Exciton-phonon coupled states in CuCl quantum cubes

Jialong Zhao,[1] Selvakumar V. Nair,[2] and Yasuaki Masumoto[1,2]
[1]*Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan*
[2]*ERATO Single Quantum Dot Project, Japan Science and Technology Corporation, Tokodai 5-9-9, Tsukuba, Ibaraki 300-2635, Japan*
(Received 12 May 2000; revised manuscript received 5 September 2000; published 29 December 2000)

The size dependence of excitonic states and vibrational modes in CuCl cubic quantum dots embedded in NaCl crystals was studied by means of site-selective persistent spectral hole burning spectroscopy. It is shown that the interaction of the longitudinal optical (LO) phonon with the exciton results in the formation of coupled exciton-phonon modes when the energy of the LO phonon approaches the energy spacings between the ground and excited states of the exciton. The energy anticrossings of the LO phonon modes with two higher optically allowed excited states of the exciton in CuCl QD's were clearly observed at confinement energies of about 10 and 6 meV, respectively. In addition, the linewidth of the LO phonon sideband in CuCl QD's in NaCl crystals was found to increase abruptly from 0.3 meV to about 1.2 meV at a confinement energy of about 23 meV, which appears to result from the exciton-phonon mixing of the LO phonon mode with the first excited state of the exciton. The experimental results are qualitatively understood by the LO phonon renormalization theory.

DOI: 10.1103/PhysRevB.63.033307 PACS number(s): 68.65.−k, 63.22.+m, 61.46.+w, 71.35.−y

Optical investigations on semiconductor quantum dots (QD's) or nanocrystals opened an exciting field of basic physics studies.[1,2] Studies of the size dependence of electronic and vibrational spectra as well as the exciton-phonon interaction in QD's are important for understanding their optical properties. The persistent spectral hole burning (PSHB) phenomenon is observed in many materials containing QD's, and PSHB provides a sensitive spectroscopic technique for the study of the size-dependent electronic states and vibrational modes in QD's.[3–10]

Since QD's containing only a few hundreds of atoms are like large molecules, the exciton formation in QD's would be expected to strongly influence the lattice vibrations. Recently, the LO phonon sidebands observed in the PSHB and photoluminescence spectra of spherical CuCl nanocrystals in glass showed an energy reduction of about 2 meV, compared with the energy of the LO phonon (25.6 meV) in the bulk crystals. The energy softening was described theoretically in terms of the phonon renormalization in the presence of a single exciton in spherical QD's.[8,11] Quantum beats of confined exciton-LO phonon complex were observed in CuCl nanocrystals and the reduction of LO phonon energy extracted from the quantum beat was interpreted in terms of LO phonon renormalization.[12] The studies of the excited-state phonons in QD's are still at an early stage and knowledge on the shape dependence of the LO phonon renormalization is lacking.

CuCl QD's embedded in NaCl crystals, unlike those in a glass matrix, show oscillatory fine structures in the inhomogeneously broadened Z_3 exciton absorption bands. These structures were assigned to the size-quantized Z_3 excitons confined in the CuCl QD's of cubic shape.[5,6,13] In this paper, we study the size dependence of the lattice vibrations in the excited states for CuCl cubic QD's in NaCl crystals by means of PSHB. We note that, unlike the conventional Raman scattering which involves the ground-state vibrational modes, the PSHB spectroscopy gives the information about phonon modes in the excited states.[8] The effect of the exciton formation on the lattice vibrations in the QD's was explored experimentally by tuning the size-dependent energy level spacings between the ground and excited states to be resonant with the LO phonon.

CuCl QD's used in the experiment were embedded in NaCl crystals. The NaCl crystals containing CuCl were grown by the transverse Bridgman method.[14] The size of the QD's was controlled by heat treatment with different temperature and time. The samples were directly immersed in superfluid helium at 2 K in an optical cryostat. A narrow-band dye laser pumped by the third harmonics of the output of a *Q*-switched Nd^{3+}: YAG laser (355 nm) was used as a pump source. The pulse duration and repetition were approximately 5 ns and 30 Hz, respectively. The spectral linewidth was about 0.014 meV. A halogen lamp was used as a probe source. The PSHB spectrum was measured as follows: First, the absorption spectrum was obtained and the sample was exposed to dye laser pulses to burn a persistent spectral hole at an excitation energy. Then, the absorption spectrum was measured again after the laser exposure was stopped. The absorption spectral change $-\Delta\alpha d$ is defined as the difference between the spectra before and after the laser exposure. The subsequent measurements were performed at the new position of the samples and not carried out at the position burnt previously. The transmitted light of the samples was detected by a liquid-nitrogen cooled charge-coupled device in conjunction with a 75-cm spectrometer involving an 1800 grooves/mm grating operated in the second order of diffraction. The spectral resolution of the experiment was about 0.13 meV.

