounds. Experiments performed in CdS^{5,6} and

CdSe⁶ confirm these predictions. The values of carriers density n and liquid binding energy ϕ are here also in fair agreement with calculations.

In this Letter, we present experimental evidence for the existence of EHL in AgBr. However, in contrast to the other cases mentioned above, the binding energy of this strongly polar compound with indirect-gap structure is significantly larger than derived from the theory.⁴ This makes it possible to observe the liquid with temperatures in excess of 100 K and even suggests a much higher critical temperature of the EHL.

But AgBr also exhibits another novel character-

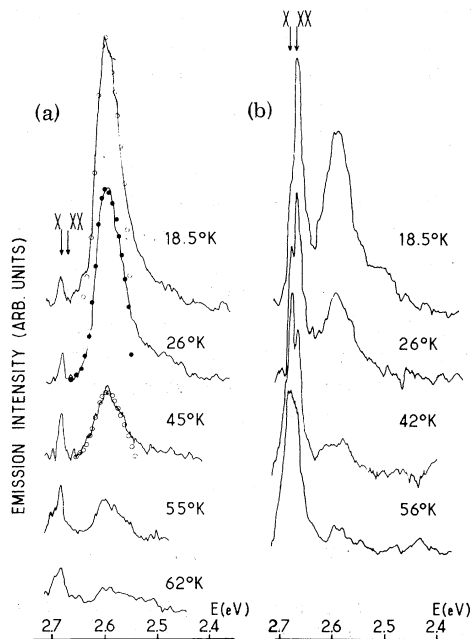


FIG. 1. Luminescence of AgBr at different cooling temperatures. The pulsed excitation intensity is ~ 50 KW/cm^2 on the left (a), and ~ 5 MW/cm^2 on the right (b). The circles show the calculated line shape for EHL recombination, at effective temperatures of 50°K ($T = 18.5^\circ\text{K}$), 70°K ($T = 26^\circ\text{K}$), and 97°K ($T = 45^\circ\text{K}$). The two arrows indicate the positions of the free exciton X and excitonic molecule XX. The intensities in (a) and (b) are not recorded at the same scale.

istic. It represents so far the only case of an indirect-gap material where excitons, biexcitons, and the EHL are simultaneously present, indicating a new, more complex behavior of the vapor phase. Surprisingly, biexcitons appear only when the electronic system is heated, being totally suppressed at low temperatures. As we will show, this is a consequence of the presence of the liquid phase, which restricts the region of the temperature-density plane, where excitonic molecules can be found in appreciable number, to a so-called biexciton pocket.

In Fig. 1, luminescence spectra of "pure" AgBr single crystals at different cooling temperatures are represented. The experimental setup is similar to that described elsewhere.^{2,7} The maximum intensity (after focusing) of the excitation pulse ($\lambda \approx 3800$ Å, pulse duration = 6×10^{-9} sec) is of the order $5 \text{ MW}/\text{cm}^2$. All emission spectra shown here have been recorded in chronological coincidence with the peak of the excitation pulse with a time resolution of 1×10^{-9} sec.

Consider first the set of spectra in Fig. 1(a).

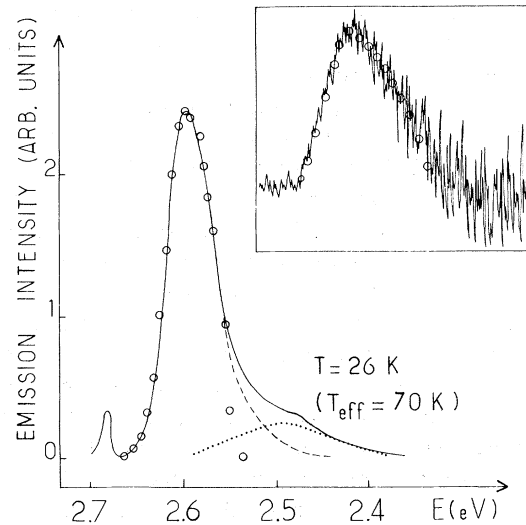


FIG. 2. EHL recombination in AgBr under pulsed excitation fitted with $T_L = 70^\circ\text{K}$ (open circles). The contribution of iodine emission (dotted line) is subtracted. Note the residual discrepancy at low energy (also observed in Ge) probably due to Auger processes. The inset is the EHL emission obtained with cw excitation at $T = 30^\circ\text{K}$ and fitted with $T_L = 59^\circ\text{K}$. The increasing noise at lower energies is due to the iodine emission band which has been suppressed here. The energy scale of the inset is 1.63 larger.

