Band-structure parameters and Fermi resonances of exciton-polaritons in CsI and CsBr under hydrostatic pressure

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Most alkali halides crystallize in the fcc sodium chloride structure. In contrast, with the exception of CsF, the Cs-halides form the simple cubic cesium chloride (CsCl) structure at ambient conditions and they have a substantially different electronic structure than other alkali halides; in particular, they have several nearly degenerate electronic levels near the Brillouin zone center. Highly resolved three-photon spectroscopy (TPS) measurements allow direct observation of the near band edge structure and, in the case of CsI, probe more states than one-photon techniques. A number of interesting phenomena, among them level repulsion (Fermi resonance), occur as these levels are tuned through one another by application of hydrostatic pressure. Doubling the photon energy range compared to a previous publication [see Yoo *et al.*, Phys. Rev. Lett **84**, 3875 (2000)] allows direct observation of the $n=1$, 2, and 3 exciton-polariton members of the Γ_8^--Γ_6^+ transition in CsI and lets us establish unambiguous values for the band gap (6.135 eV), binding energy (0.263 eV), and their pressure dependence up to 7 kbar. Similarly to CsI, the CsBr linewidth of the lowest Γ_4^- polariton (A) decreases upon compression and its bandgap must be higher than 7.20 eV.

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I. INTRODUCTION

The behavior of the cesium halides (CsI, CsBr, CsCl) under compression has been of interest to solid state physics for a long time. Their crystallographic structure (CsCl, B2) differs from other alkali halides (NaCl, B1) and their electronic band structure, especially close to the band gap, is more complicated. The valence band for all alkali halides is formed by the p state of the halide ion ($4p$ for bromine, $5p$ for iodine) and the bottom of the conduction band is mainly of s-like symmetry (e.g., cesium $6s$) but for the cesium halides bands of d-like nature are also found very close to the s-state (e.g., cesium $5d$).[1–3] The lowest (one-photon allowed) excitation is formed by the transition from the p-like (Γ_8^-) valence band of the halogen ion to the s-like (Γ_6^+) conduction band of the alkali ion. This exciton, labeled A in this work, is a singlet-triplet mixed state and its creation is dipole allowed. The electronic transitions from the p-like (Γ_8^-) valence band to the two d-like (Γ_8^+) bands of the alkali ion result in a doublet structure higher in energy, and are labeled in this work as B and D. The excitonic B state was originally thought to be a pure spin triplet and its creation thus spin forbidden; one of the first attempts to explain its observation was that fluting (nonparabolic k dependence) of the band extrema made this an optically allowed state.[1] Other assumptions are that the Coulomb energy permits B to mix with the dipole allowed singlet state belonging to the D level.[4]

The p state of the valence band does not change significantly under compression but the conduction band states reverse their symmetries: the s-band increases strongly in energy and the two d-bands experience a large redshift.[3,5–9] Therefore these levels approach each other at first during compression, their interaction increases, and a pressure induced Fermi resonance (anticrossing) results. At even greater pressures the upper level eventually takes on the s-like symmetry and starts to increase in energy with pressure, while the lower level takes on the d-like symmetry and decreases.

This inversion of the order of the $6s$-like and $5d$-like conduction bands of CsI under hydrostatic pressure was predicted almost 40 years ago[10] and was based upon the measurement of the deformation potentials of the representative exciton peaks up to 3.4 kbar. The intersection of the bands was estimated to occur at 7 kbar. Due to the similarity in the electronic structure, the same behavior should be exhibited by the other two Cs halides but, to the best of our knowledge, has not yet been observed experimentally.

Under much higher pressure, the Cs halides undergo a phase change from simple cubic to tetragonal.[11–17] Since neither KI or RbI exhibit this transition, it has been assumed that the low lying Cs $5d$-states help in distorting the $B2$ structure to the tetragonal phase.[16] Eventually, the band gap between the p and d-states closes and CsI metallizes.[18,19]

The "s-d flip" has so far been observed in optical "one-photon" (OP) experiments for CsI only.[8,9] No such data exist with regard to CsBr. In those OP experiments incoming light excites electrons out of the valence band and results in the formation of excitons that easily absorb light with energy very close to the band gap. Due to the very high absorption coefficient for direct gap insulators near the band gap (on the order of 10^7 m^{-1}) surface properties are of critical importance in OP spectroscopy.

