Linewidth Collapse in Three-Photon Exciton-Polariton Spectra of CsI under Pressure

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Unusual phenomena occurring under hydrostatic compression in the near-band-edge structure of CsI crystals were examined using the nonlinear optical technique of three-photon excitation. The lowest one-photon allowed transition to the exciton-polariton A of Γ_4^- symmetry redshifts, while the one-photon forbidden paraexciton C of Γ_5^- symmetry blueshifts to a crossing of energies at 4.4 kbar. During this process, the A level exhibits strong spectral line narrowing by more than a factor of 10, while the C level intensity increases by about the same factor. We believe this is the first reported observation of pressure induced line narrowing of deep UV electronic states in solids.

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CsI, a prototypical insulator and ionic crystal, has been the object of intensive high pressure investigations in the past, since it eventually metallizes under compression and enters a superconducting phase when compressed further [1,2]. These two effects are tied directly to the electronic structure of the crystal and to the interaction of the charge carriers with the phonons. Hydrostatic compression will tune the energies of the electronic and phonon states without necessarily changing the crystal symmetry, thus providing detailed information about their interaction. In particular, this Letter describes anomalously strong spectral line narrowing resulting from this interaction.

Among the alkali halide crystals, the cesium halides (CsI, CsBr, CsCl) form a special group not only because of their different crystallographic structure (CsCl, B2) but also because of the complexity of their electronic band structure compared with the lighter alkali halides. The p state of the halide ion forms the valence band for all alkali halides (e.g., $5p$ for iodine), and the bottom of the conduction band appears to be mainly of s-like symmetry (e.g., cesium $6s$). For the cesium halides, additional bands of d-like nature are found very close to the s-like state (e.g., cesium $5d$) [3–5]. Interactions among the levels can occur. When the CsI crystal is hydrostatically compressed, the p state of the valence band does not change significantly, but the conduction band states reverse their order. The s band increases strongly in energy while the d bands experience a large redshift [5–11].

This CsI s-d reversal has so far been observed by probing the three excitonic states of Γ_4^- symmetry below the band gap using optical one-photon spectroscopy (OPS) experiments [9,10]. Those results indicated an avoided crossing of the states, a Fermi resonance between the s and d band derived conduction band levels, at about 4–6 kbar when $T = 80$ K. A better alternative to the OPS experiments is offered by the relatively new technique of three-photon spectroscopy (TPS) [12]. This technique allows one to access states with Γ_5^- symmetry as well as Γ_4^- symmetry. The first state of $\Gamma_5^-(s)$ symmetry at 5.808 eV is the paraexciton, derived from an s band [13]. The other state of symmetry $\Gamma_5^-(d)$ at 5.96 eV requires circularly polarized light and was lost in our spectra at higher pressures. Under conditions of low temperature and zero pressure, the TPS excitation spectra of both Γ_5^- states are much less intense (several orders of magnitude in peak height) than the Γ_4^- excitations. The actual level scheme at zero pressure and low temperature has been mapped out, and values for the transverse and longitudinal energies were obtained at low temperature and zero pressure [13]. Through TPS, we are able to report for the first time behavior of low lying excitonic states of CsI under pressure. These are (a) crossing of the first triplet state (Γ_5^-) and the first singlet state (Γ_4^-) at $\approx$4.4 kbar, (b) direct observation of collapsing of the polariton linewidth of the first singlet state (by more than a factor of 10, over a pressure range of only 2800 bars), and (c) an indirect observation of the collapse of the stop gap region between the longitudinal and transverse exciton energies.

A recent description of the dispersion, $E = E(k)$, of the coupled photon-exciton entity, the exciton-polariton, is presented by Nakajima *et al.* [14]. There are three polariton branches, namely, upper and lower transverse polariton branches and a longitudinal exciton branch. The upper and lower transverse polariton branches have drastically different dispersions from that of the pure transverse exciton branch and are separated by a totally reflecting region (stopgap) between the transverse exciton and the longitudinal exciton energies. The longitudinal exciton branch has qualitatively the same dispersion as that of the transverse exciton, but with higher energies, and is nearly flat. It is also degenerate with the upper polariton branch at $k = 0$. In the conventional one-photon absorption measurements, the spectral profiles are dominated by the reflection losses in the stopgap region. These reflection losses are quite often neglected and can generate significant spectral shifts [15–17].