They are obtained under conditions of rather low input intensity ($I \approx 5 \times 10^4 \text{ W}/\text{cm}^2$). The recombination of free excitons ($h\nu = 2.68$ eV) with simultaneous emission of a momentum-conserving phonon TA_L (8.3 meV) is apparent together with a new broad emission at $h\nu \approx 2.6$ eV. Note that no excitonic-molecule emission is visible here ($h\nu = 2.67$ eV).⁷ We attribute the broad new emission (lifetime ≈ 15 nsec) to the TA_L -phonon-assisted annihilation of electron-hole pairs in the condensed liquid phase. An excellent agreement between the observed emission and the calculated line shape for EHL recombination can be obtained, provided that one introduces an effective temperature T_L for the liquid, higher than the average sample temperature T .⁸ For instance, the spectrum at $T = 26^\circ\text{K}$ is best fitted (Fig. 2) with the theoretical line shape corresponding to $T_L \sim 70^\circ\text{K}$. Other characteristics of the broad emission support the concept of a phase separation between a liquid and its excitonic vapor: By raising T , at constant excitation, a threshold temperature for the disappearance of the EHL is exhibited, as expected. Also, a stringent criterion is the existence of a threshold input intensity, below which no EHL is formed. To detect it, we have used a

cw He-Cd laser excitation. The appearance of an intense broad emission band, due to excitons bound to iodine,⁹ normally prevents the observation of the EHL luminescence. However, since the decay time of the iodine is much longer ($\tau \approx 25 \mu\text{sec}$), it is possible, by using high-frequency (100 kHz) lock-in detection techniques with appropriate phase shift, to subtract the iodine contribution (see inset in Fig. 2). The expected EHL line is seen above $I \geq 10 \text{ mW/cm}^2$ at 20°K . Here also, we have again $T_L > T$.¹⁰

From the line-shape analysis, we extract the density of carriers in the liquid phase $n \sim 8 \times 10^{18}$ particles/ cm^{-3} and the binding energy per electron-hole pair with respect to the free exciton $\varphi(0) \approx 55 \text{ meV}$. The temperature dependence of φ follows well the expected $\varphi(0) + aT_L^2$ behavior with $a \approx 2 \times 10^{-3} \text{ meV } (^\circ\text{K})^{-2}$ at least up to $T = 100^\circ\text{K}$. While the value of n is close to that found by Beni and Rice⁴ for AgBr ($n = 6 \times 10^{18} \text{ cm}^{-3}$), our value of $\varphi(0)$ disagrees with the calculated energy of an EHL in AgBr, $\varphi(0)_{\text{calc}} = 14 \text{ meV}$.⁴ It is unlikely that this discrepancy comes from poor band-structure parameters, since these are rather accurately known in AgBr.

We now consider the spectra of Fig. 1(b) recorded under identical conditions as in 1(a) but with much larger excitation intensity ($I \approx 5 \text{ MW/cm}^2$). Because of phase-separation characteristics, an isothermal increase of density should give similar spectra as in Fig. 1(a) with a larger weight given to the EHL band. Instead, for the same cooling temperature, the liquid has been further heated. This is deduced from the change of the line shape, in particular the broadening of the high-energy side.¹¹ Another striking feature is the appearance of the excitonic molecule (XX) in addition to the exciton (X) and the EHL lines, showing a change in the composition of the gas.