An alternative to the OP experiments on the alkali halides mentioned above offers the technique of three-photon excitation spectroscopy (TPS).[20] Not only can this technique access the same excitonic states as OPS but additionally can probe states of different symmetry. Since the TPS pump radiation of wide band gap materials has about 1/3 of the exciton energy and the photon energies are far from any system resonances it can propagate undisturbed through the crystal and probe a much bigger volume. OP experiments on the other hand are practically limited to probing the surface and are more suited for thin films. Thus a probing with the

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multiphoton technique has the advantage of not being critically dependent on sample preparation and surface properties.[21]

Optical pumping of the electronic levels leads to an interaction of photons with excitons, which needs to be described within the framework of the (exciton-) polariton picture that will be outlined here briefly for the convenience of the reader. In general, the interaction between different types of excitations in a crystal results in a change of the undisturbed dispersion relations that becomes more pronounced when approaching the region of intersection. If there was only one excitonic energy level in the crystal the polariton dispersion, $E=E(k)$ (with $k=n\omega/c$ as the wave vector), would then consist of three branches, namely the upper and lower "transverse" polariton branches, and a "longitudinal" exciton branch which cannot be probed in single beam experiments (n and $\omega=2\pi\nu$ are the refractive index and frequency of the corresponding laser beam). Upper and lower transverse polariton branches have quite different dispersions from that of the noninteracting transverse exciton branch and are separated by a totally reflecting ("stopgap") region stretching from the transverse exciton to the energetically higher lying longitudinal exciton branch, sometimes referred to as the LT splitting. The longitudinal exciton branch has a very similar dispersion to that of the transverse exciton and is nearly independent of k near the Brillouin zone center. In conventional OP absorption measurements, the spectral profiles are dominated by the reflection losses in the stopgap region, which are quite often ignored even though they can introduce significant spectral shifts.[22–24] However, peaks in reflection from those regions can be observed in OP reflection experiments.

Previous OP observations indicate an avoided crossing (Fermi resonance) of the three Γ_4^- states of CsI occurring at about 4–6 kbar at a temperature of about 80 K: Kuznetsov *et al.*[8] measured 5.76, 5.90, and 5.97 eV for A, B, and D with an uncertainty of ±0.02 eV at zero pressure employing a double reflection technique. Tsujimoto *et al.* observed dips in the excitation spectra of the 3.7 eV self-trapped exciton luminescence band of CsI at about 5.795, 5.92, and 5.98 eV with the same experimental uncertainty interpreting the dips as excitonic energies.[9] OP measurements of CsBr thin films have been reported for pressures up to 3 kbar at room temperature.[25]

Measurements of CsI by TPS are more precise and more detailed. At zero pressure the actual level scheme of the (exciton-) polariton energies has been mapped out at 1.5 K.[26] Besides the three states A, B, and D of Γ_4^- symmetry observed by OP techniques, TPS reveals yet two more states of symmetry $\Gamma_5^-(s)$ and $\Gamma_5^-(d)$ situated below and between the other three at 5.808 eV and 5.960 eV.[26] The $\Gamma_5^-(s)$ state at 5.808 eV was labeled as C in Ref. 27 and we follow here the same nomenclature for consistency. It has been assumed that this paraexciton state C at zero pressure is of almost entirely triplet nature originating from the same s-like conduction band.[27]

Under ambient conditions both Γ_5^- states are much less intense (factors of ~100 and 20 in peak height) than the Γ_4^- excitations. The $\Gamma_5^-(d)$ state is difficult to detect without circular polarization of the pump photons and was lost in our spectra at higher pressures. Our own TPS measurements find values of 5.875, 5.940, and 6.015 eV for the Γ_4^- polaritons at $p=0$.[28] The values are somewhat higher than those measured by OP spectroscopy for similar temperatures, an effect which is caused by the LT splitting, and the linewidths are smaller.[27]

