PHYSICAL REVIEW B VOLUME 59, NUMBER 12 15 MARCH 1999-II

Inverse exciton series in the optical decay of an excitonic molecule

Eiji Tokunaga, A. L. Ivanov,* and Selvakumar V. Nair
ERATO Single Quantum Dot Project, Japan Science and Technology Corporation, 5-9-9 Tokodai, Tsukuba 300-2635, Japan

Yasuaki Masumoto
ERATO Single Quantum Dot Project, Japan Science and Technology Corporation, 5-9-9 Tokodai, Tsukuba 300-2635, Japan
and Institute of Physics, University of Tsukuba, Tsukuba 305-8571, Japan

(Received 29 December 1998)

We report the observation of inverse exciton series (M-emission series) in the optical decay of an excitonic molecule to the exciton excited states ($n=2s$, $3s$, and $4s$). A theory is developed which relates the inverse exciton series to the molecule wave function using the bipolariton model. The components of the exciton excited states $n=2$, 3, and 4 in the biexciton wave function in CuCl are determined from the relative intensities of M_{1s}, M_{2s}, M_{3s}, and M_{4s} emission lines. This opens a way to reconstruct the internal molecule wave function. [S0163-1829(99)50412-8]

Recent experimental and theoretical works on exciton physics have focused on the exciton-exciton interaction, i.e., the biexciton effect in four-wave mixing and transient photoluminescence,[1] the polariton-polariton interaction in a semiconductor microcavity,[2] and multiexciton states in quantum dots.[3] Of these, a biexciton state in a bulk direct-band-gap semiconductor is the extreme case (strong interaction and infinite volume) and most difficult to solve because the standard perturbation approach can be applied neither to the Coulomb interaction nor to the exciton-photon coupling (polariton effect).

An excitonic molecule (biexciton, xx) in semiconductors is a singlet-state four-particle complex of two electrons (e) and two holes (h) bound together by the Coulomb direct and exchange interactions. The xx state in a semiconductor with isotropic valence and conduction bands is characterized by the e-h mass ratio σ. In the extreme limits of $\sigma=0$ and $\sigma=1$, the xx is similar to the hydrogen and positronium molecules, respectively. From a fundamental interest, first-principle quantum mechanical calculations of four-particle Coulomb-correlated states have been attempted for more than fifty years. In spite of the long theoretical efforts (see, e.g., Refs. 4–6) the four-particle wave functions, however, are not accurately determined except for the hydrogen molecule.[7] For values of σ corresponding to excitonic molecules in direct-band-gap semiconductors, the theoretical binding energy ranges from 60 to 70 % of the experimental value even for the most reliable calculation.[6] The main reasons for the absence of accurate calculations are the difficulty in treating four particles without the adiabatic approximation, and the complexity of the semiconductor band structure.[8]

For the hydrogen molecule, numerous experimental data related to the wave function have been obtained and rigorously compared with theoretical calculations. For the biexciton, in contrast, practically only two parameters are experimentally available, namely, the molecule binding energy ϵ^m and the oscillator strength of the optical transition to the xx state. The oscillator strength provides us with the absolute value $|\tilde{\Psi}(\mathbf{p}\simeq 0)|^2$.[9] Here $\tilde{\Psi}(\mathbf{p})$ is the Fourier transform of the molecule envelope wave function, which characterizes the relative motion of the two constituent excitons (x's), and refers to the excitonic representation of the molecule. In the excitonic representation, the four-particle molecule wave function is constructed in terms of the deformed or undeformed ground-state x wave functions and the envelope wave function of the relative motion, taking into account the permutation symmetry of the e and h coordinates (the antisymmetry of the total wave function is ensured by the antisymmetry in the spin coordinates). This picture holds, because $\epsilon^m/\epsilon^x \ll 1$, where ϵ^x is the x binding energy. It is practically impossible to solve the inverse problem of reconstructing the molecule wave function from the two known experimental parameters, ϵ^m and $|\tilde{\Psi}(0)|^2$. These values depend only on the gross features of the wave function. Unless the binding energy is accurately reproduced, different wave functions can yield the same value for $|\tilde{\Psi}(0)|^2$. Therefore, experimental measurements of parameters more sensitive to the molecule wave function are highly desirable.

