The Quest for an Excitonic Bose Condensate

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Abstract

The high critical temperature and adjustable symmetry of bound electron-hole pairs make excitonic Bose-Einstein condensation an interesting (though elusive) possibility. Several models have been proposed for the behaviour of excitons just above the critical density. In the interest of simplicity, these models ignore certain phenomena; namely, the expansion of the exciton gas through a crystal, interconversion between singlet and triplet states, and two-body Auger recombination. Experiments have shown that the Auger process, in particular, is especially prevalent at low temperature and high density, making it even more of a barrier to Bose condensation of excitons than their inevitable photodecay. The models of Snoke, O'Hara, and Banyai are examined here, and modifications to Banyai's model are proposed.

1 Introduction

1.1 Excitons

Excitons, or excitation quanta in semiconductors, consist of a conduction electron Coulomb-coupled to a valence hole. They exhibit a traditional Rydberg series of energy levels, and have Bohr radii typically spanning hundreds of lattice sites. Exchange forces break the singlet/triplet degeneracy, with triplet orthoexcitons at a higher energy than singlet paraexcitons.[1] In bulk semiconductors, excitons have finite lifetimes and interact strongly with phonons in the crystal. Photodecay can be direct or phonon-assisted; luminescence from orthoexciton decay is roughly 500 times stronger than for para and is a convenient experimental measure of properties of the exciton gas.

At low densities, excitons obey Maxwell-Boltzmann statistics. At low temperatures and higher densities, they can bond into H_2-like biexcitons, or undergo a first-order phase transition into a fermi liquid[2]. They are spin 1 or 0 particles and have been shown to obey Bose statistics. As the critical temperature for Bose-Einstein condensation depends on mass [1],

$$T_c = \left(\frac{N}{V}\right)^{2/3} \frac{h^2}{2\pi k_B m (2.612)^{2/3}} \propto \frac{1}{m} \tag{1}$$

[1]This energy difference is 12 meV in cuprite [3]

the critical temperature for a bound electron-hole pair is several orders of magnitude higher than for an atom. Despite this, bulk Bose condensation of excitons has not yet been achieved, largely due to two-body decay. In this so-called Auger process, two excitons collide and one recombines. The recombined exciton's energy (roughly the band gap energy) is transferred to the other, which ionizes only to recombine later. At high densities, Auger recombination is the dominant process lowering density and heating the gas.

1.2 Cuprous Oxide

The calculations in this paper will be aimed at excitons incuprous oxide, Cu_20, a cubic crystal with inversion centers about the copper atoms. Cuprous oxide, also known as cuprite, has long been considered the semiconductor of choice for excitonic condensates, due to the low effective mass, high binding energy (150 meV), and long liftetimes (up to several microsecond for paraexcitons) [6].

2 Experimental Techniques

2.1 Bulk Cuprite Experiments

The experimental setup of Wolfe et al is fairly straightforward: a laser pulse incident on a cooled single crystal of cuprous oxide creates excitons; the light emitted from exciton photodecay is then counted with a photomultiplier. The emitted light can be energy-dispersed with a diffraction grating, spatially resolved using a moving aperture, and time-resolved by coupling the experiment's electronics to the laser's cavity dumper. Combining these measurements yields an extremely versatile experiment; the gas' energy distribution and diffusion through the crystal can be studied over time.

A strain can be applied across the crystal to break the threefold degeneracy of the bands; a local shear stress also can be used to spatially vary the band gap, creating an approximately parabolic potential well. Excitons in such a well can be resonantly excited by carefully tuning the incident photon energy to be between the band gaps in stressed and unstressed regions.

Time-resolved data from this technique can be fit extremely closely to a Bose distribution using μ and T as fit parameters, yielding the appearance of a highly degenerate hot Bose gas in quasiequilibrium cooling to the lattice temperature. This led to early claims of Bose-Einstein condensation in excitons in cuprite [4,5]; however, it was later shown via numerical simulation that the same data could be reproduced entirely classically for a nonequilibrium system[6]. If the expansion of the exciton gas through the crystal, as well as two-body decay processes, are taken into account, then the energy distributions can be explained without ever invoking the Bose nature of the gas.