For CsBr, too, the energy values for the excitons have been measured at zero pressure and $T\leqslant 10$ K.[22,26,27] OPS values for the Γ_4^- polariton energies were ~6.80, 7.08, and 7.13 eV. The corresponding TPS values were determined as 6.975, 7.110, and 7.22 eV. Beyond the states of Γ_4^- symmetry a weak feature was observed at 7.136 eV with circularly polarized light, which was attributed to a state of Γ_5^- symmetry.[26]

II. EXPERIMENTAL

The present experiments for the two Cs halides were performed at a temperature of 9 K in the 0–7 kbar range.[29,30] The CsI crystals were acquired from Solon Technologies and the CsBr crystals grown by the Crystal Growth Laboratory of the University of Utah. A freshly cleaved sample was mounted in a sapphire ball cell[31] (SBC) with a maraging steel cylinder of several mm length as a sample container connected to a two-stage gas pressure intensifier. Helium was used as the pressure medium because it ensured the best hydrostatic conditions for the sample. Previous experiments with KI had shown that the use of other pressure media like Ar or even worse, no media at all, resulted in the "breakup" of the spectra with multiple peaks very different from zero pressure spectra which precluded an interpretation. The quality of the hydrostatic conditions has a direct bearing on the success of these kinds of experiments.[21,32] The TPS spectra were obtained using a pulsed nitrogen-laser pumped tunable dye-laser system generating an estimated intensity of 200 $\mathrm{MW/cm^2}$ at the sample.

Further experimental details can be found in Ref. 28 and references therein. The back reflection of the pump-laser beam from the far side of the crystal and sample chamber enabled us in principle to detect two resonances per polariton branch, one with a wave vector value of $1k$ and one with $3k$. A clear distinction between them, however, requires a significant curvature of the polariton dispersion and was not always possible. The resonances were detected through the luminescence of the self-trapped exciton states at about 3.7 eV in CsI as well as in CsBr.[33] Figures 1 and 5 show TPS spectra obtained from CsI and CsBr for different pressures. Estimated uncertainty of the $E(k)$ and $E(3k)$ peak positions themselves is ~1 meV, that of the $E(k=0)$ positions derived from them is higher caused by the data analysis (truncation of the polariton dispersion relation in k). For CsBr the detailed dependence on the dispersion was not taken into account for further analysis.

In contrast to CsI the triplet paraexciton state in the CsBr crystal could not be detected by us, in spite of extensive experimental efforts in the appropriate energy domain. Others have also tried in vain to find this excitation.[27] Nevertheless, the spectral narrowing of the lowest state A as observed

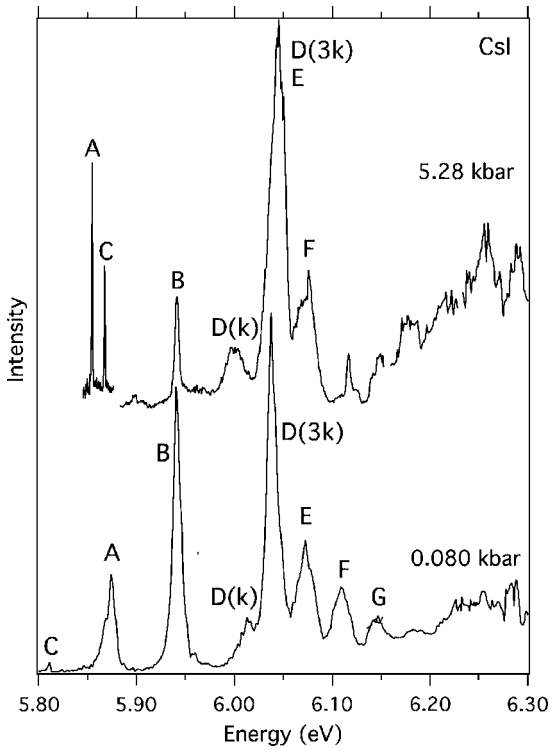

FIG. 1. CsI excitation spectra at two different pressures at 9 K. A, B, and D represent the three Γ_4^- transitions ($n=1$ exciton polaritons), C the $\Gamma_5^-(s)$ paraexciton, E and F the $n=2$ and $n=3$ members of the excitonic series of A. Possibly G is the $n=2$ member of the B exciton polariton. The two excitations on the D branch, $D(k)$, and $D(3k)$, are clearly visible whereas for the other peaks the k excitations are low energy shoulders to the dominant $3k$ resonance. At 5.28 kbar the $D(3k)$ and E level are indistinguishable.