Here we present an experimental observation, in a high-quality CuCl sample, of the inverse exciton M-emission series in the xx optical decay and describe a systematic way to build up the internal biexciton wave function from the experimental data. According to the bipolariton model,[10] the optical decay of an excitonic molecule in bulk direct-band-gap semiconductors is described in terms of the resonant dissociation ''$xx\rightarrow$ two outgoing polaritons'' (a similar physical picture of the xx radiative decay in CuCl was used in Ref. 11). If the molecule wave vector $K_m \geq \sqrt{\varepsilon_\infty}\omega_t/c$, where ε_∞ is the background dielectric constant and $\hbar\omega_t$ is the x energy, this scheme can be reinterpreted in a standard way:[12] the molecule emits a photon by the annihilation of one e-h pair, leaving behind an exciton. So far, only the xx radiative decay to the x ground state $n=1s$ (M emission) has been observed, while from the energy-momentum conservation it is also possible that the molecule emits light, decaying to the x excited states $n=2s$, $3s$, etc. ($M_{2s,3s\ldots}$ lines) as shown in Fig. 1. The M series yields unique information on

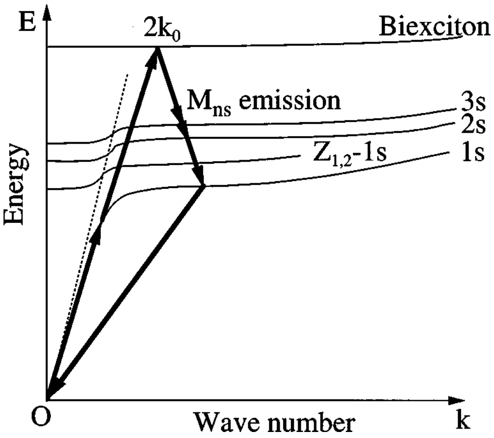

FIG. 1. Schematic of the excitation and emission process of biexcitons at $2k_0$ in the exciton-polariton dispersion curves.

the molecule wave function because the normalized intensities I_{ns}/I_{1s} are proportional to the projection of the xx wave function onto the x excited states. Here I_{ns} is the intensity of the n line in the M-emission series. In this way one can estimate the coefficients of the expansion of the molecule wave function in several excitonic eigenstates and approximate the total xx state. Note that a similar phenomenon does not exist for the hydrogen molecule. Since the first observation of the optical decay of excitonic molecules,[13] there were many unsuccessful attempts to detect the M series (see, e.g., Refs. 8 and 14) and for about three decades the experimental discovery of the M series remained a very challenging problem of biexciton optics.

Platelets of CuCl single crystal grown from gas phase with a thickness of about 20 μm were immersed in superfluid helium at 2 K in a strain-free condition. The spectra were measured with a liquid-nitrogen-cooled back-illuminated Si charge-coupled-device camera (Princeton Instruments) through a monochromator. Figure 2(a) shows the reflection and emission spectra taken by Xe-lamp illumination and by excitation with a HeCd laser (3.814 eV) above the band-gap energy ($E_g \simeq 3.4$ eV), respectively. The states $n=1s, \ldots, 4s$ of Z_3 excitons are clearly seen in the reflection spectrum (see also Ref. 15) as well as in the emission spectrum. Note that this is the first observation in CuCl of the emission from the x excited states.

