Bose-Einstein Condensation in Semiconductors: The Key Role of Dark Excitons

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Bose-Einstein condensation in semiconductors is controlled by the nonelementary-boson nature of excitons. Pauli exclusion between the fermionic components of composite excitons produces dramatic exchange couplings between bright and dark states. In microcavities, where bright excitons and photons form polaritons, they force the condensate to be linearly polarized, as observed. In bulk, they also force linear polarization, but of dark states, due to interband Coulomb scatterings. To evidence this dark condensate, indirect processes are thus needed.

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Although the possibility for a system of noninteracting massive bosons to condense into a single coherent state was predicted almost 100 years ago by A. Einstein [1], its direct observation in weakly interacting systems has taken quite a long time. Bose-Einstein condensation (BEC) requires the quantum regime to be reached, with a de Broglie wavelength comparable to the interparticle distance. For dilute systems of heavy atomic bosons, this implies a very low temperature. Elaborate cooling techniques in atomic physics have allowed the observation of BEC in atomic gases [2] and more recently in molecular systems [3] at temperatures as low as μK. These observations have opened a new field [2] of very active research on these ''ultracold gases.''

Since light particles are favorable to observe BEC, semiconductors seem very appealing. Excitons, which result from the Coulomb attraction of one conduction electron and one valence hole, are composite bosons. With an effective mass of the order of the vacuum electron mass m_e, they are much lighter than atoms, so they should condense at much higher temperature. This is why exciton BEC has been searched for for tens of years, with repeated claims of observation followed by denials [4]. Being semiconductor excitations, excitons of course have a finite lifetime. However, this lifetime is in most cases long enough to reach the thermal equilibrium necessary to approach thermodynamic aspects of BEC.

Quite recently, a similar effect has been observed through the Bose-Einstein condensation of polaritons [5,6], which are excitations resulting from the strong coupling of one photon and one exciton. In a microcavity, the extremely steep dispersion of the polariton modes induces an extremely light polariton effective mass, of order of $10^{-4}m_e$, which allows critical temperatures [7] for polariton BEC as high as 10^2 K. While 2D systems are known to never develop true long range order, coherence across a finite size polariton cloud in trapped geometry has been demonstrated [6].

To detect exciton BEC, attention has been naturally focused on bright excitons, which are the ones coupled to light. This has led to overlooking of dark excitons, which do not have this advantage. In this Letter, we point out the key role they play for BEC in semiconductors.

Selection among possible Bose-Einstein condensates results from interactions. The dominant one for excitons is the Pauli exclusion between their fermionic components. It induces dramatic exchange couplings between bright and dark states. Here we show that it forces the polariton condensate to have a linear polarization, as it produces the lowest energy, in full agreement with experiments [5,6]. In the case of exciton BEC, these bright-dark couplings also force the linear polarization of the condensate. However, dark excitons having an energy slightly lower than bright excitons, due to valence-conduction Coulomb processes, the stable condensate is actually made of dark excitons. This may well explain why exciton BEC has not yet been observed. This Letter should thus stimulate conceptually new experiments looking for a dark BEC. A possible (indirect) way to observe it is through the line shift of a bright exciton, induced by its interaction with a population of dark excitons. This shift is sensitive to the dark exciton distribution and must change when the exciton gas goes from thermal to condensed.

When the coupling between photons and excitons is weak compared to the exciton broadening, excitons are created by photon absorption according to the Fermi golden rule [8]. When it is strong, photons are not absorbed but form a mixed state with bright excitons. The resulting exciton-polaritons [9] are exact eigenstates of the coupled photon-semiconductor Hamiltonian for one excitation. Since photons do not interact, many-body effects between polaritons come from interactions between the excitonic parts of these polaritons.

