Three-Photon Magnetoabsorption of Excitons in Alkali Halides

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Three-photon magnetoabsorption measurements in fields up to 9 T are presented for the first time. A narrow exciton line of Γ_5^- symmetry is resolved in CsI at 5.8076 eV. A g value of 1.17 is deduced from the Zeeman splitting of this exciton. At high magnetic fields an exciton of Γ_3^- symmetry is detected. The analysis of the field-dependent mixing of the Γ_3^- and Γ_5^- excitons yields a zero-field shift of the Γ_3^- exciton to lower energies of 0.54 meV and an effective g value for the admixture of 1.20.

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Three-photon spectroscopy was recently introduced by Beerwerth and Fröhlich[1] as a powerful technique to study exciton polaritons in crystals with inversion symmetry. The authors measured resonances on the upper polariton branch and even the longitudinal exciton of the one-photon–allowed exciton of Γ_4^- symmetry in several alkali halides. Besides this one- and three-photon–allowed Γ_4^- exciton there are excitons of Γ_1^-, Γ_2^-, Γ_3^-, and Γ_5^- symmetry, which are only allowed in three-photon absorption, as can be easily derived with the use of the tables of Koster *et al.*[2] In this Letter we present the first demonstration of such a one-photon–forbidden transition. Again the alkali halides are chosen, since they show strong odd-parity exciton transitions. Among the alkali halides the cesium halides have attracted much interest recently, since application of hydrostatic pressure causes a drastic red shift of the band gap.[3] There are even predictions of metallization of these ionic crystals at superhigh pressures.[3,4] Kuznetsov *et al.*[5] showed that in CsI, excitons derived from the lowest d conduction band (Γ_8^+ symmetry) shift to lower energy by 0.25 eV under hydrostatic pressure of 120 MPa. We were able to resolve a new, very narrow exciton line of Γ_5^- symmetry in CsI, which is assigned to the same d conduction band. The width of this line is only 0.2 meV at 4.2 K. This small linewidth makes possible, for the first time, the direct observation of the Zeeman splitting of an exciton transition in alkali halides. In one-photon absorption, g values of the Γ_4^- exciton can only be determined by magnetoreflectance[6] or magnetoabsorption dichroism,[7] because the linewidth of about 30–50 meV is much larger than the expected Zeeman splitting (about 1 meV at 9 T).

For our measurements we used ultrapure single crystals of CsI which were cut for measurements in three orientations ([001], [110], and [111]). The crystals were oriented by use of stress-induced birefringence as described by Maier.[8] The magnetic fields for the measurements in the Faraday configuration were produced by a superconducting magnet at 4.2 K; fields up to 9 T were available. As a light source we used a frequency-doubled Nd-doped yttrium-aluminum-garnet laser (Quanta Ray model DCR-2 A) to pump a tunable dye laser (Lambda Physik model FL 2002). Three-photon absorption was detected via the luminescence of the self-trapped exciton at 290 nm.

In Fig. 1 we present a three-photon spectrum of CsI and the one-photon data of Teegarden and Baldini.[9] The three rather broad lines correspond to transitions to the upper polariton branch of the Γ_4^- excitons which are also seen in the one-photon spectrum at slightly lower energies.[1] The interesting new feature is the very narrow line at about 5.8 eV, which cannot be seen in one-photon absorption. In Fig. 2 we present three-photon spectra of this new line in zero field and in a magnetic field of 9 T for three different geometries of the crystal with respect to the magnetic field. The measurements are done with circularly polarized light. In zero field we see a narrow line at 5.8076 eV for all three orientations. In higher fields we get drastic differences for the three geometries.

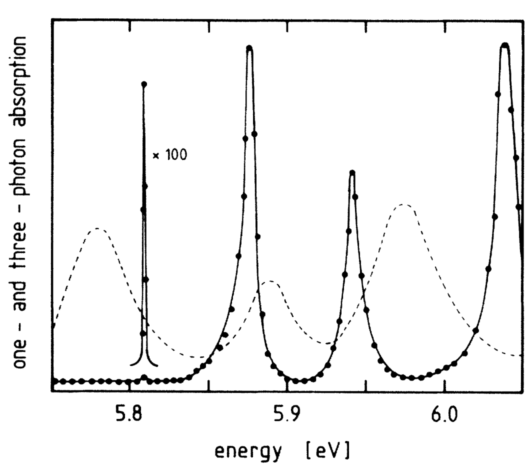

FIG. 1. Three-photon spectrum of CsI at 4.2 K. One-photon data at 10 K (dashed line) are taken from Ref. 9.