Excitonic molecules with $\mathbf{K}_m = 2\mathbf{k}_0$ ($2k_0 \simeq 0.89 \times 10^6$ cm^{-1}) were resonantly created by two-photon absorption of picosecond uv pulses from a TiS laser (Spectra Physics, Tsunami) through a doubling crystal (BaB_2O_4). The optical pulses are characterized by 2 ps duration, 82 MHz repetition, 20 mW average power, and the energy of photons $\hbar\omega_0 = 3.186$ eV. The xx emission spectra, obtained in the backscattering geometry, are plotted in Fig. 2(b). The sharp M_T and M_L emission lines indicate that the weak excitation condition is satisfied.[16] These lines refer to the emission process which involves the transverse and longitudinal 1s excitons, respectively. In the lower energy side of the M_T and M_L lines, some extremely weak emission lines ($\sim 10^{-4}$ of the M_T line intensity) are detected. The spectral position of these lines corresponds to the energies $2\hbar\omega_0 - E_{ns}$ with $n \geqslant 2$, where E_{ns} is the x excited state energy. Therefore, we identify the main biexciton-mediated lines (M_T and M_L) and the weak signals with the M-emission series M_{1s}, M_{2s}, M_{3s}, M_{4s}, and $M_{\infty s}$. Here the subscript ∞s refers to the spectral lines $n \geqslant 5$ collectively. The lines M_{ns} characterize the optical decay of the two-photon generated molecule to the ns x states. Our observation of the M-emission series clearly demonstrates why the previous attempts were unsuccessful: the $M_{n\geqslant 2}$ lines are extremely weak in intensity, requiring for their observation a highly sensitive detection technique and a high-quality sample free from impurity emissions.[17] The M series is direct evidence of the nonzero components of the x excited states $n=2,3$, etc., in the molecule wave function.

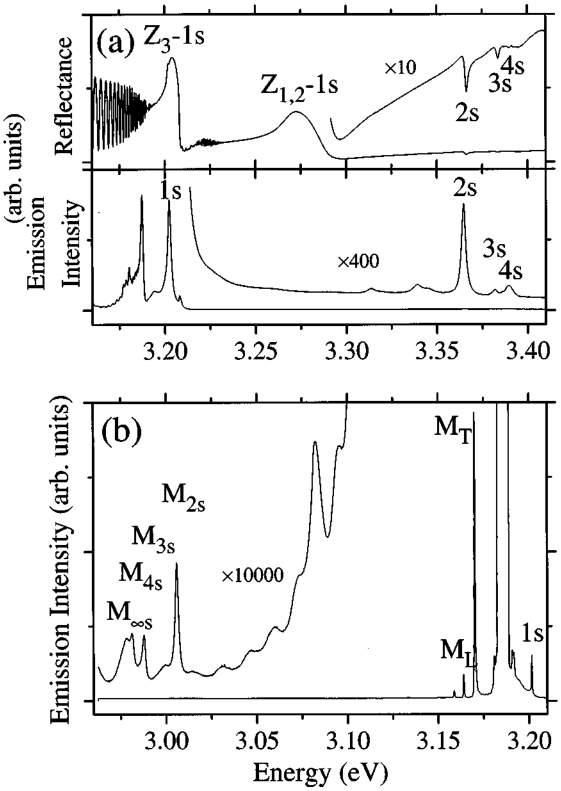

FIG. 2. (a) Reflection and emission spectra by band-gap excitation at 3.814 eV. (b) Emission spectra from two-photon excited biexcitons at $2k_0$.

In the backward direction of the xx wave vector $\mathbf{K}_m$, the M_T line is allowed while the M_L line is forbidden, owing to the geometrical selection rules. Thus, the large ratio of the intensities of the M_T and M_L lines in Fig. 2(b) means that the two-photon generated xx's do not suffer momentum relaxation and keep the initial wave vector $2\mathbf{k}_0$ before the radiative decay[18] as shown in Fig. 1. The large intensity ratio also assures that the T emissions should strongly dominate over the corresponding L emissions for M_{ns} lines with $n \geqslant 2$, although one cannot discriminate between the T and L emissions because the longitudinal-transverse splitting of the ns x state decays as $1/n^3$. Therefore, in further analysis we associate the M series with the optical decay involving only T-polarized excitons at a well-defined wave vector. The T-polarized excitons combine with the light field into the polariton eigenmodes.[19]

