Three-photon difference-frequency spectroscopy of polaritons in alkali halides

D. Fröhlich, St. Kirchhoff, P. Köhler, and W. Nieswand
Institut für Physik, Universität Dortmund, 4600 Dortmund 50, Federal Republic of Germany
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Three-photon difference-frequency generation is used to study resonances on the lower polariton branch of alkali halides. The resonances show a spectacularly small linewidth of about 0.12 meV. This small linewidth allows us for the first time to resolve the splitting of the lower polariton in a magnetic field. A pronounced dependence of this splitting on the total **k** vector is observed.

Exciton polaritons have gained much interest recently. For a review we refer to Bassani and Altarelli.[1] In a microscopic quantum theory of exciton polaritons Bassani, Ruggiero, and Quattropani[2] distinguish between "tightly bound excitons" (Frenkel type) and "shallow excitons" (Wannier type). The authors predict interesting effects considering the dispersion near $\mathbf{k}=\mathbf{0}$ for tightly bound excitons which are expected in molecular crystals or solid rare gases. Experimental results which might confirm these findings were not available up to now. Excitons in alkali halides are also tightly bound and are considered of Frenkel type. Resonances on the upper polariton and the longitudinal exciton of KI and CsI were first seen by Beerwerth and Fröhlich[3] with the use of three-photon spectroscopy (TPS). Although the linewidth of these resonances ($\Delta E \sim 22$ meV) is smaller by about a factor of 2 than the linewidth of one-photon absorption,[4] it is still much too large to resolve the dispersion of the longitudinal exciton or to get reliable data of the splitting of the upper polariton in a magnetic field.

The dynamical behavior of excitons determines the line shape, as was first discussed in detail by Toyozawa.[5] He calculated the relaxation of the exciton polariton by phonon emission to the bottleneck on the lower polariton branch. The expected much longer lifetime in the region of the bottleneck should show up in a much smaller linewidth of the resonances on the lower polariton branch. By TPS one can only reach resonances on the upper polariton and the longitudinal exciton, because the exciting laser photons give rise to polaritons on the lower branch, which bends over to higher **k** values if one gets closer to the resonance (region of normal dispersion). Therefore, the fusion of three polaritons cannot lead to resonances on the lower branch.

In this Brief Report, we report for the first time resonances on the lower polariton in a crystal with inversion symmetry. We achieved the necessary large **k** vectors by applying three-photon difference frequency generation (TP-DFG). The principle of TP-DFG to polaritons on the lower branch is shown schematically in Fig. 1. The maximum **k** vector ($K_1+K_2+K_3$) of the polariton in the direction of the total **k** vector of the "absorbed" laser photons (up-going arrows $\mathbf{k}_1$ parallel $\mathbf{k}_2$) is achieved if the **k** vector $\mathbf{k}_3$ of the "emitted photon" (down-going arrow) is antiparallel to $\mathbf{k}_1$ and $\mathbf{k}_2$. It should be noted, that $\hbar\omega_1+\hbar\omega_2$ is larger than the gap energy E_g; one, therefore, expects two-photon absorption (TPA) to higher exciton states (P excitons) or continuum states. Fast relaxation processes from these real intermediate states will certainly diminish the TP-DFG signal, since energy conservation ($\hbar\omega_{\mathrm{DF}}=\hbar\omega_1+\hbar\omega_2-\hbar\omega_3$) is no longer given for these relaxed excited states. Although possible resonances by TPA for the intermediate step lead to competing relaxation processes, they should also give rise to a considerable resonance enhancement due to the two-photon resonances in the relevant $\chi^{(3)}$ component. The experimental results show that there is a large coherent (nonrelaxed) component left which is deconverted by difference frequency (DF) generation to an outgoing polariton from the lower branch of energy $\hbar\omega_{\mathrm{DF}}$. Besides the fact that resonances on the lower polariton branch can be reached by TP-DFG, this technique has to be distinguished in another important point from TPS. In the TPS experiments[3,6] the three-photon absorption is monitored by the subsequent emission from the self-trapped exciton. Light is emitted into the whole solid angle, although a polariton with well-defined **k** vector is excited. The **k** and polarization memory is lost in the relaxation process. In TPS, the creation of a polariton by fusion of three polaritons in the crystal is monitored by the subsequent decay via its *exciton* part. In TP-DFG, on the contrary, the outcoming photon beam is highly collimated and its polarization yields information on the relevant tensor component of $\chi^{(3)}$. In this case the creation of a polariton is monitored by the subsequent decay via its *photon* part. The longitudinal exciton (LE), however, cannot be detected by TP-DFG, since the pure LE does not have a photon component. Resonances on the lower polariton and the longitudinal exciton of CuCl were measured by Hönerlage, Bivas, and Vu Duy Phach by resonant two-photon Raman scattering.[7] In this case biexcitons are virtually created by absorption of two polaritons. They decay by spontaneous emission to a longitudinal exciton or a transverse polariton. With the use of a second beam Hönerlage, Levy, and Grun[8] have induced the decay of virtual biexcitons, which leads to a strong coherent signal. Our technique can also be termed as nondegenerate four-wave mixing. Contrary to CuCl we are not close to a resonance with one pump photon (1*S* exciton in CuCl) and there is no other strong resonance for the vir-