Figures 1 and 2 show the absorption and PSHB spectra of two CuCl QD samples with different QD sizes at 2 K. Oscillatory fine structures are observed between 3.22 and 3.28 eV in the Z_3 exciton absorption bands as shown in Figs. 1(a) and 2(a), and are attributed to size-quantized exciton states in cube-shaped QD's.[5,6,13] As seen in Figs. 1(b) and 2(b), the main hole marked by *M* coincides with the energy of the pump beam. The broad hole, referred as a pseudophonon-wing[15] with a Stokes shift of a few meV was

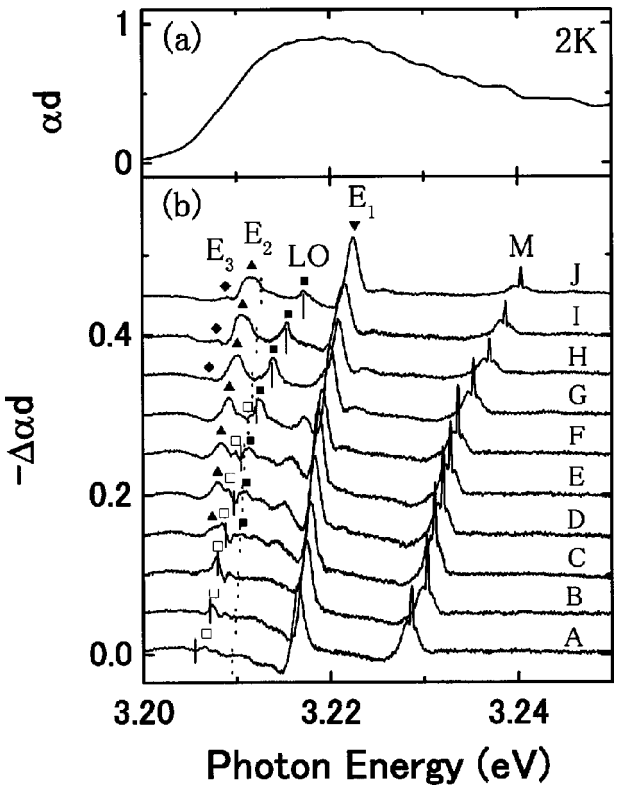

FIG. 1. Absorption (a) and PSHB spectra (b) of CuCl QD's with large size in NaCl crystals at 2 K. The excitation energies for spectra *A*, *B*, *C*, *D*, *E*, *F*, *G*, *H*, *I*, and *J* are 3.2287, 3.2303, 3.2311, 3.2320, 3.2329, 3.2336, 3.2353, 3.2370, 3.2387, and 3.2404 eV, respectively. The vertical dotted lines show the energies of the hole burning of the ground state $E_{1,1,1}$ under excitation of the excited state $E_{3,1,1}$ obtained from the relation $E_{3,1,1}-E_B=3.67(E_{1,1,1}-E_B)$. The vertical solid lines represent the energies of the LO phonon sideband holes calculated from $E_M-E_{\mathrm{LO}*}$, where $E_{\mathrm{LO}*}=23.1$ meV is the LO phonon energy in the excited state.

