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Large g value in CuCl semiconductor microcrystallites

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A magnetic circular dichroism measurement is applied to semiconductor microcrystallites. The effective g values of CuCl semiconductor microcrystallites embedded in polymer matrix are found to be 0.447 and -0.18 for the Z_3 and Z_{12} exciton states, respectively, the former being 1.49 times enhanced from the bulk value. The result is a direct consequence of the quantum confinement effect, explained in terms of the change in amplitudes of the components with higher l index in the lowest exciton state.

Efforts have been made to clarify the intrinsic nature of the confined exciton state of semiconductor microcrystallites recently, aiming to overcome extrinsic effects such as defects or surface roughness that often conceal the quantum confinement effects.[1-5]

Experiments on electroabsorption (EA) in semiconductor microcrystallites have been done by several groups.[6-11] The experiments were originally performed intending to observe lifting of degeneracy and appearance of new absorption because of the symmetry reduction by the external electric field.[6] However, it was shown by a number of experiments that an electron or a hole is influenced by defects or the surface of a microcrystallite and the lowest excited state is not described by the (s,S) state with both an electron and a hole delocalized in a microcrystallite.[1,10-12] It has been also found that CdSe and $\mathrm{CdS}_x\mathrm{Se}_{1-x}$ microcrystallites in glass show narrower hole-burning spectra after strong laser illumination than fresh samples, which was attributed to change in charge states on the surface.[13] These results suggest that the observed EA signal is most likely affected by defects or the surface.

The purpose of the present paper is twofold. First, by using a sample film of CuCl semiconductor microcrystallites embedded in polymer matrix, we reduce the above-mentioned effects. Because the surface of this sample is better defined than samples in glass, the quantum confinement effects are expected to be observed more directly. Second, we apply magnetic circular dichroism (MCD) measurements to semiconductor microcrystallites. This measurement is sensitive to angular momentum, whereas the static EA is sensitive to the spatial extent of the wave functions. MCD signals depend not only on orbital angular momentums but also on the spin part of the Bloch electron and hole. Thus MCD provides complementary information to EA.

The sample film of CuCl semiconductor microcrystallites has been prepared by the method reported in the literature.[14] In short a precursor film of CuCl/polymethyl methacrylate (PMMA) was dried in a nitrogen-flow chamber for about 26 h and was heated at 145 °C for 20 sec. The average radius of the obtained microcrystallites is estimated by a transmission electron microscope to be 46 Å with standard deviation of 12 Å.

A light beam from a xenon lamp was passed through a monochromator and a polarizer, and was led to an elastic modulator. The obtained modulated probe beam of the right and left circularly polarized light was then focused on the sample film mounted at the center of a superconducting magnet. The modulated signals were detected with a photomultiplier and a lock-in amplifier in an f mode. No smoothing of the spectra was performed. The range of the applied magnetic field was 0–6 T. All the measurements were performed at 10 K. The MCD spectrum of a bulk thin crystal of CuCl was also measured as a reference for assuring quantitative accuracy of the measurements.

The absorption spectrum of the CuCl microcrystallites at 0 T is shown in Fig. 1. Two peaks of the Z_3 and Z_{12} exciton states are clearly distinguished. The half-width of the Z_3 exciton state is 3.3 meV, which is 1.5 times larger than the width of the exciton in our reference bulk sample crystal. The peak energies of the Z_3 and Z_{12} exciton states are shifted to blue by 6 and 11 meV, respectively. The MCD spectrum is shown in Fig. 2, indicating

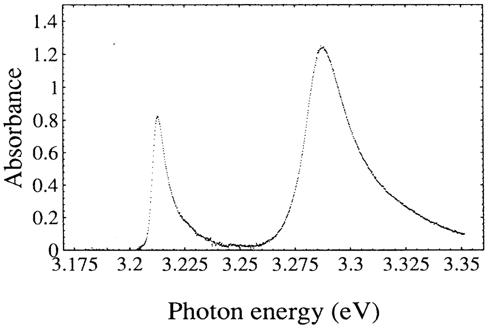

FIG. 1. Absorption spectrum of the CuCl semiconductor microcrystallites at 0 T, 10 K.