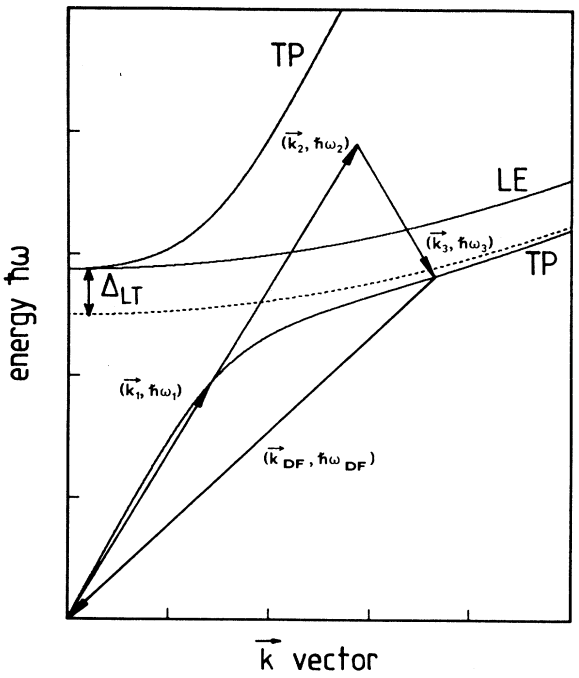

FIG. 1. Schematic polariton diagram to demonstrate TP-DFG. TP, transverse polariton; LE, longitudinal exciton; Δ_{LT}, longitudinal-transverse splitting; $(\mathbf{k}_i, \hbar\omega_i)$, $i=1,2,3$, refer to incoming polaritons; $(\mathbf{k}_{DF}, \hbar\omega_{DF})$ refers to the polariton at the difference frequency.

tual excitation by two photons (biexciton in CuCl).

In our experiments we had to use a variety of laser sources in order to span the large region in $\mathbf{k}$ space. For $\mathbf{k}$ values between 8×10^7 and 10×10^7 m^{-1} we used two tunable dye lasers (Lambda Physik FL 2002) which were pumped by the same frequency-doubled and frequency-tripled Nd-doped yttrium-aluminum-garnet (YAG) laser (Quanta Ray DCR-2A). For higher and lower $\mathbf{k}$ values (up to 12.3×10^7 m^{-1} and down to 5.5×10^7 m^{-1}) we used one fixed frequency laser (Raman-shifted YAG at 0.6497 eV, YAG at 1.164 75 eV, and third harmonic of YAG) and a tunable dye laser, which was frequency doubled. In order to achieve a spectral resolution of about 50 μeV we had to use an étalon in the YAG laser to get lasing on a single longitudinal mode. The main problem of these experiments is scattered light from the high-intensity laser sources, which has to be filtered out to allow the detection of the rather weak uv signal in the spectral region between 214 and 240 nm. A special optical filter, which consists of four Pelin Brocca prisms and a quartz prism monochromator with a solar-blind photomultiplier as a detector, was sufficient to achieve the necessary suppression of scattered laser light (about $1:10^{16}$). Measurements were done in an immersion cryostat at a temperature of about 1.5 K and in a superconducting magnet in Faraday configuration at 4.2 K: fields up to 7 T were applied.