While the time-dependent volume problem can be circumnavigated using a local strain well, the two-body Auger recombination process remains a barrier to BEC. In this process, two excitons collide and one recombines, giving its energy to the other. The remaining exciton is ionized, and the hot electron and hole recombine after emitting several phonons.

2.2 Two-Dimensional Exciton Gases

A second set of experiments should be noted here; quite a few groups have worked on two-dimensional excitonic condensates. Most of these experiments are similar to the bulk measurements described above, but use a semiconductor thin film rather than a large single crystal. Spatially-resolved luminescence measurements show "rings" of photodecay some distance from the excitation point. These rings were originally interpreted as evidence of superfluid flow [11], despite Hohenberg's assertion that the superfluid order parameters disappear in $d \leq 2$ [12], and Kohn's claim that Bose-condensed elementary excitations exhibit no off-diagonal long-range order [10]. A simpler explanation for the rings invokes the "phonon wind" effect seen in electron-hole plasmas. The absorption of the laser pulse, as well as exciton cooling, heats the lattice, creating a wind of phonons that push the excitons out in a ring, at more or less the speed of sound [6]. More recently, evidence suggesting superfluid flow has been found in semiconductor heterostructures in magnetic fields [7]. Excitons in this system are quite different from bulk excitons[2]; electrons and holes in different layers of semiconductors are coupled and placed in a large magnetic field; opposite voltages placed on the electron and hole-donor levels allow an exciton current to be established. These results are quite new, and have revitalized hopes of observing coherent effects in excitons.

3 Theory

3.1 Numerical Simulations

Due to interactions between an anisotropic phonon gas and each other, solvable solutions to exciton problems are hard to come by. Because of this, much of the theoretical work on excitonic condensates has gone into numerical simulations. Three such models are discussed here: an influential early model, a model that corrected several misinterpretations of experimental data, and a quantum-mechanical model that would be better-suited to describing an excitonic condensate if one were created.

3.2 Semiclassical scattering model

An early numerical model of exciton gases was published by Snoke and Wolfe in 1988 [8]. While drastic simplifications were made due to the computing limitations of the day, this model has influenced much later work [9]. Working within a random-phase approximation, a simple low-density two-exciton scattering probability is assumed:

[2]They are certainly bound electron-hole pairs, but aren't excitation quanta.

Probability to scatter=(matrix element)×(probability to be in initial state)

×[1+(probability to be in final state)]×(energy and momentum conserving delta functions)

This becomes:

$$S(\vec{k}_1, \vec{k}_2; \vec{k}_3, \vec{k}_4) = M^2 f(\vec{k}_1) f(\vec{k}_2)[1 + f(\vec{k}_3)][1 + f(\vec{k}_4)]\delta(\vec{k}_1 + \vec{k}_2 - \vec{k}_3 - \vec{k}_4)\delta(E_1 + E_2 - E_3 - E_4) \quad (2)$$

The total scattering rate into $\vec{k}$ is then just an integral over the other the probabilities of all the ways an exciton could scatter into $\vec{k}$:

$$\Gamma_i(\vec{k}) = \int d^3k_1 d^3k_2 d^3k_3 S(\vec{k}_1, \vec{k}_2; \vec{k}_3, \vec{k}) \quad (3)$$

A similar expression can be written for the scattering rate out of $\vec{k}$. Starting from these scattering rates, a computer was used to iteratively update a given occupation function. Note that the rates are defined in terms of scattering events, not time; the frequency of scattering events changes drastically with the degeneracy of the gas. In all of the low density simulations, the gas was able to equilibrate to a Maxwellian distribution within five scattering events.