In order to describe theoretically the inverse x series, we generalize the bipolariton model of the excitonic molecule[10] to include the x excited states. The four-particle xx

wave function is given by $\Gamma_{\mathbf{K}_m}(\mathbf{R}_m,\mathbf{R},\mathbf{r_1},\mathbf{r}_2)=\Gamma(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)\exp(i\mathbf{K}_m\mathbf{R}_m)/V^{1/2}$, where $\mathbf{R}_m$, $\mathbf{R}$, and $\mathbf{r}_{1,2}$ are the coordinates of the *xx* translational motion, the relative motion of the two *x*'*s*, and the *e*-*h* relative motion, respectively, and *V* is the volume. $\Gamma(\mathbf{R},\mathbf{r_1},\mathbf{r_2})$, which describes the internal structure of the molecule, is constructed in terms of a deformed ground-state *x* wave function ϕ_1^d and an envelope wave function Ψ as $\Gamma(\mathbf{R},\mathbf{r_1},\mathbf{r_2})=\Psi(\mathbf{R})\phi_1^d(\mathbf{r_1})\phi_1^d(\mathbf{r_2})+\Psi(\mathbf{R}')\phi_1^d(\mathbf{r}_1')\phi_1^d(\mathbf{r}_2')$, where $\mathbf{R}'$, $\mathbf{r}_1'$, and $\mathbf{r}_2'$ are obtained from $\mathbf{R}$, $\mathbf{r_1}$, and $\mathbf{r_2}$ by *e*-*e* exchange, respectively. In the bipolariton model, which treats the *xx* radiative decay as a resonant fission of the molecule into two outgoing polaritons under the condition of total energy-momentum conservation, the intensity of the *xx* emission signal at energy E_1 and spectral interval ΔE_1 is given by

$$\Delta I(\mathbf{K}_m,E_1,\Delta E_1)\propto\int_{\Delta\mathbf{k}_1}d\mathbf{k}_1\int d\mathbf{k}_2\,\delta(\mathbf{K}_m-\mathbf{k}_1-\mathbf{k}_2)\times\delta[E_m(\mathbf{K_m})-E_1^{pol}(\mathbf{k}_1)-E_2^{pol}(\mathbf{k}_2)]\times|\langle\Gamma|W|\chi_1\chi_2\rangle|^2, \tag{1}$$

where $E_m(\mathbf{K}_m)$ is the molecule energy, $E_1^{pol}(\mathbf{k}_1)$ and $E_2^{pol}(\mathbf{k}_2)$ are the dispersions of signal (photonlike) and idle (excitonlike) polaritons, respectively, and $\mathbf{\Delta k}_1=\mathbf{\Delta k}_1(\Delta\Omega,E_1,\Delta E_1)$ is the phase space volume of the signal modes $\mathbf{k}_1$ which contribute to the intensity collected in the solid angle of observation $\Delta\Omega$. The four-particle potential $W=W(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)$ describes the *x*-*x* Coulomb interaction and

$$\langle\Gamma|W|\chi_1\chi_2\rangle=\int d\mathbf{R}d\mathbf{r}_1d\mathbf{r}_2\Gamma^*(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)W(\mathbf{R},\mathbf{r_1},\mathbf{r_2})\times\chi(\mathbf{k}_1,\mathbf{r}_1)e^{i\mathbf{k}_1\mathbf{R}/2}\chi(\mathbf{k}_2,\mathbf{r}_2)e^{-i\mathbf{k}_2\mathbf{R}/2}. \tag{2}$$

Here $\chi(\mathbf{k},\mathbf{r})=\Sigma_nB_n(\mathbf{k})\phi_{ns}(\mathbf{r})$, where $\phi_{ns}(\mathbf{r})$ is the *ns x* wave function and $B_n(\mathbf{k})$ is the Hopfield coefficient[19] which characterizes the relative contribution of the excitonic component to the polariton associated with the *ns x* state. From Eqs. (1) and (2), and using the four-particle Schrödinger equation for the internal *xx* wave function $\Gamma(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)$, we derive the frequency-integrated intensity of the emission signal located at energy $E_1^{(0)}$:

$$I(\mathbf{K}_m,E_1^{(0)},\Delta\Omega)\propto\Delta\Omega\rho^{(1,2)}(k_1^{(0)})\times\left|\sum_{i,j}B_i(k_1^{(0)})B_j(k_2^{(0)})W_{i,j}C_{i,j}\right|^2, \tag{3}$$