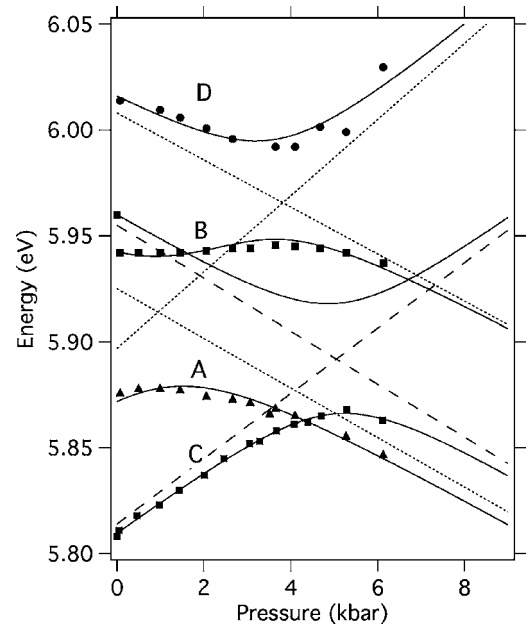

FIG. 2. The behavior under pressure of the four lowest polariton excitation energies, C, A, B, and D, in CsI. The solid lines represent the best fit to the data. The dotted lines show the asymptotic behavior of A, B, and D in the limit of vanishing interaction. The dashed lines describe the intersection of the $\Gamma_5^-(s)(C)$ level with its unobserved counterpart, the $\Gamma_5^-(d)$ level.

for[28] CsI was also observed for CsBr with increasing pressure, though not as dramatic as for CsI.

III. RESULTS

The spectra of Figs. 1 and 5 show the three prominent Γ_4^- peaks (A, B, and D) corresponding to the transitions from the p-like valence band of the halogen ion (symmetry of Γ_8^- at the center of the Brillouin zone) to either the $6s$-like (Γ_6^+) or the $5d$-like (Γ_8^+) conduction bands mainly derived from the Cs ion. These three maxima are also observed in OP absorption measurements for CsI and were originally assumed to be the only constituents involved in the level repulsion (Fermi resonance) under pressure. No such OP measurements exist for CsBr.

IV. Fermi resonance

A. CsI

Four levels are observed by us directly and one indirectly. These five split up into two separate groups: The three peaks (A, B, and D) of Γ_4^- symmetry are found to interact and exhibit pressure induced level repulsion. This can be seen from Fig. 2 where the excitations are labeled as paraexciton C (5.808 eV), and polaritons A (5.875 eV), B (5.940 eV), and D (6.015 eV). As already reported in Ref. 28, the paraexciton C increases at first linearly in energy with pressure, approaching the A level and growing rapidly in intensity. Eventually the intensity becomes about a factor 100 stronger than the initial one. C then appears to intersect the dispersion relation of A without any sign of level repulsion confirming the difference of their symmetry assignments of Γ_4^- and Γ_5^-.

C proceeds to a maximum in energy at ~5.3 kbar and then turns over, due to the redshift of the second paraexciton of $\Gamma_5^-(d)$ symmetry which has an energy of 5.960 eV at zero pressure. The second paraexciton is thus observed indirectly and one can estimate its energy decrease to be close in value to the energy increase of C with pressure.

The A polariton at first does not decrease in energy under compression, however, it decreases dramatically in linewidth and intensity.[28] The linewidth of the $A(E_{3k})$ at zero pressure is ~11 meV and it decreases at a rate of 3.5 meV/kbar assuming linear behavior.[28] The straightening (leveling) of the dispersion relation of the upper polariton branch of A under compression is indicated by the amalgamation of the $A(E_k)$ and $A(E_{3k})$ resonances which makes the distinction between them increasingly difficult at higher pressures.[28]

The B polariton is not sensitive to compression up to ~4.5 kbar at which point it starts decreasing in energy.