As transparent from the exciton many-body theory we have recently constructed [10–13], interactions between excitons are predominantly due to Pauli exclusion between their fermionic components, departing in this way from the standard elementary boson picture. Pauli exclusion indeed drives all semiconductor optical nonlinear effects, Coulomb interactions only producing corrective terms

[14–17]. The associated carrier exchanges, which can take place between many more than just two excitons, can be visualized through Shiva diagrams [18], which not only help to select the dominant processes but also allow to calculate them readily.

The actual Bose-Einstein condensate in semiconductors is selected in the degenerate exciton subspace through many-body effects between excitons, since the condensate with the lowest energy is the one that occurs. Hence, the composite nature of the excitons through Pauli exclusion between its constituents plays a key role in this selection.

In quantum wells, the exciton degeneracy is 4; the conduction electron having a spin $s = \pm 1/2$ and the valence hole an angular momentum $m = \pm 3/2$; the light holes, with angular momentum $m = \pm 1/2$, having a higher energy in confined geometry. Among these four exciton states, the two with total spin ± 2 are not coupled to light, so they are not concerned with the polariton BEC. Hence to characterize the polariton condensate, we must find the linear combination of the two bright excitons leading to the lowest energy; i.e., the prefactors $a_{\pm 1}$ of

$$B^\dagger = a_1 B_1^\dagger + a_{-1} B_{-1}^\dagger, \tag{1}$$

where $B_{\pm 1}^\dagger$, defined as

$$B_{\pm 1}^\dagger = \sum_{\mathbf{k}} \langle \nu_0 | \mathbf{k} \rangle a_{\mathbf{k}, \mp 1/2}^\dagger b_{-\mathbf{k}, \pm 3/2}^\dagger, \tag{2}$$

creates a $S = \pm 1$ ground state bright exciton with zero center-of-mass momentum, in the relative motion ground state $|\nu_0\rangle$ with energy $-E_0$, made of a ($\mathbf{k}$, $s = \mp 1/2$) electron and a ($-\mathbf{k}$, $m = \pm 3/2$) hole.

As obvious from Fig. 1(a), the Pauli scattering for carrier exchanges of two bright excitons (± 1) generates two dark excitons (± 2). This escape into dark states reduces all diagonal matrix elements between n bright excitons $B^\dagger$ by a factor ($|a_1|^{2n} + |a_{-1}|^{2n}$), as readily seen from the Shiva diagrams [18] of Fig. 2. Since $|a_1|^2 + |a_{-1}|^2 = 1$ for normalization, so that $a_1 = e^{i\varphi_1} \cos\xi_1$ and $a_{-1} = e^{i\varphi_{-1}} \sin\xi_1$, where ξ_1 is the ellipticity of the exciton linear combination $B^\dagger$, this factor reduces [19] for $n = 2$ to

$$|a_1|^4 + |a_{-1}|^4 = 1 - 2|a_1 a_{-1}|^2 = 1 - \frac{1}{2}\sin^2 2\xi_1. \tag{3}$$

According to [20], this leads to an energy expectation value for N excitons given by

$$\langle H \rangle_N = \frac{\langle v | B^N H B^{\dagger N} | v \rangle}{\langle v | B^N B^{\dagger N} | v \rangle} = N E_0 \left[-1 + \eta \left(1 - \frac{1}{2} \sin^2 2\xi_1 \right) x_1 + O(\eta^2) \right], \tag{4}$$

where $\eta = N(a_x/L)^2$ is the dimensionless parameter associated to the exciton density, a_x is the exciton Bohr radius, L the sample size, and $x_1 = \pi - 315\pi^3/4096 \simeq 0.75$ in 2D [21]. The η term in Eq. (4) comes from the exchange Coulomb scattering between $n = 2$ excitons shown in Fig. 1(b). This is why it appears with the reduction factor for carrier exchanges given in Eq. (3). Equation (4) thus shows that the minimum energy is reached for $\xi_1 = \pi/4$, i.e., for linearly polarized excitons, the selection of the polarization axis being due to the breaking of rotational invariance.