In Fig. 2 we present as an example two resonances on the lower polariton branch and for comparison a resonance on the upper branch and the one-photon spectrum from Teegarden and Baldini.[4] The most striking result is

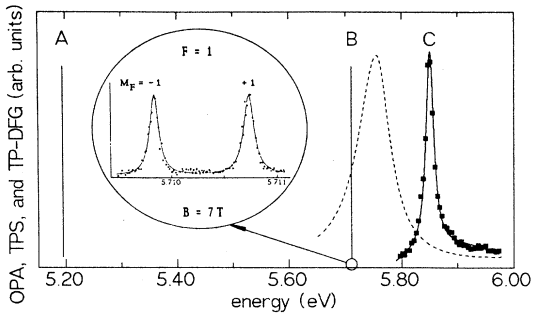

FIG. 2. TP-DFG spectra of two resonances on the lower polariton branch (A, 5.195 eV; B, 5.710 eV) in RbI at 4.2 K. For comparison one resonance on the upper polariton (C, 5.850 eV) is also shown. The one-photon spectrum (dashed line) is taken from Ref. 4. The inset shows the splitting of the B resonance in a magnetic field of 7 T.

the very narrow linewidth (about 120 μeV) of the new lines as compared to about 22 meV for resonance on the upper polariton and even 50 meV for the one-photon data. These narrow lines allow one to measure for the first time the splitting of the polariton in a magnetic field as indicated in the inset in Fig. 2. There are several attempts to determine g values for the first exciton in alkali iodides by one-photon experiments. Ahrenkiel and Teegarden[9] were the first who derived an effective g value of about 0.9 for KI and RbI by magnetoreflectance. Later measurements of the magnetic circular dichroism by Onaka and Kita[10] yielded temperature- and even thickness-dependent values for the effective g values. At 77 K the authors report for KI g values between 0.57 and 1.0 and for RbI g values between 0.56 and 0.67. Due to the high accuracy of our experimental data, we were able to derive a significant $\mathbf{k}$ dependence of the splitting as shown in Fig. 3 for two $\mathbf{k}$ values (5.5×10^7 and 11.9×10^7 m^{-1}). Without taking the polariton character into account and other complications due to field-induced mixing, the two slopes correspond to g values of 0.86 and 1.12, respectively. The corresponding values for KI at

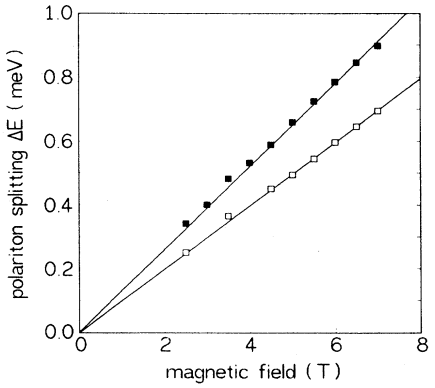

FIG. 3. Field-dependent splitting of resonances on the lower polariton branch in RbI. Open squares, resonance A at $\hbar\omega=5.195$ eV; $K=5.5\times10^7$ m^{-1}; solid squares, resonance B at $\hbar\omega=5.710$ eV, $K=11.9\times10^7$ m^{-1}.