To proceed further we consider a gas of excitons and biexcitons in thermal equilibrium with an electron-hole liquid. Let $-E_X$, $-(E_X + \Delta)$, and $-(E_X + \varphi)$ be the binding energies of a pair of $e-h$ in the X, XX, and EHL states, respectively. We consider only the case where the liquid is the most stable state, i.e., $\varphi > \Delta$. At low density, the chemical potential of X or XX is

$$\mu_i = -E_i + kT \ln[(n_i/n_{i0})T^{3/2}], \quad (1)$$

with $i = X$ or XX, $E_i = E_X$ or $2(E_X + \Delta)$, and $n_{i0} = h^{-3} g_i (2\pi m_i k)^{3/2}$, g_i being the degeneracy. The equilibrium between the gas and the liquid reads

$$\frac{1}{2} \mu_{XX} = \mu_X = -E_X + \varphi.$$

This gives the ratio biexcitons over excitons

$$R = n_{XX}/n_X = (n_{XX0}/n_{X0}) \exp[-(\varphi - 2\Delta)kT]. \quad (2)$$

If the binding energy of the molecule is large ($\Delta < \varphi < 2\Delta$), R is a decreasing function of T : Biexcitons exist at the lowest temperatures and transform into X at higher T , as one would usually guess. More peculiar is the case $2\Delta < \varphi$ where R is an *increasing* function of T along the coexistence curve; at the lowest T , the gas is made of X, the observation of XX being possible only at higher T . Of course, R will finally decrease along the coexistence curve, leading to the concept of the biexciton pocket: The increase of φ with T alone already leads to a peaked function for R , but other effects such as the interactions in the gas would also lead to a dissociation of XX into X and finally into $e-h$ (Mott transition).¹²

This model explains well the main features observed in AgBr. It predicts the existence of a pocket, since the condition $\varphi > 2\Delta = 7 \text{ meV}$ is fulfilled. Using Eq. (2) and the measured T dependence of φ , we find that R reaches its maximum value at $T_M \approx 150^\circ\text{K}$.¹² In Fig. 1(a), the effective temperatures of the liquid are lower than T_M . The set of curves corresponds to a vertical path in the (T, n) diagram to the left of the biexciton pocket, where R is small (see Fig. 3); and, indeed, no biexciton emission is observed. At higher laser intensity [Fig. 1(b)], the electronic system has been heated and the density increased. Molecular emission is now apparent and stays even when the EHL band has disappeared. This

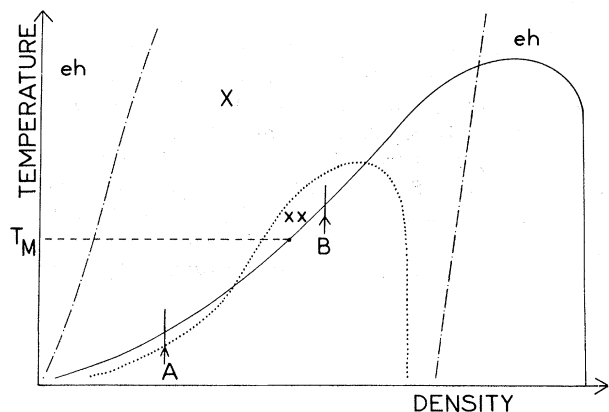


FIG. 3. Schematic representation of the phase diagram. The dotted curve corresponds to $R = \text{const}$. The dotted and dashed lines give an indication of the regions where the excitonic gas transforms into an electron-hole gas (or plasma) (see text).

can be explained by the vertical path intercepting the pocket as shown in Fig. 3.

All considerations so far are based on the assumption of a regime of thermodynamic equilibrium. Unfortunately, this situation is hardly achieved in our samples, in view of the short lifetime of the particles. Therefore, one should not expect to find a quantitative agreement between the theory and our results. For instance, we evaluate at T_M a value $R_M \sim 0,1$ and experimentally R is of the order of 4.¹⁴ Also, we wish to point out that we have not observed situations where R increases as the sample temperature is raised (path between A and B). This is perhaps not surprising, however, if we consider that impurities ($n_i \approx 10^{17} \text{ cm}^{-3}$) like iodine act as very efficient trap centers for excitons, but less for excitonic molecules.¹⁵ This capture is important only at low lattice temperature, and gradually diminishes if the sample is heated. The thermal release of bound exciton leads to an *apparent* decrease of R for all vertical paths. In other words, heating the whole sample is different from heating the electronic system only.