In our single pump beam experiment, three polaritons, together in the forward direction, $\rightarrow\rightarrow\rightarrow$, create a polariton on the upper transverse polariton branch having total energy E and wave vector $3k$, where k represents the wave vector of the photon within the crystal. Also, a polariton of similar energy is formed but with wave vector $1k$,

$\rightarrow\rightarrow\leftarrow$, which is produced with the help of the reflected beam from the exit surface of the pressure cell window (highly polished sapphire). Since the reflected beam has significantly smaller intensity than the incoming beam, our spectra will always show greater intensity for the $3k$ than the $1k$ peak. These k and $3k$ energy values are used to find the longitudinal exciton energy, E_L, using the expansions $E_{1k} = E_L + Ak^2$ and $E_{3k} = E_L + A(3k)^2$, where A is the polariton curvature parameter, and E_{1k} and E_{3k} are measured energies corresponding to the wave vectors k and $3k$, respectively.

The present experiments for CsI were performed at 9 K in the 0–6 kbar range using TPS. The sample was mounted in a sapphire ball high pressure cell connected to a two-stage gas pressure intensifier [18]. Helium was used as the pressure medium because it ensured the best hydrostatic conditions for the sample. The quality of the hydrostatic conditions is important for the success of the TPS experiments [19]; e.g., the use of argon instead of helium would probably destroy the spectra as was observed to be the case for KI [20]. More details about the method and experiment can be found in Ref. [21]. The resonances were detected through the luminescence of the self-trapped exciton (STE) state at 3.7 eV [22]. Figure 1 shows the TPS spectra of CsI obtained in this way for three different pressures. The three polariton peaks of Γ_4^- symmetry [at $P = 0$: 5.875 eV (peak A), 5.940 eV (peak B), and 6.015 eV (peak D)] are the prominent ones. The weak and narrow paraexciton peak C (pure triplet state) is at 5.808 eV (at $P = 0$). The nomenclature for A, B, and C has been kept the same as in Ref. [23] for consistency.

The most dramatic observation in the present hydrostatic pressure investigation of CsI pertains to the behavior of the A polariton and the C paraexciton. Their longitudinal exciton energies are plotted in Fig. 2. The paraexciton band is blueshifted with pressure, approaching the A level with an initial rate of 14 meV/kbar and growing rapidly in strength. Eventually the intensity becomes about a factor of 20 stronger than that at zero bar. Initially, the A polariton energy does not decrease under compression; however, its integrated intensity decreases rapidly. The FWHM of A_{3k} and A_k both drop at least a factor of 10 from more than 11 and 19 meV, at 80 bar to the resolution limit of our original dye-laser setup of less than 1 meV, at 2.8 kbar (see Fig. 3). The C paraexciton band and A appear to intersect without interaction at about 4.4 kbar, within the rather tight resolution limits of the experiment. Shortly after the crossing, the $\Gamma_5^-(s)$ paraexciton starts turning around. This possibly is due to the Fermi repulsion from the redshifted $\Gamma_5^-(d)$ state (the pressure dependence of this peak energy is not available). Assuming a linear relationship, linewidth of A decreases at about 3.7 meV/kbar.

At 2.8 kbar, the lattice constant has changed by less than 1%, but the linewidth of A has collapsed to 1 meV while the two states are still separated by 20 meV. The linewidth of the C paraexciton does not experience the same dramatic change. In fact, up to the highest pressure measured, the FWHM stays at the same (instrument broadened) value near 1 meV. Figure 4 displays the pressure dependence of the linewidths. It is difficult to draw quantitative values

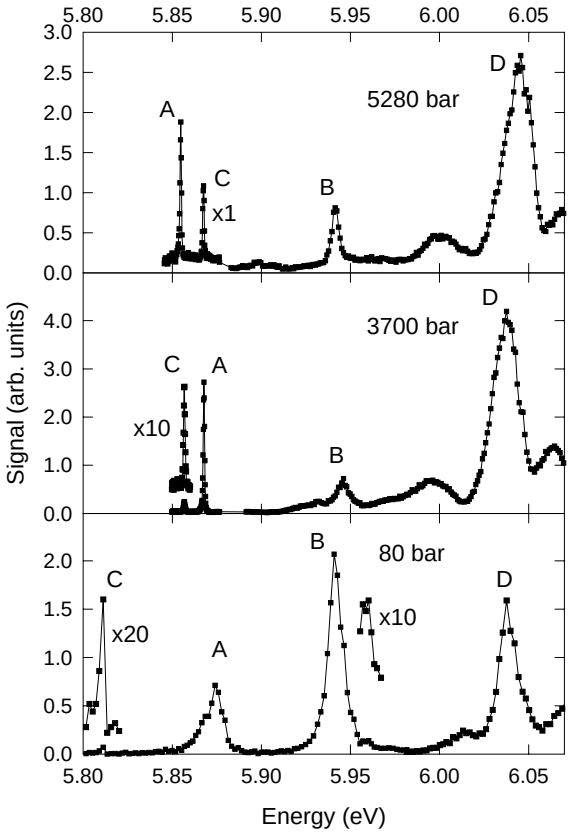

FIG. 1. CsI excitation spectra at three different pressures at 9 K.