Figure 1 also clearly shows the two resonances of the upper D polariton branch, $D(k)$ and $D(3k)$. At 5.28 kbar the curvature of the upper polariton branch has increased significantly, $D(k)$ and $D(3k)$ are further apart than at 80 bar (Fig. 1). D and the related longitudinal exciton energy at first decrease with pressure, reach a minimum in energy at ~4 kbar and then increase again rapidly.

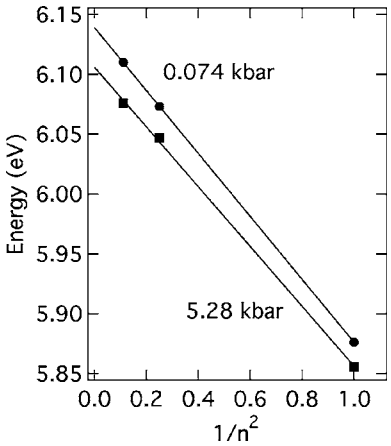

FIG. 3. Energies of the A, E, and F resonances plotted versus $1/n^2$ providing evidence for the identification of E and F as the $n=2$ and $n=3$ exciton-polaritons of the $A(n=1)$ level. Plotted are the longitudinal energies since the exact transverse energies are not known.

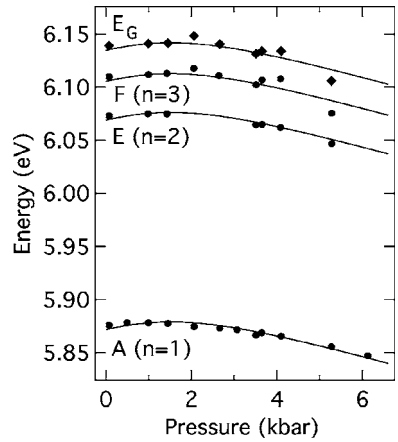

FIG. 4. Pressure dependence of the A, E, and F peaks in CsI further establishing E and F as the $n=2$ and $n=3$ exciton polaritons of A. Also shown is the bandgap energy E_G calculated from the $n=2$ and $n=3$ exciton polaritons of A. The solid line for A is the best fit from Fig. 3; for E, F, and E_G the solid lines are obtained by adding the appropriate fraction of the binding energy to the fit for A.

Figure 1 shows a few more excitations beyond D labeled E, F, and G. G was very weak and lost in the spectra at higher pressures. Plotting the energies of A (the Γ_8^--Γ_6^+ transition), E and F in Fig. 3 versus $1/n^2$ confirms the E level as the $n=2$ exciton-polariton of A and F as the $n=3$ member of the series. Strictly speaking, they are the longitudinal energies and in order to find the transverse energies (the excitonic energies without photon interaction) one would have to subtract the values of the LT splitting for each one. The LT splitting of A was calculated by Fröhlich *et al.* from a fit to his data to be 38 ± 10 meV.[26] However, the LT splitting values for the 2nd and 3rd member of the series are expected to be much smaller. Neglecting this small LT splitting of the $n=2$ and $n=3$ resonances one can calculate the values for the energy gap and binding energy and thus avoid the "hydrogenic defect" problem affecting the $n=1$ member for which the effective mass approximation might not be appropriate. For comparison, the hydrogenic defect for the isoelectronic Xe was determined to be 7%.[34,35] We found that based on the $n=2$ and $n=3$ members of the series the hydrogenic defect of the $n=1$ member is on the order of the LT splitting of A itself, namely $\sim$38 meV. Thus we can establish the bandgap energy of CsI at 6.135 eV for a temperature of 9 K and 80 bar and determine the binding energy to be $\sim$263 meV based on the $n=2$ and $n=3$ members of the series, values that should also hold well for 0 K and 0 bar. Figure 4 shows the energies of A, E, and F alone under compression as well as the behavior of the energy gap itself. Their pressure dependence is very similar, again indicating that they are related with each other. Within the accuracy of the experiment the binding energy stays approximately constant throughout the pressure range whereas the band gap energy first increases slightly, reaches a maximum of $\sim$6.145 eV at $\simeq$2 kbar of pressure and then decreases. The pressure behavior of these two important band structure parameters is therefore determined for a pressure range from 0 to 6 kbar, which corresponds to a decrease in the lattice constant from 4.57 Å to $\sim$4.49 Å.[36]