In conclusion, we have shown that the EHL exists in AgBr with a very large binding energy. The liquid coexists with a gas of excitons only at low temperatures, excitonic molecules appearing in the gas at higher temperatures and generated densities.

We are grateful to Professor Malinowski, Bulgarian Academy of Sciences, Sofia, for the samples used in this experiment.

^(a)Permanent address: Charles University, Faculty of Mathematics and Physics, 121 16 Prague 2, Czechoslovakia.

¹See for instance M. H. Pilkuhn, in *Proceedings of the Thirteenth International Conference on the Physics of Semiconductors, Rome, Italy, 1976*, edited by F. G. Fumi (North-Holland, Amsterdam, 1977).

²M. Maaret, J. Barrau, M. Brousseau, J. Collet, and J. Mazzaschi, *Solid State Commun.* **22**, 593 (1977); J. Shah, R. F. Leheny, W. R. Harding, and D. R. Wight, *Phys. Rev. Lett.* **38**, 1164 (1977); D. Hulin, N. Bontemps, M. Combescot, and A. Mysyrowicz, *Phys. Lett.* **61A**, 349 (1977).

³L. V. Keldysh and A. P. Silin, *Zh. Eksp. Teor. Fiz.* **69**, 1053 (1975) [*Sov. Phys. JETP* **42**, 535 (1975)].

⁴G. Geni and T. M. Rice, *Phys. Rev. Lett.* **37**, 874 (1976).

⁵V. G. Lysenko, V. I. Revenko, T. G. Tratas, and V. B. Timofeev, *Zh. Eksp. Teor. Fiz.* **68**, 335 (1975) [*Sov. Phys. JETP* **41**, 163 (1975)].

⁶R. F. Leheny and J. Shah, *Phys. Rev. Lett.* **37**, 871 (1976); R. F. Leheny and J. Shah, *Phys. Rev. Lett.* **38**, 511 (1977).

⁷I. Pelant, A. Mysyrowicz, and C. Benoît à la Guillaume, *Phys. Rev. Lett.* **37**, 1708 (1976); T. Baba and R. Masumi, in *Proceedings of the Taormina, Research Conference on the Structure of Matter: Recent Developments in Optical Spectroscopy of Solids, Taormina, Italy, 1976* (to be published).

⁸A similar effect ($T_{\text{eff}} > T_{\text{bath}}$) has already been observed for excitons and biexcitons in AgBr, even with cw excitation [W. vonder Osten and J. Weber, *Solid State Commun.* **14**, 1133 (1974)]. It indicates that a thermalization of the particles with respect to the lattice is not achieved during their short lifetime.

⁹F. Moser and S. Lyu, *J. Luminesc.* **3**, 447 (1971).

¹⁰The observation of a constant line shape over such a large excitation range (10^{-3} – 10^3 W/cm^2) is a strong argument in favor of EHL.

¹¹We have not attempted to extract the liquid effective temperature under these conditions, because of the overlap of the EHL with excitonic molecule emission. A decomposition of the lines involves, in our view, too much arbitrariness. Note, however, that the EHL temperature is probably higher than 100°K even at the lowest coolant temperature.

¹²J. Shah, M. Combescot, and A. Dayem, *Phys. Rev. Lett.* **38**, 1497 (1977); G. A. Thomas and T. M. Rice, to be published; M. Combescot, to be published.

¹³Note that the assumed variation of φ may not hold at this temperature. The value quoted here gives an upper limit for T_M .

¹⁴To estimate R , we take equal radiative coefficients for X and XX decay. They are probably comparable because according to {A. A. Golovin and E. I. Rashba, *Pis'ma Zh. Eksp. Teor. Fiz.* **17**, 690 (1973) [*JETP Lett.* **17**, 478 (1973)]} the radiative decay of XX has giant oscillator strength in direct-gap materials but this effect should not occur in indirect-gap semiconductors.

¹⁵This is evidenced by the study of the time evolution of the emission after the end of the excitation pulse. We have observed a preferential capture of X over XX. It could explain also the discrepancy between the calculated and estimated values of R .