Evidence for Bose-Einstein Condensation of Biexcitons in CuCl

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(Received 22 December 1978)

Evidence for the occurrence of a Bose-Einstein condensation of biexcitons in evaporated CuCl films is reported. It involves several unusual properties of the molecular luminescence under strong excitation.

An intriguing property of an ensemble of particles with integral spin is the occurrence at sufficiently low temperatures of a phase transition in which all particles exceeding a critical density $n_c(T)$ condense into a single quantum state. This may lead to the observation of quantum effects on a macroscopic scale. Systems in which this phenomenon have been observed are superfluid helium and the Cooper pairs of electrons in superconductors.

It has been realized by several authors[1] that excitronic particles in nonmetallic crystals might provide a new system for the observation of a Bose-Einstein condensation. Interesting new characteristics here are the small effective mass of the particle (this leads to high critical temperatures for the onset of the phase transition), and the fact that one deals with destructible particles (this allows the condensate to be directly probed through the optical emission).

In this Letter we present strong evidence for the occurrence of a Bose-Einstein condensation of biexcitons in CuCl. We show that the condensate can occur either at $K = 0$ or in a state of collective motion in analogy with superfluid helium.[2] The evidence relies on a number of peculiar characteristics of the luminescence of the excitonic molecules in highly excited CuCl.

Since its discovery in 1968,[3] the excitonic molecule has been the subject of a considerable study in CuCl. It is now well established that this quasiparticle decays by emitting a photon, restituting a free exciton to the system. If the biexciton has some kinetic momentum $\hbar K_{xx}$, the final exciton may have a longitudinal or transverse character,[4] leading to the appearance of two characteristic bands M_L and M_T near 3.170 eV. The shape of the bands yields directly the momentum distribution function of the decaying molecules. At low densities, they are represented by Maxwell-Boltzmann functions, and one expects a ratio in the M_T to M_L intensities of the order 2:1, because of the twofold degeneracy of the transverse exciton.

In our experiments, generation of a high density of biexcitons ($n_{max} \gtrsim 10^{19}$ cm^{-3}) in ~2-μm-thick, evaporated CuCl films is performed via two-photon absorption either at $K = 0$, using two counterpropagating laser beams of identical frequency $\hbar\omega = \frac{1}{2}E_{xx}$ but opposite circular-polarization vectors,[5] or at $K = 2K_0$, where K_0 is the photon wave vector, using a single linearly polarized laser beam. In *both instances, at sufficiently low power levels* ($I_0 \lesssim 10^5$ W/cm^2 at 2°K), broad M_T and M_L luminescence bands with nearly Maxwellian shape and ~2:1 ratio are observed as shown in Fig. 1. This indicates that the created molecules interact quickly among themselves and with the lattice to reach a thermodynamical equilibrium.[6] As the laser intensity is increased one observes for $K = 0$ excitation, an increase of the relative height of the M_L line, but no substantial broadening or narrowing. At the highest available excitation power, of the order of 10^7 W/cm^2, M_L takes a more asymmetric shape with a rather steep high-energy edge [see Fig. 1(a)]. Various spectra obtained with one-beam excitation are shown in Figs. 1(b) and 2. A sharp line N_T (width $\Delta\omega \sim 0.3$ Å) develops on the high-energy side of M_T with increasing laser intensity both in the backward and 90° geometry. By contrast the M_L emission is weak in collinear geometry, but shows indication of a sharp structure in 90° geometry. Whereas M_L is unpolarized in back-

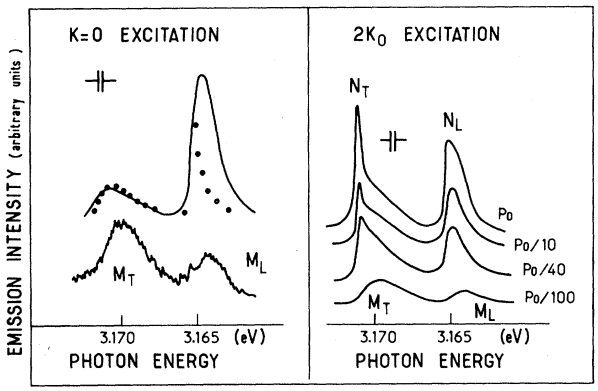

FIG. 1. Luminescence spectrum of CuCl at $T = 4°K$ at various excitation intensities P when the molecules are created at $K = 0$ or $2K_0$. In both cases, at low input intensity (bottom curves) the lines fit a Maxwell distribution. Note the different spectra at higher intensity, which depend upon the type of excitation. The open circles correspond to a numerical integration, using a Bose distribution with $\mu = 0$ (see text). Detection is at 90° from incident light vector.