where $\mathbf{k}_1^{(0)}$ is the carrier wave vector determined by the dispersion equation $E_1^{(0)}=E^{pol}(k_1^{(0)})$ for the signal polariton and by the angle of observation, $\mathbf{k}_2^{(0)}=\mathbf{K}_m-\mathbf{k}_1^{(0)},\rho^{(1,2)}$ is the joint density of polariton states proportional to $[k_1^{(0)}]^2/[v_g^{pol}(k_1^{(0)})+v_g^{pol}(k_2^{(0)})](v_g^{pol}$ is the polariton group velocity), $W_{i,j}=\epsilon^m+\epsilon^x(2-1/i^2-1/j^2)$, and

$$C_{i,j}(\mathbf{k}_1^{(0)}-\mathbf{K}_m/2)=\int d\mathbf{R}d\mathbf{r}_1d\mathbf{r}_2\Gamma^*(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)\times\phi_i(\mathbf{r}_1)e^{i\mathbf{k}_1^{(0)}\mathbf{R}/2}\phi_j(\mathbf{r}_2)e^{-i\mathbf{k}_2^{(0)}\mathbf{R}/2}. \tag{4}$$

TABLE I. Components of the exciton excited states in the biexciton wave function in CuCl.

Emission intensity	I_2/I_1	I_3/I_1	I_4/I_1
	1.4×10^{-4}	4.0×10^{-5}	1.5×10^{-5}
Component	$\|C_2/C_1\|^2$	$\|C_3/C_1\|^2$	$\|C_4/C_1\|^2$
	1.6×10^{-4}	4.4×10^{-5}	1.8×10^{-5}

$C_{i,j}$ can be experimentally determined using Eq. (3). Thus, in principle, one can construct the total *xx* wave function in the basis of the *x* eigenfunctions $\{\phi_n\}$ $(n=1s,2s,2p,\ldots)$ as

$$\Gamma_{\mathbf{K}_m}(\mathbf{R}_m,\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)=\sum_{i,j}\sum_{\mathbf{k}}C_{i,j}(\mathbf{k})\phi_i(\mathbf{r}_1)e^{i(\mathbf{K}_m/2+\mathbf{k})\mathbf{R}_1}\times\phi_j(\mathbf{r}_2)e^{i(\mathbf{K}_m/2-\mathbf{k})\mathbf{R}_2}, \tag{5}$$

where $\mathbf{R}_1=\mathbf{R}_m+\mathbf{R}/2$ and $\mathbf{R}_2=\mathbf{R}_m-\mathbf{R}/2$ are the coordinates of the translational motion of the two constituent *x*'*s*. Equations (3), (4), and (5) provide a complete description of the *xx* emission intensity for all K_m's and for all energy regions including the inverse *x* series in terms of the *xx* wave function.

For frequency-degenerate two-photon creation of molecules, used in the experiment, one has $\mathbf{K}_m=2\mathbf{k}_0$ and the idle polariton is strongly excitonlike, i.e., $B_j(\mathbf{k}_2^{(0)}\simeq3\mathbf{k}_0)=\delta_{jn}$ (δ_{ij} is the Kronecker symbol) and $E_2(k_2^{(0)})=E_{ns}=E_g-\epsilon^x/n^2$ is the energy of the *ns x* state. In this case, Eq. (3) reduces to I_n for the M_{ns} emission as

$$I_n(2\mathbf{k}_0,E_m-E_{ns},\Delta\Omega)\propto\Delta\Omega\rho^{(1,2)}(k_1^{(0)})|B_1(k_1^{(0)})W_{1s,ns}C_n|^2, \tag{6}$$

where $W_{1s,ns}=\epsilon^m+\epsilon^x(1-1/n^2)$, and

$$C_n\equiv C_{1s,ns}(0)=\int d\mathbf{R}d\mathbf{r}_1d\mathbf{r}_2\Gamma^*(\mathbf{R},\mathbf{r}_1,\mathbf{r}_2)\phi_{1s}(\mathbf{r}_1)\phi_{ns}(\mathbf{r}_2). \tag{7}$$

In Eq. (7) we approximate $k_0\simeq0$, because the photon wave vector is much smaller than the inverse *xx* radius. We use Eq. (6) to estimate from the experimental data the coefficients C_n given by Eq. (7).