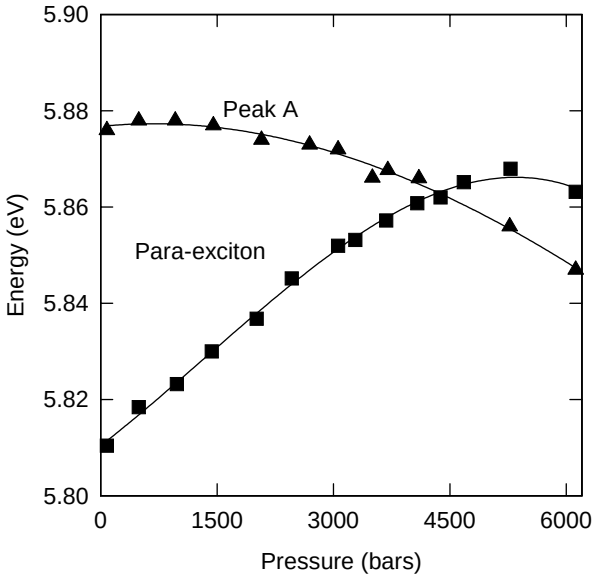

FIG. 2. Pressure dependence of the Γ_5^- paraexciton C and of the Γ_4^- polariton A in CsI.

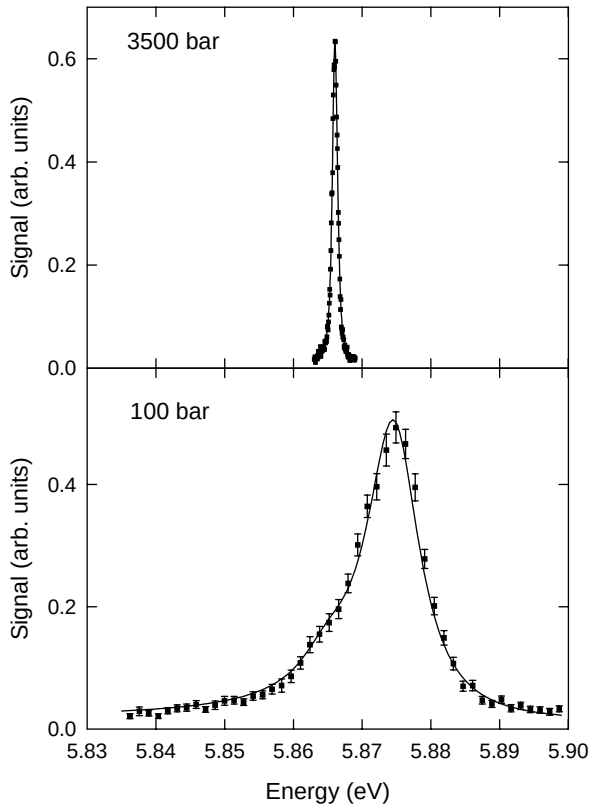

FIG. 3. The CsI Γ_4^- A polariton ($\Gamma_8^- \rightarrow \Gamma_6^+$) and its reduction in linewidth demonstrated at two different pressures. The bottom panel shows $A(k)$ as a shoulder to the larger $A(3k)$.

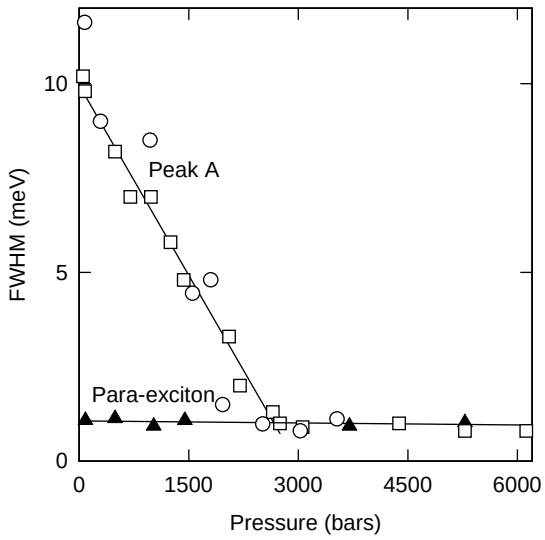

FIG. 4. CsI $A(3k)$ polariton: Linewidth dependence on pressure at 9 K. Hollow symbols represent the linewidth of A and solid ones the linewidth of the paraexciton, C. Square and circle symbols represent different runs. The linewidth data for $A(k)$ are not shown but it also collapses at 2.8 kbar.