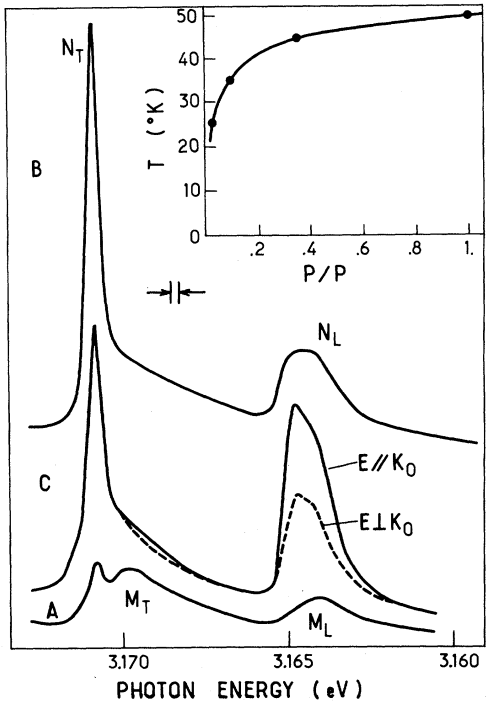

FIG. 2. Luminescence spectra of CuCl at 4°K excited at $2K_0$. Curves A, B, and C correspond to cases A, B, and C of Fig. 3. Line M_L is unpolarized in A and B, contrary to noncollinear detection geometry. Inset: Lattice temperature threshold for N_T vs laser intensity P/P_0.

ward geometry, it is predominantly polarized along K_0 in the noncollinear geometry. We have verified that the sharp lines do not shift in frequency as the laser frequency is tuned away from the two-photon absorption peak. Finally, the maximum temperature T_0 for appearance of N_T increases with laser power (and, consequently the biexciton density) as shown in the inset of Fig. 2.

All our results are simply explained if we assume that the gas of biexcitons has undergone a Bose-Einstein condensation. What will the emission from this condensed state look like? First consider the decay from the condensate at $K_{xx} = 0$. Referring to Fig. 3 the decay to the longitudinal exciton X_l is forbidden, since the Γ_1 symmetry of the biexciton requires the dipole moments of the created photon and exciton to be parallel. Momentum conservation requires that their kinetic momenta be opposite, so the final exciton must be, like the photon, strictly transverse, as shown in diagram A' of Fig. 3. A surprising conclusion, then, is that the $K = 0$ condensate can only decay by reemitting a pair of counterpropagating photons, predominantly at exactly the pumping laser frequency.

On the other hand, the *uncondensed* part of the biexciton distribution $N_{xx}(\vec{K}_{xx})$ can decay towards the lower X_t exciton polariton (for all biexcitons with $K_{xx} > K_0$). It can also give rise to the M_L emission, as the emitted photon may have a polarization component parallel to that of the longitudinal exciton dependent on α (α is the angle between K_{xx} and K_0) or it can terminate on the up-

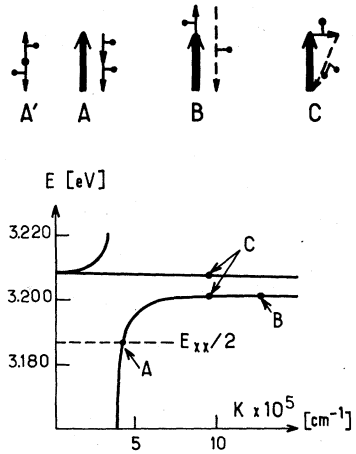

FIG. 3. Exciton-polariton dispersion curve of CuCl. A, B, and C indicate the final states reached in biexciton decay for the three geometrical configurations depicted: heavy arrow, biexciton K vector; light arrow, emitted-photon K vector; dashed arrow, exciton K vector; line with disk, direction of dipole moment.