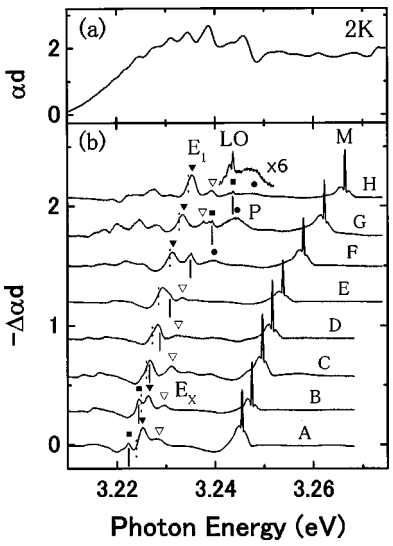

FIG. 2. Absorption (a) and PSHB spectra (b) of CuCl QD's with small size in NaCl crystals at 2 K. The excitation energies for spectra *A*, *B*, *C*, *D*, *E*, *F*, *G*, and *H* are 3.2454, 3.2474, 3.2496, 3.2517, 3.2538, 3.2580, 3.2623, and 3.2664 eV, respectively. The vertical dotted lines show the energies of the hole burning of the ground state $E_{1,1,1}$ under excitation of the excited state $E_{2,1,1}$ obtained from the relation $E_{2,1,1}-E_B=2(E_{1,1,1}-E_B)$. The vertical solid lines represent the energies of the LO phonon sideband holes calculated from $E_M-E_{\mathrm{LO}*}$, where $E_{\mathrm{LO}*}=23.1$ meV is the LO phonon energy in the excited state.

suggested to originate from the confined acoustic phonon-assisted absorption of the QD's.[16,17]

The Stokes shifts of the holes E_1, E_2, E_3, LO, and P as a function of the exciton confinement energy are shown in Fig. 3. The confinement energies of the satellite holes, $E_{\mathrm{hole}}-E_B$, where E_{hole} is the photon energy of the hole and E_B is the bulk Z_3 exciton energy ($E_B=3.2022$ eV at 2 K), were obtained from the PSHB spectra. According to the size dependence of the Stokes shift between the main hole and the satellite hole in the QD's, the exciton- and phonon-related holes can be distinguished. If an infinitely high potential barrier is assumed, the quantized exciton energy levels for a quantum cube are given by

$$E_{n_x,n_y,n_z}=E_B+\frac{\hbar^2\pi^2}{2M(L-a_B)^2}(n_x^2+n_y^2+n_z^2), \qquad (1)$$

where $M=2.3m_0$ is the translational mass of the bulk exciton and quantum numbers n_x, n_y, and n_z take values 1, 2, 3,.... L is the side lengths of the quantum cube and $L-a_B$ is used for the dead-layer correction. For a quantum cube the ground state $E_{1,1,1}$ and the first and higher excited states, $E_{2,1,1}$, $E_{2,2,1}$, $E_{3,1,1}$, $E_{2,2,2}$, and $E_{3,3,1}$, satisfy relations $E_{2,1,1}-E_B=2(E_{1,1,1}-E_B)$, $E_{2,2,1}-E_B=3(E_{1,1,1}-E_B)$, $E_{3,1,1}-E_B=3.67(E_{1,1,1}-E_B)$, $E_{2,2,2}-E_B=4(E_{1,1,1}-E_B)$, and $E_{3,3,1}-E_B=6.3(E_{1,1,1}-E_B)$. As seen in Figs. 1(b) and 2(b), the main hole burnt resonantly at the laser energy E_M and the satellite hole E_1 almost obeys the equation $E_M-E_B=2(E_1-E_B)$. Thus, the dominant satellite hole E_1 is

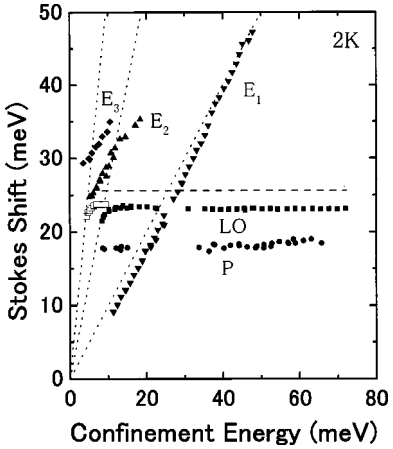

FIG. 3. Stokes shifts of the satellite holes E_1, E_2, LO, and P in CuCl QD's in NaCl crystals as a function of the exciton confinement energy. The dashed line represents the energy of LO phonon in a bulk CuCl crystal. The dotted lines represent the size dependence of the energy spacings between the ground and excited states in the CuCl QD's on the quantum cube model.