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the difference in the absorbance for σ^+ ($\Delta m = 1$) and σ^- ($\Delta m = -1$) light. The magnetic field was varied from 1 to 6 T by 1-T steps. The signal intensity was proportional to the magnetic field in the measured range. The measurements were also carried out with opposite direction of the magnetic field so as to eliminate any background signals possibly caused by slight anisotropy of the quartz windows. The MCD signals clearly show the Zeeman shift of the Z_3 and Z_{12} exciton states, having positive and negative g values according to the exciton states in bulk crystals.[15,16]

The effective g values are obtained by numerical fitting procedures. The width of the absorption spectrum of the microcrystallites film is dominated by the homogeneous width and a part of it is inhomogeneously broadened by fluctuation in the size of the microcrystallites. Then we assume for simplicity a Fano profile function to give the absorption profile as a function of the photon energy E. The best fitted curve for 6 T is shown in Fig. 3. As for the Z_{12} exciton state, a small constant term was added to the fitted curve. The constant term and the small structures near 3.27 eV presumably originate from the excited states of the Z_3 exciton state. The effective g values obtained are 0.447 and -0.18 for the Z_3 and Z_{12} exciton states, respectively. The same procedures were also followed for the bulk thin crystal, and the effective g value of 0.3 obtained for the Z_3 exciton state is in agreement with the value in the literature.[17] The value for the Z_{12} bulk exciton state was not obtained with sufficient accuracy to be presented here because of the strong absorption; however, it reasonably agreed with the reported value of -0.2 (Ref. 18) within the experimental accuracy.

Another result different in the microcrystallites from the bulk crystal is the lack of the MCD signal below the lowest exciton states in the microcrystallites. There are distinct structures around 3.185 eV in the bulk crystal, which are attributed to the signal due to bound exciton states. The lack of this bound exciton states also shows the high quality of our sample.

The bulk CuCl crystal is in the zinc-blende lattice structure with T_d symmetry. The CuCl microcrystallites are considered to have the same crystal structure as the bulk crystal. The Z_3 (Z_{12}) exciton state is composed of the Γ_6 conduction electron and Γ_7 (Γ_8) valence-hole states and is twofold (fourfold) degenerate including the spin. The effective masses for the Γ_6 conduction electron and Γ_7 valence hole are $0.50m_0$ and $1.8m_0$, respectively, where m_0 is the electron mass in vacuum. The effective Bohr radius for the Z_3 exciton is 6.8 Å.[19] The Γ_8 valence-hole state is split into heavy- and light-hole states for $k \neq 0$, but because of the large broadening by phonon scattering, those states are not resolved and the band parameters for the Z_{12} exciton state are less well known. It is often useful to apply the spherical approximation neglecting cubic contributions, in which case Γ_6, Γ_7, and Γ_8 states are approximated by the total angular momentum of $F = \frac{1}{2}$, $\frac{1}{2}$, and $\frac{3}{2}$ states, respectively.

It is well known that the intensity ratio of the Z_{12} to Z_3 exciton states in the bulk crystal[20] is 3.7, and larger than the factor of 2 which is expected from degeneracy of the states, and that it depends on the spin-orbit energy and the exchange energy. The intensity ratio of the lowest to the second-lowest absorption bands is 4.3 for the present microcrystallites, and hence the deviation from 2 is even larger in the microcrystallites.

The exchange energy in a microcrystallite is shown to be proportional to $1/R_0^3$ in the case $R_0 \ll a_B$ and to approach the bulk value in the case $R_0 \gg a_B$, where R_0 is a microcrystallite radius.[21] The difference in the exchange energy is negligibly small between the bulk and the present microcrystallites. The energy separation between the Z_{12} and Z_3 exciton states does not differ from the bulk crystal, either. Thus it is concluded that the observed large intensity ratio of the lowest to the second-lowest absorption bands is due neither to the change in the exchange energy nor to the spin-orbit energy but to the size quantization of the exciton states. Similar arguments were made by Itoh, Iwabuchi, and Kirihara.[22] They explained the change in the intensity ratio of the lowest to the second-lowest absorption band by the transfer of the optical transition probability from the 1s to 2s exciton state. Here we will develop their arguments further in view of the inseparability of the exciton wave functions.

In the case of $R_0 \gg a_B$, the separation of the center-of-mass and the relative coordinates is often carried out. However, the complete separation of the coordinates cannot explain the effect of the finite size on the ratio of the exciton intensities or the change in the effective g values,

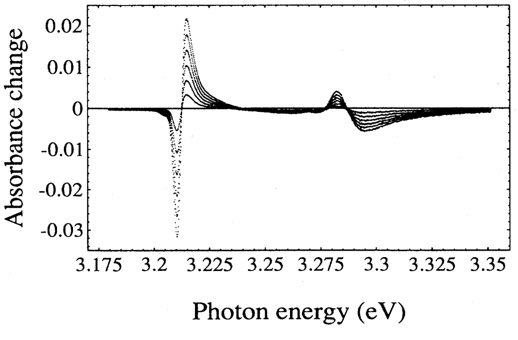

FIG. 2. Absorbance change spectra ($\sigma^+ - \sigma^-$) for the magnetic field $H = 1, 2, \ldots, 6$ T, respectively (dots).