per X_t branch for small $K_{xx}<K_0$ (M_{2T} emission). The point is that for small chemical potential $|\mu|$ most of the distribution is confined in a small volume in K space around $K=0$ and thus will only contribute to M_L and M_{2T} emission. One expects, therefore, with increasing density of biexcitons (decreasing $|\mu|$) to observe an increase of M_L to M_T ratio, as observed in Fig. 1(a), reflecting a deviation from classical statistical behavior. For the line shape around M_L, we obtain from geometrical considerations

$$I(\hbar\omega)=C\iint|M|^2N_{xx}(\overline{K}_{xx})\delta(E_{xx}-E_x-\hbar\omega)\delta(\overline{K}_{xx}-\overline{K}_x-\overline{K}_0)d^3\overline{K}_{xx}d^3\overline{K}_x, \quad (1)$$

where

$$|M|^2=(K_{xx}^2\sin^2\alpha)/(K_{xx}^2+K_0^2-2K_{xx}K_0\cos\alpha),$$

is the probability that the final exciton has longitudinal character. The subscripts x, xx, and 0 denote the properties of excitons, biexcitons, and photons, respectively; and C is a constant. A similar expression is obtained for M_T by changing $|M|^2$ into $2-|M|^2$. In Fig. 2(a) we have plotted the result of a numerical integration of Eq. (1), assuming for N_{xx} the well-known Bose statistical distribution with $\mu=0$.

We now turn our attention to a condensate occurring at $K_C=2K_0$. The condensate can be observed in luminescence, but it will be strongly dependent upon the direction of observation with respect to K_0, in agreement with the data of Fig. 2. In the backward detection geometry, cases B of Figs. 2 and 3, the transition to X_t with momentum $K_x=3K_0$ is possible, but no emission can occur to X_l for the reasons given above. In the forward geometry, the situation is similar to decay from $K_C=0$, as is readily seen from diagram A in Fig. 3, and observed experimentally in Fig. 2, case A, where little sharp emission is observed. An interesting situation is encountered for a noncollinear configuration, diagram C in Fig. 3. Here, the condensate can decay towards X_t, as before, but also towards X_l *if the emitted photons are polarized in the plane containing* $\vec{K}_0$. This is a stringent test of the model, which is partially satisfied in Fig. 2, case C. The sharp lines[7] in Figs. 1(b) and 2 result from annihilation of particles inside a condensate which has a wave-vector $K_C\sim 2K_0$, as it is directly deduced from the angular dependence of the emission spectra. We estimate from the polarization property of M_L at 90° observation that more than 15% of the particles are locked to a common wave vector. The highest critical temperature for the phase transition, $T_c\sim 50$°K, is in good order-of-magnitude agreement with the predictions from the ideal-Bose-gas theory, $T_c=25$°K, for 10^{19} particles cm^{-3}.

While the simple Bose-gas theory gives the basic features, it is evident that a more elaborate model is needed for a quantitative description of the system. The occurrence of a condensate at $K_C\neq 0$ alone requires interactions between the particles. Another example is given by the emission spectrum obtained with $K=0$ excitation. A numerical integration of Eq. (1) reproduces well the line M_T, but yields a line M_L too narrow, and of too small integrated intensity [see Fig. 2(a)]. We believe this illustrates the fact, predicted in the weakly interacting Bose-gas model,[8] that a considerable number of biexcitons are ejected out of the condensate into a K volume of the order $4\pi K_s^3/3$, where $K_s\sim d^{-1}(a/d)^{1/2}\lesssim K_0$. (Here d is the mean distance between biexcitons and a the scattering length.) In that case the contribution of the M_{2T} emission increases rapidly, leading to a broadening of the M_L line, as a result of the strong dispersion of the upper transverse branch near $K=0$.

To summarize, a number of peculiar characteristics in the molecular emission of CuCl are interpreted in terms of a Bose-Einstein condensation. As the density of particles is easily controlled by optical means, this system offers considerable advantages for the study of this phenomenon.

This work was partially supported by NATO Grant No. 1483 and National Science Foundation Grant No. DMR 78-09426.