from the hole burning of the ground state $E_{1,1,1}$ under excitation of the first excited state $E_{2,1,1}$ in the quantum cubes. Further, the holes marked by E_2 and E_3 in larger CuCl QD's are assigned to the hole burning of the exciton ground states under excitation of the excited states $E_{3,1,1}$,[5] and $E_{3,3,1}$, respectively. Strictly speaking, direct optical excitation of the first excited state $E_{2,1,1}$ in ideally cubic nanocrystals is forbidden and its oscillator strength should be zero. Therefore, the observation of the hole burning of the ground state under excitation of the first excited state suggests that the QD's are not ideal cubes.[5,6] Recently, the holes E_1 and E_X observed in Fig. 2(b) were suggested to be from the hole burning of the exciton ground states under excitation of the degenerate first excited states $E_{2,1,1}$ and $E_{1,1,2}$ in nearly cubic CuCl quantum boxes.[18]

A pronounced nonresonant hole labeled by LO with a Stokes shift of 23.1 meV is located at the low-energy side of the main hole and is almost size-independent over a wide size range as shown in Fig. 3. From the size dependence, the hole is assigned to a LO phonon sideband of the exciton ground state, which is slightly smaller than the phonon energy of 23.5 meV in CuCl QD's in glass.[8] In addition, a broad hole denoted by *P* with a Stokes shift of about 18 meV was observed in the PSHB spectra. The Raman spectrum of CuCl crystals in the transverse optical (TO) phonon regime is anomalous, consisting of a sharp [TO(γ), ~21.3 meV] and a broad [TO(β), ~18.7 meV] line at low temperature.[19,20] The Stokes shift of the hole *P* measured in the PSHB spectra is close to the energy of the TO(β). Therefore, the satellite hole *P* may be from the optical absorption together with simultaneous emission of a TO(β) phonon.

As seen in Figs. 1(b) and 2(b), the PSHB spectra are very complex because the hole burning of the ground states under excitation of various excited states was clearly observed at the lower energy side of the spectra, in contrast to the simple PSHB spectra of spherical CuCl QD's in glass.[8] We can easily demonstrate the LO phonon mixes with the excited states of the excitons in CuCl cubic QD's in NaCl crystals when the LO phonon is close to the energy differences between the ground and excited states. In the PSHB spectra of large CuCl QD's in Fig. 1(b), the holes E_2 and LO become close to each other when the dot size is increased. Then the LO phonon energy becomes small and the LO phonon mode clearly anticrosses with the optically allowed excited state $E_{3,1,1}$ of the exciton at an energy of about 3.212 eV. The Stokes shift of the hole E_2 is the energy difference between the ground state $E_{1,1,1}$ and the next optically allowed state $E_{3,1,1}$ in cubic QD's, and may be compared to the energy spacing between the ground state $(1S)$ and the excited state $(2S)$ in spherical nanocrystals, whose principal quantum number n and angular momentum quantum number l are taken as $n=1, l=0$, and $n=2, l=0$, respectively.[2] An anticrossing between the phonon sideband of the exciton ground state and the higher excited state $E_{3,1,1}$ is clearly observed at a confinement energy of about 10 meV in Fig. 3.

Further, it is noted that a sharp peak marked by an open square arises between holes E_2 and LO in spectra ranging from *G* to *C* in Fig. 1(b). The sharp peak becomes dominant with the increase of the dot size. The Stokes shift of the peak is about 23.7 meV and is not dependent on the dot size in the smaller QD's as shown in Fig. 3. Therefore, the peak is considered to be an LO phonon mode of CuCl QD's. The energy of the LO phonon mode is decreased rapidly when the dot size is further increased. As a result, the LO phonon mode shows a clear anticrossing with a higher optically allowed excited state $E_{3,3,1}$ of the exciton at a confinement energy of about 6 meV. The above result clearly shows that the renormalization of LO phonon exists in CuCl cubic QD's in NaCl crystals, resulting in clear anticrossings of the LO phonon mode of the exciton ground states with two higher optically allowed excited states, $E_{3,1,1}$, and $E_{3,3,1}$. The observed anticrossings are consistent with the renormalization theory of the LO phonon.[8,11]

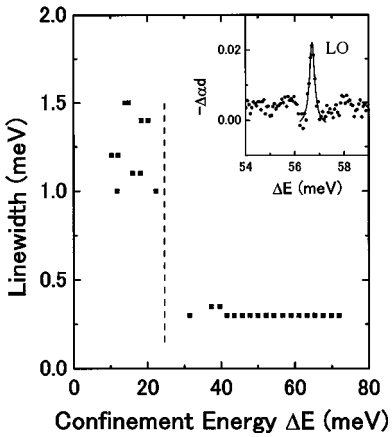

FIG. 4. Size dependence of the linewidth of LO phonons in CuCl QD's in NaCl crystals. The vertical dashed line shows the energy of the phonon that is equal to the energy spacing between the ground and the first excited state $E_{2,1,1}$. The inset shows the LO phonon sideband (closed circles) at the confinement energy of 56.7 meV and a Lorentzian fit (solid curve), respectively.