This effect is enhanced in the case of polaritons. As pointed out in [21], these mixed particles also have a photon-assisted exchange scattering, free from any Coulomb process [see Fig. 1(c)], with the same symmetry as the Coulomb exchange scattering of Fig. 1(b). This scattering is actually dominant when one of the polaritons has a strong photon character. Consequently, the condensate of microcavity polaritons constructed on the two bright states (± 1) must exhibit a linear polarization, in full agreement with experimental results [5,6]. Through a quite convincing experiment in which excitons are created by a circularly polarized pump beam, Balili *et al.* observe [6] a linearly polarized light from a region different from the excited one, thanks to a pinned geometry that collects the excitons in a parabolic trap. In these experiments, the exciton gas, created by a circularly polarized pump, loses

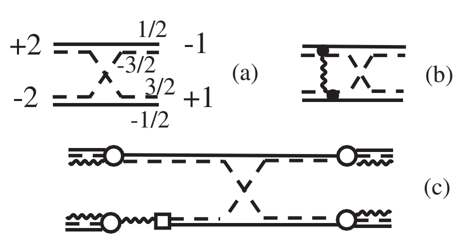

FIG. 1. (a) Pauli scattering for carrier exchange between two bright "in" excitons (∓ 1). The "out" excitons with spins (± 2) are dark. Solid line, electron; dashed line, hole; double solid-dashed line, exciton. (b) Exchange Coulomb scattering between two excitons. (c) Photon-assisted exchange scattering between two polaritons (triple solid-dashed-wavy line); wavy line, photon; empty square, exciton-photon coupling; empty dot, polariton—photon (or exciton) coupling.

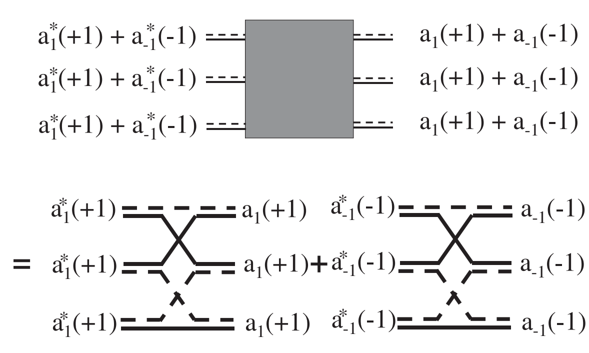

FIG. 2. Shiva diagram for carrier exchanges between 3 coherent excitons $B^\dagger = a_1 B_1^\dagger + a_{-1} B_{-1}^\dagger$. Since, according to Fig. 1(a), exchanges between opposite spin bright excitons generate dark states, this Shiva diagram reduces to diagonal terms between (+1) excitons and between (−1) excitons.

its coherence while traveling to the trap, where it condenses into a different coherent state. The linear polarization actually observed is along the (110) crystal axis, due to a small anisotropy that lifts the degeneracy with respect to the orientation of the polarization axis, i.e., which fixes the relative phase $\varphi_1 - \varphi_{-1}$. In other experiments [5] the degeneracy with respect to the direction of the polarization axis is lifted by the microcavity anisotropy.

The situation is more complex in the case of exciton BEC, because there is no reason to eliminate the dark excitons. To characterize a Bose-Einstein condensate possibly formed in quantum wells out of the four excitons (±1, ±2), we thus have to look for the minimum of $\langle H\rangle_N$ with $B^\dagger$ now given by

$$B^\dagger = a_1 B_1^\dagger + a_{-1} B_{-1}^\dagger + a_2 B_2^\dagger + a_{-2} B_{-2}^\dagger, \qquad (5)$$