slightly different **k** values (5.6×10^7 and 12.3×10^7 m^{-1}) are 0.85 and 1.09. Contrary to the results of Onaka and Kita,[10] we find very similar values for KI and RbI. Taking the polariton dispersion into account we expect a g value close to 1.12. A final analysis would have to consider the heavy-light hole mixing as discussed by Fishman[11] and Uihlein and Feierabend.[12] At the present it is not clear if a field-induced mixing of the ortho- and paraexciton or a mixing between the orthoexciton of the Γ_8^- valence band ($j=\frac{3}{2}$) and the orthoexciton of the Γ_6^- valence band ($j=\frac{1}{2}$) also has to be considered in order to account quantitatively for the **k**-dependent splitting. Measurements at still higher **k** values should help to clarify this point, since the lower polariton is expected to cross the paraexciton [$E_p=5.7266$ eV (Ref. 6)] at about $k=15\times10^7$ m^{-1}. Further measurements (possibly for different crystal orientations) will be necessary to clarify if it is sufficient to consider only the Γ_8^- ($j=\frac{3}{2}$) valence band, as was done in the case of CuBr by Merle *et al.*[13] or if the split-off band of Γ_6^- symmetry ($j=\frac{1}{2}$) has to be included in the analysis.

In Fig. 4 we present the polariton dispersion of RbI. The solid and dashed lines represent a fit to a two-oscillator model as discussed in Ref. 6. The narrow resonances on the lower polariton allow us to determine the longitudinal-transverse splitting Δ_{LT} and the exchange interaction Δ_{ex} with higher accuracy than was possible in the TPS experiments.[6] A first analysis, which has to be refined by including spatial dispersion and possible mixing effects mentioned before, yields $\Delta_{LT}=98$ meV for KI and RbI. For Δ_{ex} we get 29 and 33 meV for KI and RbI, respectively. The Δ_{LT} values agree quite well with results of Itoh and Hashimoto,[14] who determined the polariton dispersion from the analysis of interference fringes, as measured in thin samples by one-photon absorption. They get $\Delta_{LT}=105$ meV for KI and RbI. The Δ_{ex} values have to be compared to recent data of Itoh[15] who derived Δ_{ex} from the position of the free-exciton luminescence. He got $\Delta_{ex}=20$ and 26 meV for KI and RbI, respectively.

The difference in linewidth by more than 2 orders of magnitude between resonances on the upper and lower polariton can be explained by considering phonon interaction as the main decay process. Phonon emission processes which are the dominant decay mechanism at low temperatures are much less probable for the lower polariton states because there are no excitonlike states below these polaritons as final scattering states available contrary to the polaritons on the upper branch. A detailed study of the temperature dependence of the linewidth should clarify this point.

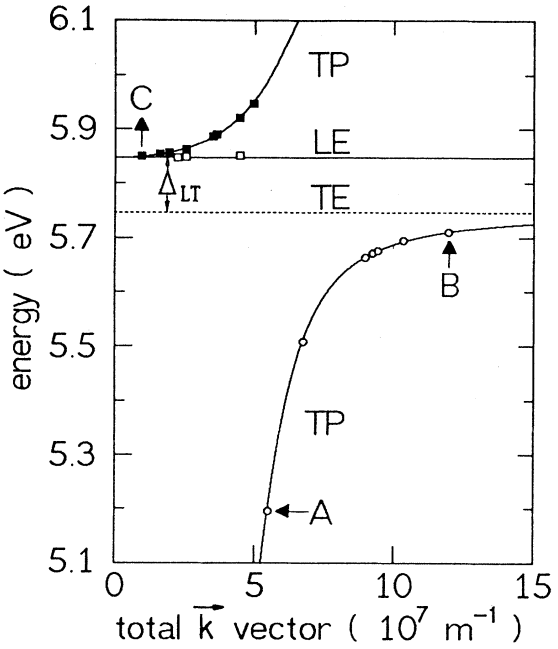

FIG. 4. Resonances on the upper and lower polariton branches and the longitudinal exciton in RbI. $A-C$ refer to the resonances as indicated in Fig. 2.

We are convinced that this technique of three-photon difference spectroscopy can be applied to many other interesting substances. Polaritons in semiconductors and possibly two-dimensional structures as multiple quantum wells are good candidates for further experiments.

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