In the following, we studied the change of the energy and the linewidth for the LO phonon when the LO phonon is resonant with the energy separation between the exciton ground state $E_{1,1,1}$ and the first excited state $E_{2,1,1}$, which may be considered to correspond to the ground state $1S$ and the first excited state $1P$ (quantum numbers $n=0$ and $l=1$) in spherical nanocrystals, respectively.[2] As seen in spectra *C*, *D*, and *E* of Fig. 2(b), when the LO phonon is close to the energy difference between the ground state $E_{1,1,1}$ and the first excited state $E_{2,1,1}$, it is difficult to distinguish the holes E_1 and LO owing to broader width of the hole E_1. Thus, Fig. 3 does not show a clear energy anticrossing as the theory predicted.[11] However, it is found that the linewidth of the LO phonon is increased abruptly at a confinement energy of about 23 meV, as shown in Fig. 4. When the energy of the LO phonon in the small QD's is smaller than the energy difference between the ground state $E_{1,1,1}$ and the first excited state $E_{2,1,1}$, the LO phonon is very narrow and its linewidth is about 0.3 meV, as is shown in the enlarged spectrum *H* of Fig. 2(b) and the inset of Fig. 4. The LO phonon becomes broad with a linewidth of about 1.2 meV in the spectra *A* and *B* of Fig. 2(b) after the phonon is resonant with the

energy difference between the ground state $E_{1,1,1}$ and the first excited state $E_{2,1,1}$. At the same time, it is noted that the intensity of the LO phonon sideband is enhanced near the exciton-phonon resonance.

In spherical QD's, the coupling of $l=1$ phonons with exciton P states leads to a renormalization of the latter, as predicted in Ref. 11, but the P states having a zero oscillator strength are not expected to show up in the PSHB spectrum. In the similar manner, the phonon sideband of the ground state in ideally cubic QD's can interact with the first excited-state $E_{2,1,1}$ with a zero oscillator strength. However, the PSHB experiment reported earlier[5,6] shows that the oscillator strength of the first excited state in CuCl QD's in NaCl crystals is not zero. Therefore, the coupling between the ground state $E_{1,1,1}$ and the first excited state $E_{2,1,1}$ through phonons of appropriate symmetry will cause a weak energy anticrossing that can be observed in the PSHB spectrum. Although we do not see a clear anticrossing of the LO phonon with the first excited state $E_{2,1,1}$, we interpret the observed broadening of the LO phonon sideband as due to exciton-phonon mixing. This interpretation is backed by the lineshape analysis of Zimin *et al.*[21] around the LO-phonon-exciton anticrossing region.

In conclusion, we have studied the LO phonon modes and exciton states in nearly cubic CuCl QD's in NaCl crystals by the PSHB spectroscopy. The exciton formation in the QD's has influenced the lattice vibrations, leading to a mixing of the LO phonon with the excitons near the exciton-phonon resonance. At larger sizes, the resonant mixing of the optically allowed excited states $E_{3,1,1}$ and $E_{3,3,1}$ of the exciton and the phonon modes shows clear anticrossing behaviors. At smaller sizes, the significant linewidth broadening of the LO phonon probably results from the mixing of the LO phonon with the exciton when the phonon is resonant with the transition between the ground and the first excited state. This indicates that the interaction of the LO phonons with excitons in QD's depends on the shape of QD's. Because the energy levels of the exciton excited states in nearly cubic QD's are more complex than those in spherical nanocrystals, further theoretical studies on the nearly cubic QD's are required to understand the interaction of the LO phonon with excitons in CuCl QD's in NaCl crystals.

One of the authors (J. Z.) sincerely thanks Dr. A. V. Fedorov, Dr. T. Mishina, Dr. T. Okuno, Dr. J. Qi, and Dr. M. Ikezawa for valuable discussions. This work was partially supported by the ''Research for the Future'' Program JSPS-RFTF 97P00106 from the Promotion of Science.

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