where $B_{\pm 2}^\dagger$ reads as $B_{\pm 1}^\dagger$ in Eq. (2), with $a_{\mathbf{k},\mp 1/2}^\dagger$ replaced by $a_{\mathbf{k},\pm 1/2}^\dagger$. Since $|a_1|^2 + |a_{-1}|^2 + |a_2|^2 + |a_{-2}|^2 = 1$ for normalization, we can split the bright and dark states as $|a_1|^2 + |a_{-1}|^2 = \cos^2\theta$ and $|a_2|^2 + |a_{-2}|^2 = \sin^2\theta$, so that $a_1 = e^{i\varphi_1}\cos\xi_1\cos\theta$ and $a_{-1} = e^{i\varphi_{-1}}\sin\xi_1\cos\theta$, with similar expressions for $a_{\pm 2}$. The angles (θ, ξ_1, ξ_2) can always be taken between 0 and $\pi/2$. The reduction factor in the exchange scatterings of two linear combinations of excitons, given in Eq. (3), is then replaced by

$$1 - 2|a_1 a_{-1} - a_2 a_{-2}|^2 = 1 + (1 + \cos\phi)X - \frac{1}{2}(\sin 2\xi_1 \cos^2\theta + \sin 2\xi_2 \sin^2\theta)^2, \qquad (6)$$

where $\phi = \varphi_2 + \varphi_{-2} - \varphi_1 - \varphi_{-1}$, while $X = \sin 2\xi_1 \sin 2\xi_2 \cos^2\theta \sin^2\theta$ is positive for $0 \leq (\xi_1, \xi_2) \leq \pi/2$. Its minimum value with respect to ϕ thus occurs for $\cos\phi = -1$. The remaining factor of Eq. (6) is minimum for $\xi_1 = \pi/4 = \xi_2$; i.e., when the two bright excitons (±1) have the same weight in $B^\dagger$, and similarly for the two dark excitons (±2). However, since for these values of (ξ_1, ξ_2) the reduction factor does not depend on θ, the fraction of bright to dark excitons in $B^\dagger$, controlled by θ, is not determined by this $\langle H\rangle_N$ minimization.

We then note that, when considering the Bose-Einstein condensate possibly formed out of the four excitons (±1, ±2), we implicitly assume that these four excitons have the same energy. This is true if we take into account only intraband Coulomb interactions. However, interband Coulomb processes also exist [see Fig. 3(a)]. While they are much weaker, they are crucial in the exciton BEC because they push the bright exciton slightly above the dark exciton [22]. Indeed, these interband processes only exist between conduction and valence electrons having the same spin [see Fig. 3(b)]. Since, in quantum wells, a bright exciton ($+1$) is made of a ($-1/2$) electron and a ($+3/2$) hole, i.e., a valence electron ($-3/2$) in an orbital state

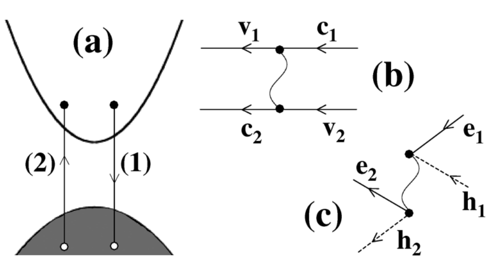

FIG. 3. (a) Interband valence-conduction Coulomb process. (b) Feynman diagram for process (a); (c) same as (b) in terms of electrons and holes: an electron-hole pair recombines while another one is created. In these repulsive processes, the spin of the electron is conserved, so that they do not exist for dark excitons (±2) made of ($\pm1/2$) electron and ($\pm3/2$) hole, i.e., ($\mp3/2$) valence electron with spin ($\mp1/2$).

($l_z = -1$) and a spin state ($-1/2$), valence-conduction Coulomb processes do exist for bright excitons. On the contrary, they do not exist for dark excitons: the exciton ($S = 2$) is made of the same ($+3/2$) hole, but its electron now has a spin ($+1/2$). Since Coulomb interaction between electrons is repulsive, this makes the bright exciton energy slightly above the one of the dark exciton. Consequently, the Bose-Einstein condensate can only be formed out of dark states. It then follows from $\langle H\rangle_N$, calculated with $B^\dagger = a_2 B_2^\dagger + a_{-2} B_{-2}^\dagger$, that the minimum is obtained from $|a_2| = |a_{-2}|$; i.e., excitons condense in a linearly polarized dark state.