This model conserves total gas energy, which hardly describes a cooling gas, so phonon interaction was also introduced. The probability for an exciton to scatter from $\vec{k}_1$ to $\vec{k}_2$ by emitting or absorbing a phonon is related to the phonon occupation number F:

$$\begin{aligned} S(\vec{k}_1, \vec{k}_2, \vec{k}_p) = M_p^2[&\delta(\vec{k}_1 + \vec{k}_p - \vec{k}_2)\delta(E_1 + E_p - E_2) f(\vec{k}_1) F(\vec{k}_p)[1 + f(\vec{k}_2)] \\ &+ \delta(\vec{k}_1 - \vec{k}_p - \vec{k}_2)\delta(E_1 - E_p - E_2) f(\vec{k}_1)[1 + F(\vec{k}_p)][1 + f(\vec{k}_2)]] \end{aligned} \quad (4)$$

A modified simulation considering both exciton-exciton elastic and exciton-phonon inelastic scattering was then constructed. The initial distributions used took more than 80 scattering events to equilibrate; however, as the $[1 + f(\vec{k})]$ stimulated scattering rate is much larger here, the time between scattering events is expected to be much smaller.

Snoke and Wolfe concluded that exciton-exciton scattering could allow a gas to partially condense well within the expected lifetime of an exciton. The phonon interaction mainly affected the higher end of the kinetic energy spectrum, and thus had little effect on condensation time. They predicted that these effects are stronger than the competing Auger process; however, the Auger constant was later measured to be two orders of magnitude higher than was thought at the time [3].

3.3 Boltzmann Equation Model

Over a decade after Snoke's model, O'Hara and Wolfe used another simulation employing the Boltzmann equation to look for ways that a low-density exciton gas could mimic Bose statistics [6]. The spatial dependence of the occupation function $g(\vec{x}, \vec{k})$ in the Boltzmann equation allows the intensity profile of the incident laser pulse, as well as the changing volume of the gas, to be modelled. A number of scattering rates are considered:

- Exciton-phonon scattering rates were calculated as before, but taking into account the anisotropic deformation potential for TA phonon emission.
- An empirically derived relation for Auger decay is used:

$$\frac{\partial g_{\vec{k}}}{\partial t} = -2Ang_{\vec{k}} \tag{5}$$

- Elastic scattering cross-sections were quoted from another group's Monte-Carlo simulation.

For a relatively long, Gaussian laser pulse (7.0ns at FWHM), excitons that diffused well into the crystal were able to cool to the lattice temperature. Meanwhile, local Auger heating in the dense near-surface region maintained a wide energy distribution there. Data integrating over both the surface and bulk of this intensely *non-equilibrium* gas results in an energy distribution identical to an *equilibrium* Bose-Einstein distribution. This result can be double-checked by looking at total particle numbers; the fit Bose-Einstein distribution implied a much larger total particle number than the luminosity suggests. O'Hara concludes that the Auger process limits exciton densities to roughly one percent of the critical density for Bose-Einstein condensation, but that resonantly exciting a low-energy excition gas could still result in quantum phenomena.

3.4 Second-Quantization Model

If quantum effects are possible in an exciton gas, then a quantum mechanical treatment will be necessary to describe them. For this reason, the model of Banyai et al [9] should be mentioned. Similar in basic concept to Snoke's model, the occupation distribution of the exciton gas is recursively time-evolved using an expression for scattering rates. Banyai starts with a basic Hamiltonian for a BEC;

$$H - \mu N = \sum_{\vec{k}} (e_{\vec{k}} - \mu) a_{\vec{k}}^{\dagger} a_{\vec{k}} + \lambda^* \sqrt{V} a_0 + \lambda \sqrt{V} a_0^{\dagger} \tag{6}$$

Where λ is the symmetry-breaking unobservable Bose field, and the expectation value of the ground state lowering operator $< a_0 >$ is the order parameter, taken to be a large c-number when there is macroscopic occupation at $\vec{k} = \vec{0}$. Temporarily setting the symmetry breaking parameter to 0, a modified Hamiltonian is derived that incorporates a long-wavelength interaction potential with the crystal's thermal phonons:

$$H = \sum_{\vec{k}} e_{\vec{k}} a^\dagger_{\vec{k}} a_{\vec{k}} + \sum_{\vec{q}} \hbar\omega_{\vec{q}} b^\dagger_{\vec{q}} b_{\vec{q}} + \frac{1}{\sqrt{V}} \sum_{\vec{k},\vec{q}} g_{\vec{q}} a^\dagger_{\vec{k}+\vec{q}} a_{\vec{k}} (b_{\vec{q}} + b^\dagger_{-\vec{q}}) \tag{7}$$