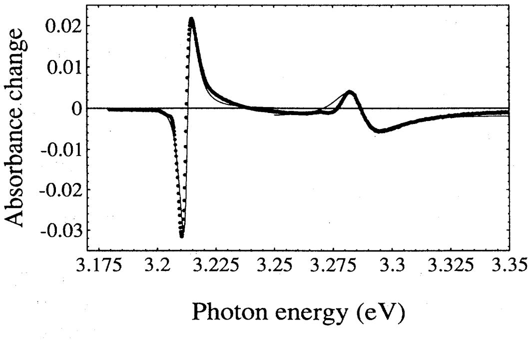

FIG. 3. Absorbance change spectrum at 6 T (dots), and the best fitted curve (solid curve).

where the internal motion of excitons is concerned. Moreover, even in a bulk crystal, the exciton wave function in the presence of the external magnetic field is inseparable, because the interaction with the magnetic field cannot be written solely in terms of the relative coordinates in the case of different effective masses for an electron and a hole.

We have found by numerical calculations that the energy of the $(p_{1/2},P_{1/2})$-like state of the Z_3 exciton overlaps with the Z_{12} exciton states and has comparable optical transition probability to the lowest $(s_{1/2},S_{1/2})$-like state of the Z_3 exciton as well as a similar distribution of the optical transition probability among the lowest and higher $(s_{1/2},S_{1/2})$-like state of the Z_3 exciton. The $(p_{1/2},P_{1/2})$-like state is not resolved in the absorption spectrum (Fig. 1); however, a small peak at 3.270 eV in the MCD signal (Fig. 3) is most probably due to the $(p_{1/2},P_{1/2})$-like state. The large intensity ratio is thus explained by the change in the optical transition probability of the exciton states by the quantum confinement effect. Here we have introduced notations, $(s_{1/2},S_{1/2})$- or $(p_{1/2},P_{1/2})$-like state, since these states are not purely $(s_{1/2},S_{1/2})$ or $(p_{1/2},P_{1/2})$ state, but are linear combinations of basis wave functions with $l=0,1,2,\ldots$.

The large effective g value of the Z_3 exciton state is also explained in the same context in terms of mixing of components with higher l index. The Hamiltonian for the Zeeman splitting is given by

$$H^{(1)}=\frac{e}{2m_0c}\mathbf{H}\cdot\left[g_1\mathbf{s}_1+g_2\mathbf{s}_2+\frac{1}{m_1^*}l_1-\frac{1}{m_2^*}l_2\right], \quad (1)$$

where $e=|e|$, m_1^* (m_2^*) is the effective mass divided by m_0, g_1 (g_2) is the gyromagnetic factor, l_1 (l_2) is the orbital angular momentum operator, and $\mathbf{s}_1$ $(\mathbf{s}_2)$ is the spin operator for an electron (a hole). First, we consider two limiting cases: $R_0 \gg a_B$, and $R_0 \ll a_B$ for the spherical confinement, where the orbital momentum l and its z component m are good quantum numbers. In the former case, the wave function for the lowest exciton state is just the hydrogenic 1s state. There is no contribution from the orbital angular momentum. In the latter case, there is no contribution from the orbital angular momentum, either, since the lowest exciton state is the pure $(s_{1/2},S_{1/2})$ state.

Now, let us consider the intermediate case. There are two equivalent approaches: one starts from basis functions for strong confinement where an electron and a hole are individually confined, and the other from basis functions for the hydrogenic states. First, we consider from the first viewpoint. The wave function for the exciton state in the case of $R_0 \approx a_B$ is composed of the superposition of $(s,S),(p,P)(d,D),\ldots$ exciton states when expanded into multipolar spherical waves. The amplitudes of these components are mainly determined by the kinetic energy and the Coulomb interaction, which mixes states with any orbital angular momentum. The off-diagonal terms, i.e., the Coulomb interaction terms, become larger as the size of a microcrystallite increases. Then the relative amplitudes of higher-l index components $[(p,P),(d,D),\ldots]$ increase with the particle size. What is important here is that an electron state is more substantially affected by the confinement than a hole state because the effective Bohr radius of the former is usually larger. Then the evolution of the higher index components is different for an electron and a hole, giving a larger expectation value, $\langle H^{(1)}\rangle$, in the intermediate case than in the limit of the strong confinement. If the radius of a microcrystallite becomes sufficiently large for both an electron and a hole not to be affected by the confinement, then the amplitudes of high-l index components for an electron and a hole satisfy the condition that the contribution to $\langle H^{(1)}\rangle$ from the orbital angular momentums is zero. Therefore, there exists an optimum radius of a microcrystallite for the largest g value.