We also want to note at this point that additional poorly defined lines appeared *beyond* the energy band gap in both the CsI and CsBr crystals which were not reproducible from one run to the next. TPS therefore does not appear to be a straight-forward tool for studying the energetic states beyond the band gap at the present stage of its application, possibly because radiation induced "damage" is introduced to the system when the combined photon energy exceeds the band gap threshold. This was also found to be true for other alkali-halides investigated by our TPS experiments.

B. CsBr

The general behavior described above for CsI was to a large degree repeated for CsBr as can be seen from Figs. 5 and 6. The critical pressure in CsBr for the point of closest approach of all levels appears to be at about 6 kbar. The lowest energy paraexciton band (C) was not detected.[27]. At zero pressure the longitudinal energies are approximately: 6.965 eV(A), 7.112 eV(B), and 7.212 eV(D). The initial increase with pressure for the A peak was about 16 meV/kbar. This behavior of the A polariton is quite different from the A in CsI where the A peak practically starts out at a maximum already.

As was previously reported for CsI,[28] the linewidth of the A peak in CsBr also narrows significantly over the pressure range measured (see Fig. 7): While the full width at half maximum (FWHM) at 100 bar in CsBr still amounts to 34 meV, it has shrunk to 8 meV at 6.90 kbar. In addition to the linewidth narrowing of the A peak in CsBr, the D peak linewidth first decreased and then increased as pressure was applied. In general, the Fermi repulsion for CsBr appears to be spread out over a bigger pressure range and shows the onset of the resonance much clearer.

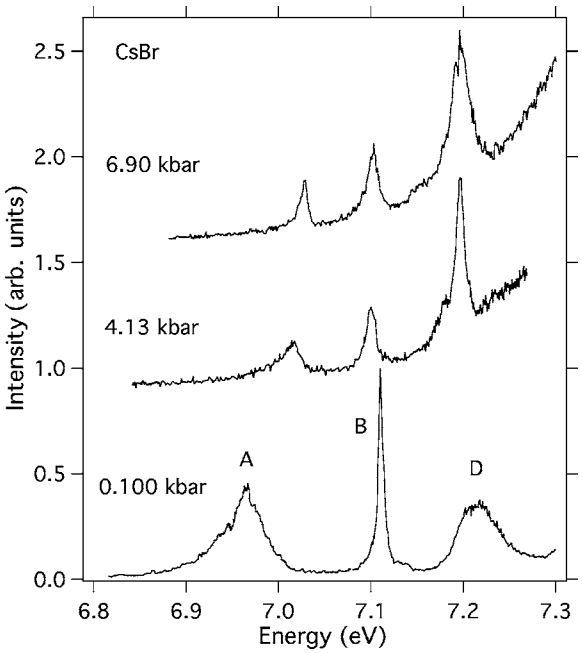

FIG. 5. CsBr excitation spectra at three different pressures at 9 K. A, B, and D represent the three Γ_4^- transitions ($n=1$ exciton polaritons) similarly to CsI. Other excitations were not observed.