The normalized intensities I_n/I_1 of the *M*-emission series are listed in Table I for $n=2$, 3, and 4. In order to treat the normalized intensities with Eq. (6) we calculate $k_1^{(0)}$ and $B_1(k_1^{(0)})$ by a five-resonance polariton model (Z_3 excitonic series with $n=1s,2s,3s,4s$, and ground-state $Z_{1,2}$ exciton) with CuCl parameters from Fig. 2 and Ref. 20. The normalized squared coefficients $|C_n/C_1|^2$ found from the experimental data are collected in Table I. The ratio $|C_n/C_1|^2$ characterizes the relative contribution of the *ns x* state to the molecule wave function providing direct information on the internal structure of the molecule. The estimate of $|C_1|^2\propto|\tilde{\Psi}(0)|^2$ from the oscillator strength of the optical transition to the *xx* state is a very delicate problem which deals with absolute values of the optical signals.[9] In contrast, $|C_{n=2,3,4}/C_1|^2$ are obtained from the measurements of the relative optical intensities, and are much more reliable and stable to the experimental conditions.

TABLE II. Calculation of the components for the A-H wave function and two model wave functions $\Gamma=\Psi(R_h)(e^{-r_{1a}}e^{-r_{2b}}+e^{-r_{1b}}e^{-r_{2a}})$ with $\Psi(R_h)=e^{-0.5008R_h}$ (model 1) and $\Psi(R_h)=R_he^{-0.8641R_h}$ (model 2), where R_h and $r_{1a,2b,1b,2a}$ are the h-h and e-h distances, respectively. All coordinates are scaled by a_x, the exciton Bohr radius, and the average values of R_h are set to $2.7a_x$, the same as for the A-H wave function.

	C_1		C_2		$\lvert C_2/C_1\rvert^2$
	Direct	Exchange	Direct	Exchange	
Model 1	1	0.0817	0	-0.0344	1.01×10^{-3}
Model 2	1	0.1048	0	-0.0472	1.83×10^{-3}
A-H wave function	1	0.1304	0.0283	-0.0442	2.00×10^{-4}

In the first-order approximation, the xx may be considered as made up of two $1s$ x's. As the two $1s$ x's interact, their wave functions become deformed and e-e and h-h exchanges become frequent between the two x's. These deformation and exchange effects are responsible for the appearance of the x excited state components in the wave function. In order to see the contributions of these effects, we compare three trial xx wave functions; the Akimoto-Hanamura (A-H) wave function,[4] which includes both deformation and exchange effects, and two simpler model wave functions without exciton deformation (model 1 and model 2) as shown in Table II. The parameters in the two model wave functions are chosen to give the same average radius of the molecule as the A-H wave function. We obtain $|C_2/C_1|^2$ by analytical calculation of Eq. (7). For the A-H wave function, we see that exchange and deformation contributions partially cancel each other leading to a significant reduction of $|C_2/C_1|^2$. Consequently, deviation from the experimental observation for the A-H wave function is much smaller than for the model wave functions. This analysis shows $|C_n/C_1|^2$ provides a very sensitive measure of the accuracy of the xx wave function and the cancellation of the exchange and deformation contributions is crucial for the proper construction of the xx wave function.

In summary, we have observed the inverse exciton series in CuCl and developed a theory for determining the biexciton wave function from the inverse series using the bipolariton model. From the M_{ns}-emission series, we have obtained the magnitudes of ns exciton components in the molecule wave function and provided bench marks for testing the wave function: The relative intensities of the M_{ns} lines give constraints on a four-particle trial wave function. Here we investigated the inverse emissions from biexcitons only at $K_m=2k_0$, but further investigation of the K_m dependence of the inverse series will lead to a complete experimental determination of the molecule wave function.

We thank K. Kurihara for sample purification, and appreciate valuable discussions with H. Haug, L.V. Keldysh, M. Kuwata-Gonokami, and N. Nagasawa.

---

*Present address: TCM, Cavendish Laboratory, University of Cambridge, Cambridge, U.K.