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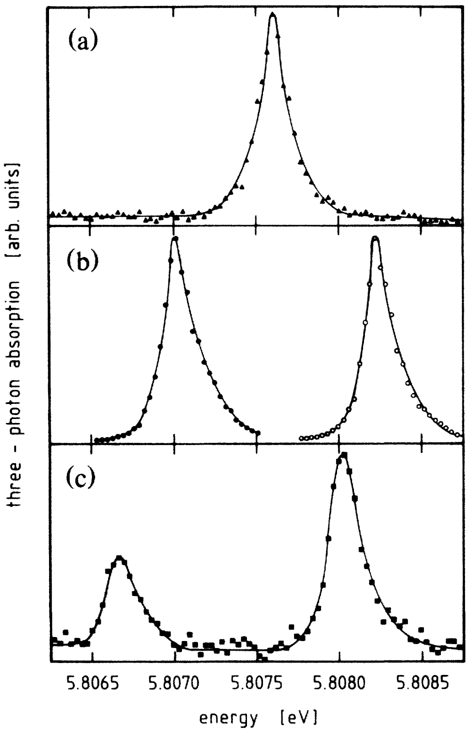

FIG. 2. Three-photon absorption of narrow exciton structure in CsI at 4.2 K for different orientations and strengths of magnetic field in Faraday configuration: (a) Γ_5^- exciton transition in zero field. (b) Zeeman splitting of $\Gamma_5^-(\pm 1)$ excitons in a magnetic field of 9 T and [001] orientation. The lower-energy component (filled circles) is excited with right-handed circularly polarized light, the higher-energy component (open circles) with left-handed circularly polarized light. (c) Spectrum of $(\Gamma_5^-(0), \Gamma_3^-)$ mixed states in magnetic field of 9 T and [110] orientation.

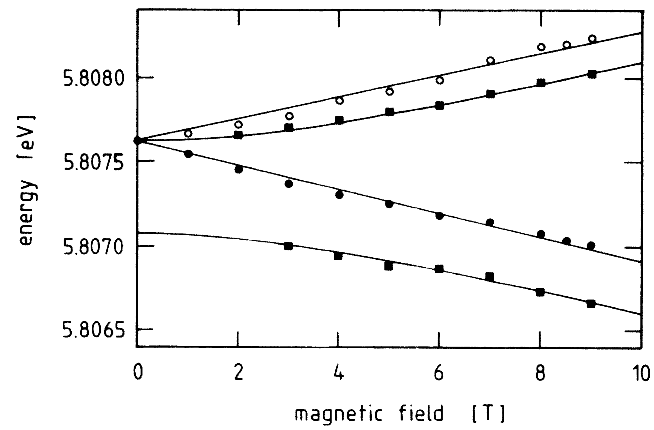

FIG. 3. Field dependence of $\Gamma_5^-(\pm 1)$ splitting and $(\Gamma_5^-(0), \Gamma_3^-)$ mixing. Filled and open circles show $\Gamma_5^-(+1)$ and $\Gamma_5^-(-1)$ components, respectively, filled squares the $(\Gamma_5^-(0), \Gamma_3^-)$ mixed states. Solid lines represent fit with parameters given in the text.

For a field parallel to a [001] direction two Zeeman components are selectively excited with use of light of different helicity. With [111] orientation we find only one line which coincides with the line in zero field within the present reproducibility of our spectroscopic data. Interesting behavior is seen in the [110] orientation, where a new line is detected at slightly lower energies, which apparantly gains oscillator strength from the main line in a magnetic field.