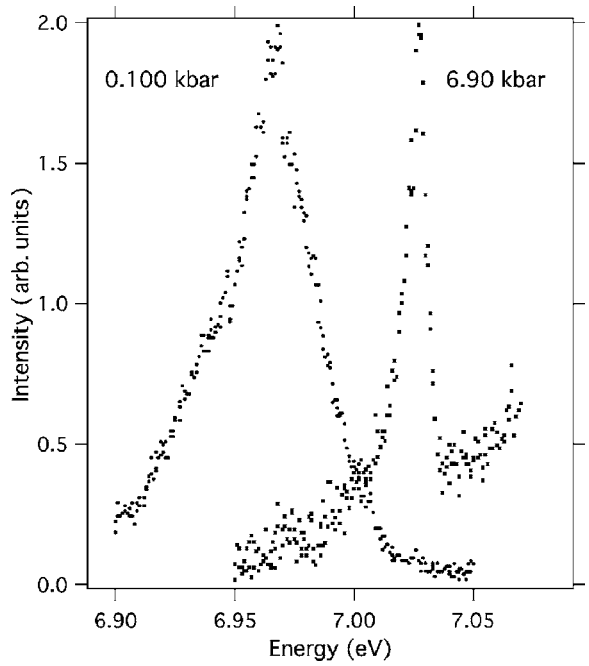

FIG. 7. The CsBr A polariton ($\Gamma_8^- \rightarrow \Gamma_6^+$) and its reduction in linewidth by a factor 4 demonstrated at two different pressures (0.100 and 6.90 kbar).

V. DISCUSSION

A. CsI

1. Fermi resonance

The close spacing between the s-like and the d-like conduction bands in CsI at the Γ-point, a consequence of the CsCl structure and the heavy C_s^+ ion, creates an ideal situation for the study of the Fermi resonance.[1–3] This contrasts with the fcc alkali halide crystals where the minima of the d-bands are located at the X-point of the Brillouin zone allowing a less complicated interpretation of the TPS spectra.

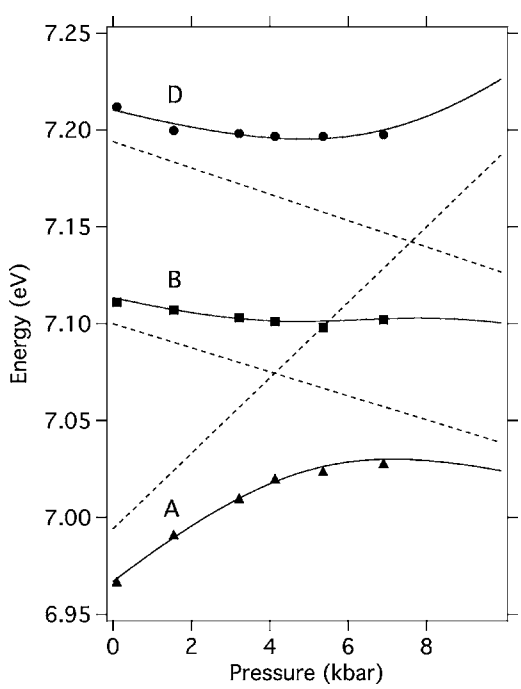

FIG. 6. The shift of the CsBr excitation energies of the A, B, and D polaritons with pressure. The solid lines represent the best fit to the data. The dotted lines show the asymptotic behavior of A, B, and D in the limit of vanishing interaction.

The repulsion of three levels with energies E_A, E_B, and E_D and corresponding pressure shifts α_A, α_B, and α_D and their mutual interaction matrix elements β_{AB}, β_{AD}, and β_{BD} is described by diagonalizing the following matrix Hamiltonian:

$$Det\begin{vmatrix} E_A+\alpha_A P-\lambda & \beta_{AB} & \beta_{AD} \\ \beta_{AB} & E_B+\alpha_B P-\lambda & \beta_{BD} \\ \beta_{AD} & \beta_{BD} & E_D+\alpha_D P-\lambda \end{vmatrix}=0. \tag{1}$$

The resulting expressions for the three roots of the equation were fitted against the data and optimized with respect to the energies E_A, E_B, and E_D, their respective pressure shifts, α_A, α_B, and α_D, and the interaction matrix elements β_{AB}, β_{AD}, and β_{BD} as adjustable parameters. Table I(a) lists the values for the Γ_4^- excitations in CsI. The uncertainties are single standard deviation values as obtained from the fitting routine. The dotted lines in Fig. 2 depict the behavior of the energy levels in the limit of vanishing interaction: The exact resonance of A and B takes place at a pressure of 1 kbar and at 4 kbar for the B and D levels.