[1] E.J. Mayer, G.O. Smith, V. Heuckeroth, J. Kuhl, K. Bott, A. Schulze, T. Meier, D. Bennhardt, S.W. Koch, P. Thomas, R. Hey, and K. Ploog, Phys. Rev. B **50**, 14 730 (1994); A.L. Ivanov, H. Wang, J. Shah, T.C. Damen, H. Haug, L.N. Pfeiffer, and L.V. Keldysh, *ibid.* **56**, 3941 (1997).

[2] M. Kuwata-Gonokami, S. Inouye, H. Suzuura, M. Shirane, R. Shimano, T. Someya, and H. Sakaki, Phys. Rev. Lett. **79**, 1341 (1997).

[3] E. Dekel, D. Gershoni, E. Ehrenfreund, D. Spektor, J.M. Garcia, and P.M. Petroff, Phys. Rev. Lett. **80**, 4991 (1998).

[4] O. Akimoto and E. Hanamura, J. Phys. Soc. Jpn. **33**, 1537 (1972). From Fig. 1 of this paper, the binding energy of excitonic molecules in CuCl is estimated as $\epsilon^m\simeq11$ meV for $\sigma=m_e/m_h=0.28$ (in CuCl $m_e=0.5m_0$ and $m_h=1.8m_0$, where m_0 is the free electron mass).

[5] W.F. Brinkman, T.M. Rice, and B. Bell, Phys. Rev. B **8**, 1570 (1973).

[6] M.A. Lee, P. Vashishta, and R.K. Kalia, Phys. Rev. Lett. **51**, 2422 (1983). From the data reported in this paper, we estimate $\epsilon^m\simeq18$ meV for CuCl.

[7] W. Kolos and C.C.J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960).

[8] B. Hönerlage, R. Lévy, J.B. Grun, C. Klingshirn, and K. Bohnert, Phys. Rep. **124**, 161 (1985); F. Bassani, J.J. Forney, and A. Quattropani, Phys. Status Solidi B **65**, 591 (1974).

[9] H. Akiyama, T. Kuga, M. Matsuoka, and M. Kuwata-Gonokami, Phys. Rev. B **42**, 5621 (1990); N. Nagasawa, M. Kuwata, E. Hanamura, T. Itoh, and A. Mysyrowicz, Appl. Phys. Lett. **55**, 1999 (1989).

[10] A.L. Ivanov, H. Haug, and L.V. Keldysh, Phys. Rep. **296**, 237 (1998); A.L. Ivanov, in *Microscopic Theory of Semiconductors: Quantum Kinetics, Confinement and Lasers*, edited by S.W. Koch (World Scientific, Singapore, 1996), pp. 359–399.

[11] D.S. Chemla, A. Maruani, and E. Batifol, Phys. Rev. Lett. **42**, 1075 (1979); A. Maruani, D.S. Chemla, Phys. Rev. B **23**, 841 (1981).

[12] M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa, and E. Hanamura, *Excitonic Processes in Solids* (Springer, Berlin, 1986), Chap. 2 and 3.

[13] A. Mysyrowicz, J.B. Grun, R. Levy, A. Bivas, and S. Nikitine, Phys. Lett. A **26**, 615 (1968).

[14] M. Kuwata-Gonokami (private communication).

[15] K. Saito, M. Hasuo, T. Hatano, and N. Nagasawa, Solid State Commun. **94**, 33 (1995).

[16] H. Akiyama, M. Kuwata, T. Kuga, and M. Matsuoka, Phys. Rev. B **39**, 12 973 (1989).

[17] I.S. Gorban *et al.* [Solid State Commun. **98**, 941 (1996)] claim the observation of the M series in ZnP_2. They found, however, $I_2/I_1\sim1/10$. This value is too large for the M inverse series: our first-principle numerical estimates yield about 1/1000 for I_2/I_1 in ZnP_2. Furthermore, the experimental data by Gorban *et al.* were not confirmed in a similar experiment by K. Kondo (M.S. thesis, Okayama University, 1998).

[18] K. Kurihara, E. Tokunaga, M. Baba, and M. Matsuoka, Phys. Rev. B **52**, 8179 (1995).

[19] J.J. Hopfield, Phys. Rev. **112**, 1555 (1958).

[20] D. Fröhlich, P. Köhler, W. Nieswand, and E. Mohler, Phys. Status Solidi B **167**, 147 (1991).