from the decrease in integrated intensity since we observe luminescence from only one particular STE. The linewidth values, however, should be trustworthy provided the efficiency for the 3.7 eV STE decay channel remains approximately constant across the line. We expected the linewidth to decrease even further, e.g., to about the same FWHM value that the paraexciton exhibited under low pressure and temperature (0.2 meV at $T = 4$ K and $p = 0$ bar [23]). Changing the dye laser to one with a smaller linewidth, however, revealed that the linewidth of 1 meV was not caused by the new instrument resolution (approximately 0.1 meV) but appears to be intrinsic.

The rather large linewidth observed for the first exciton peak using OPS for many alkali halides prompted Onodera and Toyozawa [24] to suggest that there must be a hidden exciton state (triplet state) below the first exciton peak. The first measurement confirming the prediction of such a state in CsI was made by Beerwerth and Fröhlich [25] using TPS. In their work, the paraexciton state was assigned tentatively as Γ_5^- belonging to the d-like conduction band of the Cs ion. They suggested that a pressure dependent measurement may give a definite assignment to paraexciton state. In a later work, they assigned the paraexciton peak as Γ_5^- belonging to the s-like conduction band which followed from their analysis of the temperature dependent measurements [13]. Our pressure dependent measurements support this latter conclusion, since the paraexciton peak is shown to be blueshifted with pressure, a characteristic which marks it as likely belonging to the s-like conduction band. The narrow linewidth of the paraexciton peak C is attributed to a potential barrier hindering a fast relaxation to the STE which is reached from the paraexcitonic state by tunneling with a rate of 5×10^{10} s^{-1} at zero pressure [23].

Possible scattering mechanisms of the A polariton are (a) interbranch phonon assisted scattering from the upper to the lower polariton branch, (b) interband phonon assisted scattering to the paraexciton band, (c) trapping by impurities, and (d) direct self-trapping of the excited electron-hole pair. The broad linewidth of the A polariton leads to the prediction of the paraexciton band below it. It is interesting to note, however, that the broad linewidth of A at low temperature and pressure was initially attributed to a fast decay by emission of LO phonons to the lower polariton branch, and not to the paraexciton branch [23], indicating that mechanism (a) is the dominant decay channel at zero bar. Our pressure dependent measurements seem to support this conclusion as well, even though the collapsing of the A linewidth occurs as the paraexciton C rises to and above the A state. By the time the linewidth has collapsed, the A and C states are still 20 meV apart, and the highest energy LO phonons (at the zone center) in CsI are $\approx$11 meV. The one-phonon density of states (DOS) itself has maxima for phonon energies of about 6 and 8 meV. A decay from A to C would therefore require at least two LO phonons. The two-phonon DOS is not directly known but is likely to have maxima near sums of one-phonon spectrum singularities. Therefore, it is more likely that the longitudinal-transverse (LT)

splitting has decreased to a value $\leq$ the LO phonon energy, about 10 meV, thus eliminating decay mechanism (a). This is supported by our observed reduction in oscillator strength of *A*, which indicates a decrease in the LT splitting between the upper and lower polariton branches under compression. In an approximation, the microscopic polarizability α (which is related to the oscillator strength) is directly proportional to the longitudinal-transverse energy splitting, Δ_{LT}; i.e., for small α, we have $\Delta_{\mathrm{LT}} = E_L - E_T \approx \omega_T(\alpha/2\epsilon_b)$, where ϵ_b is the background dielectric constant. To support this conjecture further, it would be very helpful to obtain direct experimental data of the LT splitting under hydrostatic compression.

The most fascinating observation of our high pressure investigation of CsI was the decrease of the *A* polariton (the lowest singlet excitonic state of Γ_4^- symmetry) linewidth by more than a factor of 10 over a pressure range of only 2.8 kbar. The observations demonstrate that in CsI the linewidth and thus the electronic structure are very sensitive to hydrostatic compression since the lattice constant has changed by only about 0.8% over the same pressure region and no phase transition is observed. The dominant relaxation mechanism via LO-phonon creation to both the lower polariton branch and possibly the paraexciton branch is already turned off $\approx$1.7 kbar before the intersection of the *A* and the *C* states at 4.4 kbar. Further experiments should clarify whether the present observations pertain to CsI only or can be extended to other Cs halides like CsBr and CsCl.

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