If we turn to bulk samples, the four holes ($\pm3/2$, $\pm1/2$) now have the same energy. They give rise to four bright excitons and four dark excitons, degenerate in energy if we only take into account intraband Coulomb processes. However, since the two dark excitons (±2) are the only ones in which repulsive interband Coulomb interactions do not take place, these (±2) excitons again are the lowest energy states out of which the condensate must be made. Consequently, in bulk samples also, excitons condense in a linearly polarized dark state made of (±2) excitons.

Although the energy difference between dark and bright excitons is quite small ($\simeq 0.1$ meV in GaAs quantum wells), it is of importance to stress that it is multiplied by the number N of condensed excitons, leading to a very large total energy difference between dark and bright condensates, so a bright exciton BEC cannot take place. Bright excitons, however, are of importance for excited states, since the dark-bright energy difference is going to be small compared to the thermal energy.

Since dark states are not coupled to light, they cannot be seen through luminescence. However, just for this same reason, their lifetime is much larger that the bright exciton lifetime. This should allow us to build up the density necessary for BEC rather easily. The exchange scatterings producing the dark states out of the photocreated bright excitons being of the same order of magnitude as the ones ensuring thermalization among excitons, the buildup time should be comparable to the thermal relaxation time. Actually, we are led to believe that Bose-Einstein condensates have already been formed in some of the experiments designed to see the exciton BEC, but they were not evidenced due to lack of understanding of its dark nature.

As a possible way to provide evidence for this dark condensate, we suggest the following. Since dark excitons are similar to bright excitons with respect to Pauli exclusion and Coulomb interaction, the existence of a dark condensate must be felt by a bright exciton through a change of its energy, because the energy of an exciton is modified by the presence of a density of other excitons. The magnitude of the corresponding energy shift should be comparable to what is found in the optical Stark effect and accordingly likely to be observable. A pinned geometry experiment, similar to the one realized by Balili *et al.*, seems very appropriate. Indeed the exciton line shift, which depends on the distribution of the surrounding excitons, must change when this distribution goes from thermal to condensed; the larger the exciton density, the larger the shift change. The appearance of a marked shift increase at the center of the trap would provide a good evidence for the existence of a dark BEC, in analogy with ultracold atoms BEC [2].

In various works Kavokin and co-workers [23,24] have reached the conclusion that the condensate should be linearly polarized. Their work regards the dynamics of the system, while we here focus on the statics of the condensate, looking for the true ground state, through exciton many-body effects induced by Pauli exclusion between composite particles. Their work is based on a boson-exciton phenomenological Hamiltonian (see Eq. (1) in Ref. [24]), which from the choice of the parameters contains the fact that the N exciton ground state is linearly polarized, while we reach this conclusion through a fully microscopic approach. The lack of relation with our work is also clear from the fact that they neglect dark excitons, while, as we have seen, they play a key role, even for polariton BEC where bright excitons are the only ones coupled to photons.

In conclusion, our Letter shows the crucial role played by dark excitons ($S = \pm 2$) in the BEC possibly formed in semiconductors. Although they are not generated by photon absorption, they appear in a natural way through carrier exchanges between bright excitons with opposite spins. In the case of microcavity polaritons, which can only be formed out of bright excitons, the coherent polariton state leading to the minimum energy has a linear polarization due to exchange couplings between bright and dark states. For exciton BEC, the (small) repulsive interband valence-conduction Coulomb processes that exist for all excitons, except the ones with (± 2) spins, make these dark excitons slightly lower in energy. Consequently, the exciton condensate has to be made from these (± 2) dark states, with again a linear polarization, due to the same dark-bright couplings. Since dark excitons have a much larger lifetime than bright excitons, the critical density necessary for exciton Bose-Einstein condensation should be easier to reach. However, its observation implies indirect processes, as, for example, those arising in the energy shift change it induces to a bright exciton line when the exciton distribution goes from thermal to condensed.

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