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[4]S. Suga and T. Koda, Phys. Status Solidi (b) 61, 291 (1974).

[5]For a description of the experimental setup see L. L. Chase *et al.*, to be published.

[6]Note that the effective temperature $T_{\mathrm{eff}}\sim 10$–20°K associated with the Maxwell distribution is different from the ambient. This effect, reported in many crystals, indicates an incomplete thermalization with respect to the lattice during the particles' lifetime. Heat-

ing of the particles here is most probably due to Auger effects.

[7]Other authors have reported narrow emission lines in strongly excited CuCl. We briefly consider their alternative explanations below. *Raman scattering:* We do not observe a shift $\Delta\omega = 2\Delta\omega_L$ of N_T or N_t as was the case in Nagasawa *et al.* [J. Phys. Soc. Jpn. 41, 929 (1976)]; furthermore, a scattering process should not lead to a threshold behavior varying with temperature. *Emission from a cold gas:* A narrow line resulting from the recombination of an ensemble which has not completely thermalized should be observed first at low densities [R. Levy *et al.*, Phys. Status Solidi (b) 77, 381 (1976)]. We observe the opposite behavior. Furthermore, the polarization and angular dependence of M_L indicates a well-defined kinetic momentum of the molecule at the time of the luminescence decay. *Stimulated emission:* While it is difficult to exclude the presence of any gain at our highest excitation levels [M. Ojima *et al.*, J. Phys. Soc. Jpn. 45, 884 (1978)] the presence of N_T with a *similar width* on the high-energy edge of M_T near appearance threshold makes this explanation unlikely. Also, the behavior of M_L with angle of detection, the lack of sharp structure in the case of $K=0$ excitation, and the temperature-dependent threshold cannot be accounted for by stimulated emission. We also point out that the sample thickness (2–3 μm) and small excitation spot size (<50 μm) represent an unfavorable condition for substantial gain. At the present time, it is a matter of speculation as to why no Raman effect or cold-gas emission is apparent in our samples. Perhaps our thin polycrystalline films are good for fast thermalization. We point out that almost no ν_2 emission (due to exciton decay at impurity sites) was observed with band-to-band excitation, an indication of the good chemical quality of the samples.

[8]See, for example, E. Hanamura and H. Haug, Phys. Rep. 33C, 211 (1977).

Electric-Field-Dependent Thermopower of $NbSe_3$

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(Received 31 October 1978)

We have measured the thermoelectric power of $NbSe_3$ in the temperature range, 10–70 K, where charge-density-wave formation and strongly nonlinear conductivity has been reported. We report the first observation of an electric-field-dependent thermopower. Our results for $NbSe_3$ show that in the presence of an electric field there is an additional negative contribution to the thermopower. Possible mechanisms which may account for this are discussed.

There has been a great deal of recent interest in the non-Ohmic behavior observed in systems which undergo charge-density-wave (CDW) instabilities.[1,2] Upon application of an electric field, the electrical conductivity is found to rise dramatically when a certain threshold is surpassed. This effect is often found in quasi-one-dimensional conductors with tetrathiafulvalene tetracyanoquinodimethane[2] (TTF-TCNQ) and $NbSe_3$ (Ref. 1) as primary examples. A variety of models have been proposed to explain the nonlinear characteristics.[3-5] Since the models predict different types of charge carriers, thermoelectric power (TEP) measurements can contribute to the understanding of the nature of the carriers.

In this Letter we report on TEP measurements performed on $NbSe_3$ in the presence of an electric field. This is the first time that thermopower has been used to probe nonlinear effects in any material and consequently the first time that an electric-field-dependent TEP has been observed. Below the 59-K CDW transition the measurements show an increase in the magnitude of the TEP as electric field is increased, the limiting value approaching the TEP observed above the 59-K transition. Since a collective mode (i.e., sliding CDW) by itself would produce a reduced (or zero) TEP, the present work implies that some other mechanism is responsible for the observed increase in TEP and conductivity.

In the experiments we have measured both the electrical resistance and the TEP of $NbSe_3$ as a function of both temperature and electric field. The experimental situation is governed by the transport equation

$$\vec{E} = \vec{J}\rho(E) + S(E)\nabla T,$$