Where the first two terms are the exciton and phonon energies, respectively, and the final term sums over all the ways that an exciton could scatter by emitting or absorbing a phonon. The term $g_{\vec{q}}$ is related to the material parameters D, the band gap deformation potential, ρ, the density, and c, the speed of first sound, by:

$$g_{\vec{q}} = \frac{D}{c} \sqrt{\frac{\hbar\omega_{\vec{q}}}{\rho}} \tag{8}$$

Transition amplitudes from $\vec{k}$ to $\vec{k}'$ from the this Hamiltonian give the scattering matrix elements; Fermi's golden rule is used to construct scattering rates from them:[3]

$$W_{\vec{k}\vec{k}'} = \frac{2\pi G_2}{\hbar} |e_{\vec{k}} - e_{\vec{k}'}| [N_{\vec{k}-\vec{k}'} \delta(e_{\vec{k}} - e_{\vec{k}'} + \hbar\omega_{\vec{k}'-\vec{k}}) + (1 + N_{\vec{k}-\vec{k}'}) \delta(e_{\vec{k}} - e_{\vec{k}'} - \hbar\omega_{\vec{k}'-\vec{k}})] \tag{9}$$

where the phonon occupation number $N_{\vec{q}}$ is expected to be a Bose distribution at $\mu = 0$. A phenomenological broadening parameter γ is introduced to change the delta distributions into sharply peaked but finite-width functions, yielding a new scattering matrix element:

$$W_{\vec{k}\vec{k}'} = \frac{2G_2}{\hbar} \frac{|e_{\vec{k}} - e_{\vec{k}'}|}{|e^{\beta(e_{\vec{k}'} - e_{\vec{k}})} - 1|} \times \frac{\gamma}{(|e_{\vec{k}} - e_{\vec{k}'}| - \hbar\omega_{\vec{k}-\vec{k}'})^2 + \gamma^2} \tag{10}$$

These scattering elements were applied similarly to the matrix elements in Snoke's model, with one main change: scattering probabilities into and out of the ground state are considered separately from the excited states, to effectively deal with macroscopic occupation. Some of the results of the numerical simulation are unsurprising: in a world with no edge effects, changing volumes, or two-body processes, a gas above the critical density and below the critical temperature will always condense. What is interesting is the condensation time: the simulation predicts that the gas will quickly "overshoot" and condense too far before it reaches equilibrium, making the condensation time easily reachable within paraexciton lifetimes. An equation of motion for the order parameter $< a_0 >$ was also derived using the Heisenberg picture:

$$\partial_t < a_0 >_t \propto < a_0 > \tag{11}$$

The proportionality constant (a complicated sum over $\vec{k}$) has been omitted to draw attention to the important result: *the equation is homogeneous*, so the system will not condense unless there is some

[3] In the paper, the substitution $\hbar\omega_{\vec{q}} = |e_{\vec{k}} - e_{\vec{k}'}|$ is made. This seems odd, as it is an energy-conservation argument, applied *before* the energy-conserving delta function, which is later broadened.

initial condensate seed. Banyai argues that this problem can be circumnavigated by introducing stochastic fluctuations that could create such a seed.

4 Proposed modifications to Banyai's model

Banyai's model is attractive because it is easily extensible to include more relevant phenomena, and uses a descriptive language commonly used in manuscripts on emergent states of matter. The modifications suggested below would add to the number of calculations in the model, without otherwise changing its function. Computational cost is not considered here, as Moore's law will heavily alter that cost before the author has the requisite free time to code such a simulation. The changes are as follows:

Excitons as a two-component gas This is probably the most important modification. The occupation information stored in $n_0(t)$ and $\{f_k(t)\}$ should be replaced by separate functions for ortho and paraexcitons; $n_0^o(t)$,$\{f_k^o(t)\}$, $n_0^p(t)$, and $\{f_k^p(t)\}$. An acoustic phonon spin flip process has been suggested by Jang[4], so scattering between spin states will be included in an expanded phonon interaction term. Sums over the total angular momenta are now included (variables α and β), where $l_{para} = 0$ and $l_{ortho} = 1$:

$$U^{(phonon)} = \frac{1}{\sqrt{V}} \sum_{\vec{k},\vec{q},\alpha,\beta} g_{\vec{q}} a^{\dagger}_{\vec{k}+\vec{q},\alpha} a_{\vec{k},\beta} [(b_{\vec{q}}(\delta_{\alpha\beta} + \delta_{|\alpha+\beta|-1}\delta(e_{\vec{k}+\vec{q},\alpha} - e_{\vec{k},\beta} - \hbar\omega_{\vec{q}})) + b^{\dagger}_{-\vec{q}}(\delta_{\alpha\beta} + \delta_{|\alpha+\beta|-1}\delta(e_{\vec{k}+\vec{q},\alpha} - e_{\vec{k},\beta} + \hbar\omega_{\vec{q}}))] \tag{12}$$

Here, the $\delta_{\alpha\beta}$ terms describe phonon scattering without spin-flips, and the $\delta_{|\alpha+\beta|-1}$ allow for spin-flips (with an extra energy-conserving delta function). The orthoexciton single-particle energy eigenvalues are shifted from paraexciton levels both by exchange interaction and by the triplet state's coupling to an external magnetic field:

$$e_{\vec{k},1} = e_{\vec{k},0} + \Delta_{exchange} - 2\mu_B H_z \tag{13}$$

Exciton-exciton elastic scattering Snoke's model suggests that elastic scattering between excitons might be even more important than phonon scattering, so this should be included as well:

$$U^{(elastic)} = \frac{\gamma}{\sqrt{V}} \sum_{\vec{k},\vec{k}',\vec{q},\alpha,\beta} a^{\dagger}_{\vec{k}-\vec{q},\alpha} a^{\dagger}_{\vec{k}'+\vec{q},\beta} a_{\vec{k}',\alpha} a_{\vec{k},\beta} \tag{14}$$

where the parameter γ is determined by the scattering cross-sections of the excitons (and may also be a function of the magnetic field [13].)

Auger decay Of course, the phenomenon believed to be the limiting factor for excitonic BEC should be included. A simple sum describing two-body decay is proposed here. The temporarily ionized electron-hole pair remaining after an Auger collision is treated by its center

[4] Not yet published

of mass momentum, and treated as part of the exciton Fock space. It is expected that this treatment will break down at densities high enough that the ionized electrons have a high probability to recombine with holes from other Auger collisions.

$$U^{(auger)} = \frac{1}{\sqrt{V}} \sum_{\vec{k},\vec{k}',\vec{q},\alpha,\beta} \sqrt{A_{\alpha\beta}} a^{\dagger}_{\vec{k}+\vec{k}'+\vec{q},\alpha} a_{\vec{k},\alpha} a_{\vec{k}',\beta} b_{\vec{q}} \tag{15}$$

The Auger constant[5] $A_{\alpha\beta}$ is weighted differently depending on whether the collision is ortho-ortho, para-para, or ortho-para. Jang makes the argument[6] that indistinguishability requires these relative weights. If both colliding excitons have the same spin quantum number, then both direct and exchange terms must be considered; only direct terms contribute if the two excitons can be distinguished. Hence, if the para-para rate is given a relative weight of 1, then the ortho-para rate (distinguishable) must be given a relative weight of $\left(\frac{1}{2}\right)^2$. There are nine possible spin combinations for two orthoexcitons, three of which are indistinguishable; this gives A_{11} a relative weight of $\frac{1}{2}$. These weights correspond to measured Auger constant values.

An important detail to notice is that ortho-ortho Auger recombination should occur at half the rate of para-para recombination. It's possible, then, that BEC could be achieved in an exciton gas in a magnetic field, where the orthoexciton density will be higher. Wolfe's group at UIUC is currently modifying their bulk cuprite experiment to test this!

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