From the analysis of the orientation and polarization dependence we assign the narrow line to an exciton of Γ_5^- symmetry, which splits in a magnetic field into three components, $\Gamma_5^-(0, \pm 1)$. In the [001] orientation only $\Gamma_5^-(\pm 1)$ can be seen. This fact can be understood by consideration of three-photon absorption as a two-step process via a Γ_5^- intermediate state (two-photon allowed). As was shown in detail by Fröhlich and Kenklies,[10] one reaches with $(++)$ or $(--)$ light in the [001] orientation only the $M=0$ component of the Γ_5^+ intermediate state. With the third photon the transition from $\Gamma_5^+(0)$ to the final states $\Gamma_5^-(+1)$ or $\Gamma_5^-(-1)$ is then induced depending on the polarization. In the [110] and [111] orientations, however, one can excite only the $M=\pm 1$ components of the Γ_5^+ intermediate state if both photons have the same helicity. With the third photon one induces the transition from $\Gamma_5^+(\pm 1)$ to the final state $\Gamma_5^-(0)$. The field-induced mixing of the Γ_3^- state into the $\Gamma_5^-(0)$ component in the [110] orientation can also be understood by group theory with use of the tables of Koster *et al.*[2] In Fig. 3 the field dependence for the different lines in various orientations is shown. From the linear field dependence of the splitting of the $\Gamma_5^+(\pm 1)$ components ([001] orientation) one can deduce an effective g value of $g_{\text{eff}} = 1.17 \pm 0.03$. The g value is defined by $\Delta E = E(-1) - E(+1) = 2 g_{\text{eff}} \mu_B B$ (μ_B is the Bohr magneton). For the [110] orientation one has to consider the field-induced mixing of the $\Gamma_5^-(0)$ component and the Γ_3^- state. From the fit of the data by a square-root dependence (which follows from the diagonalization of a 2×2 matrix), we deduce for the zero-field splitting

$$\epsilon_p = E(\Gamma_5^-) - E(\Gamma_3^-) = 0.54 \pm 0.04 \text{ meV}.$$

For the off-diagonal g value, which is equal to the off-diagonal matrix element in units of $\mu_B B$, we find $g(\Gamma_5^-, \Gamma_3^-) = 1.20 \pm 0.03$.

To begin discussion of our results, we refer to the publication of Iwamoto and Onaka,[7] who determined g values of the one-photon-allowed Γ_4^- excitons (T_{1u} symmetry in Ref. 7). We tentatively assign the new Γ_5^- line (T_{2u} symmetry in Ref. 7) to a spin-allowed transition (orthoexciton) from the upper valence band (Γ_8^- symmetry) to the second conduction band (Γ_8^+

symmetry). The Γ_3^- line which is seen only in a magnetic field is interpreted as a transition to a paraexciton due to the same $\Gamma_8^- \rightarrow \Gamma_8^+$ transition. Other paraexcitons of Γ_1^-, Γ_2^-, and Γ_5^- symmetry are expected from group theory, and should be detectable in high magnetic fields of proper orientation. We plan to do further experiments using also the Voigt configuration to identify these excitons. Another challenging task is to look for the paraexcitons of the lowest ($\Gamma_8^+ \rightarrow \Gamma_6^+$) transition. These excitons also have Γ_5^- and Γ_3^- symmetry and are expected below the first exciton in the one-photon spectrum. Our g values cannot be compared directly to the one-photon results of Iwamoto and Onaka,[7] since they investigated the Γ_4^- excitons. A detailed theoretical analysis of all three-photon measurements along the lines of Ref. 7 has to be done, which will then allow us to compare the different g values. For this comparison it might be of interest to take the polariton character of the Γ_4^- excitons into account in the calculation of g values. A wave-vector–dependent splitting of polaritons can be expected, as was recently demonstrated for CuCl by Fröhlich, Hölscher, and Mohler.[11]

It would certainly be very interesting to study the temperature dependence of the linewidth of the Γ_5^- exciton. At 4.2 K it is smaller by a factor of 100 than those of the Γ_4^- excitons. A detailed analysis of the linewidth of the Γ_5^- and Γ_4^- excitons should give information about exciton-phonon interactions. It would be particularly interesting to explain why the linewidth of the polariton and longitudinal exciton of Γ_4^- symmetry is so much larger than the linewidth of the Γ_5^- exciton.

The narrow Γ_5^- line would be ideally suited for study of its pressure dependence. The comparison with the one-photon data of Kuznetsov *et al.*[5] would allow a definite assignment of the Γ_5^- exciton to the *d*-conduction band.

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