A similar argument can be repeated starting from the hydrogenic states. Since the exciton wave function is not separable in the presence of the external magnetic field in the case of different effective masses for an electron and a hole, the mixing of the relative and the center-of-mass motions should be considered. The imposition of the confinement gives rise to the coupling term[23]

$$V=\delta E\mathbf{r}\cdot\mathbf{R}+(e/Mc)\mathbf{H}\cdot(\mathbf{r}\times\mathbf{P}), \quad (2)$$

where δE represents the difference in the confinement energy of an electron and a hole, $\mathbf{r}$ and $\mathbf{R}$ are the relative and the center-of-mass coordinates, respectively, M is the total mass, and $\mathbf{P}$ is the center-of-mass momentum. The Hamiltonian for the Zeeman splitting, (1), is written in terms of the orbital angular momentum for the relative coordinate l as

$$H^{(1)'}=\frac{e}{2m_0c}\mathbf{H}\cdot\left[g_1\mathbf{s}_1+g_2\mathbf{s}_2+\left(\frac{1}{m_1^*}-\frac{1}{m_2^*}\right)l\right]. \quad (3)$$

The coupling term (2) mixes $s,p,d,\ldots$ states and thus the Zeeman splitting (3) increases because of the contribution from the orbital momentums in the case $m_1^* < m_2^*$. In the limit of the strong confinement, the mixing between different orbital momentums become significant and the amplitudes of each component is determined such that the contribution from the second term in (2) cancels the contribution from the orbital momentums in (3), the net Zeeman splitting given by just the spin part.

The mixing of components with higher-l index is further increased by symmetry-lowering effects. In a system with nonspherical symmetry, l is not a good quantum number. This is the case for the surface effects[12] or the nonspherical confinement.[19,24] A calculation showed that the amplitude of $l=1$ components in the wave function increases when an exciton approaches a surface in a bulk crystal.[25] Similar results were obtained in the case of a microcrystallite.[26] If we assume the excitons in microcrystallites are likely to approach the surface, the relative amplitude of higher-l index components increases and result in larger $\langle H^{(1)}\rangle$. In the nonspherical confinement, the amplitude of the higher-l components increases with the decrease in size depending on the deviation from the spherical confinement.

The observed enhancement of the effective g value and the deviation of the intensity ratio of the lowest to the second-lowest absorption band from a bulk crystal show that the sample microcrystallites are in the intermediate case, and separation of the relative and center-of-mass motion is not applicable.

A calculation has been done starting from multipolar wave functions for an electron and a hole based on the effective-mass approximation. The infinite high square well is assumed as a confinement potential and the electron-hole Coulomb interaction is introduced. The lowest 2317 basis functions are used. The cutoff energy is $10E_{\mathrm{Ry}}$ for $R_0=25$ Å, giving sufficient convergence. Exciton states are obtained by numerical diagonalizations. We have obtained a qualitative agreement with our experimental results that there is an optimum size ($R_0=20\pm5$ Å) giving the largest effective *g* value for the lowest Z_3 exciton state than in a bulk crystal. The calculated upper limit for the effective *g* value in a spherical confinement is obtained to be 0.325. This result shows that the experimentally obtained effective *g* value of 0.447 is too large to be solely explained by the spherical confinement. Since the CuCl sample in the present study is embedded in a polymer film, the surface is considered to be more well defined than conventional samples in glasses, but this result shows that the surface pining effects cannot be totally excluded. The shape effect may also partly explain the additional enhancement of the effective *g* value for the lowest Z_3 exciton state. Semiconductor microcrystallites in alkali-chloride matrices are found to be elliptic,[19] but the shape of microcrystallites in a polymer film is currently not well investigated. Our work may motivate further investigations of the symmetry-lowering effects.

The experimentally obtained effective *g* value of -0.18 for the Z_{12} exciton state is interpreted by the following two reasons. First, the effective mass for the Γ_8 valence-hole state is reported to be smaller than that for the Γ_7 valence-hole state.[22] This gives the smaller mixing of the relative and the center-of-mass motions, resulting in the smaller enhancement of the effective *g* value for the Γ_8 valence-hole state than for the Γ_7 valence-hole state. Second, as has been previously discussed, the absorption at 3.28 eV is composed of the quantized state of the Z_3 and Z_{12} exciton states. The small reduction of the experimentally obtained *g* value for the Z_{12} exciton state is explained by the partial cancellation of the negative Zeeman shift of the component of the Z_{12} exciton state by the positive shift of that of the Z_3 exciton state.

In conclusion, we have observed the Zeeman shift of the Z_3 and Z_{12} exciton states by the measurement of the MCD spectra of CuCl semiconductor microcrystallites embedded in a polymer film. The effective *g* values are found to be 0.447 and -0.18 for the Z_3 and Z_{12} exciton states, respectively. The *g* value for the Z_3 exciton state in microcrystallites is found to be larger than in a bulk crystal. This result and the observed deviation of the intensity ratio of the lowest to the second-lowest absorption band from a bulk crystal show that separation of the relative and center-of-mass motion is not applicable in the sample microcrystallites. Mixing of the components with higher-*l* index is responsible for the enhancement of the *g* value.

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