Unfortunately our values cannot be compared directly to those of Kuznetsov *et al.*[8] and Tsujimoto *et al.*[9] since their measurements were performed at 80 and 77 K, respectively. Neglecting the possibility of a dependence on temperature, our values for the pressure shifts compare more favorably with those of Ref. 9 which were found to be 18 meV/kbar

TABLE I. (a) CsI level repulsion parameters for the Γ_4^- excitations A, B, and D. (b) CsI level repulsion parameters for the Γ_5^- excitations $\Gamma_5^-(s)$ (also called C) and $\Gamma_5^-(d)$.

(a)		
E_A (eV)	E_B (eV)	E_D (eV)
5.897±0.002	5.925±0.002	6.008±0.002
α_A (meV/kbar)	α_B (meV/kbar)	α_D (meV/kbar)
18.0±0.5	−11.7±0.3	−11.1±0.3
β_{AB} (meV)	β_{BD} (meV)	β_{AD} (meV)
36±1	12±1	20±1
(b)		
$E[\Gamma_5^-(d)]$ (eV)	$E[\Gamma_5^-(s)]$ (eV)	
5.955±0.002	5.814±0.002	
$\alpha[\Gamma_5^-(d)]$ (meV/kbar)	$\alpha[\Gamma_5^-(s)]$ (meV/kbar)	
−12.5±1.0	15.4±0.9	
β (meV)		
26±5		

for α_A and −11 meV/kbar for both α_B and α_D. Kuznetsov *et al.* had found 21 meV/kbar for α_A and −8.5 meV/kbar for α_B and −19 meV/kbar for α_D. No values were given for the interaction matrix elements β_{ij} in Ref. 9 and the ones listed in Ref. 8 were assumed to be linearly pressure dependent by the authors (β_{AB}=4.6 meV/kbar·**p**, β_{AD}=0 meV/kbar·**p** and β_{BD}=3.3 meV/kbar·**p**).

The two levels of Γ_5^- symmetry also exhibit level repulsion behavior but appear otherwise unaffected by the excitations of Γ_4^- symmetry. While the dependence of the $\Gamma_5^-(d)$ state on pressure was not observed directly by us, the $\Gamma_5^-(s)$ state exhibits the classic behavior of the lower state participating in a two-level Fermi resonance. The repulsion of two levels with energies E_1 and E_2, pressure shifts α_1 and α_2 and the mutual interaction matrix element β_{12} is described in many introductory physics textbooks. The fit of the resulting expression for the lower level to our data for the Γ_5^- excitation in CsI suffers somewhat from the missing data for the upper level if we assume two different values for the pressure shifts for $\alpha[\Gamma_5^-(d)]$ and $\alpha[\Gamma_5^-(s)]$. Table I(b) summarizes the results. The dashed lines in Fig. 2 describe the asymptotic behavior of the $\Gamma_5^-(s)$ (C) level and its intersection with the unobserved counterpart, the $\Gamma_5^-(d)$ level, in the limit of no interaction.

If we make the assumption that the absolute value for the pressure shift is the same, i.e., $\alpha[\Gamma_5^-(d)]=-\alpha[\Gamma_5^-(s)]$, one obtains: $E[\Gamma_5^-(d)]=(5.958\pm0.002)$ eV; $E[\Gamma_5^-(s)]=(5.813\pm0.001)$ eV; $\alpha[\Gamma_5^-(d)]=-\alpha[\Gamma_5^-(s)]=(-14.1\pm0.3)$ meV/kbar; $\beta=(18.3\pm1.1)$ meV. The value for the pressure shift of the lower level stays the same within the uncertainty even if one relaxes on the absolute equality of the pressure shifts. The solid lines in Fig. 2 represent the fits to the data with different pressure shifts and the dotted and dashed lines the asymptotic behavior in the limit of vanishing interaction. Above values imply that the C level might again intersect with the A excitation at higher pressure. The value of ∼−14 meV/kbar for the pressure shift of C is close in value for the pressure shifts of the band gap observed at higher pressures up to 10 GPa.[37] At pressures beyond 30 GPa the pressure shift has decreased to −4.8 meV/kbar.[15]

TABLE II. CsBr level repulsion parameters for the Γ_4^- excitations A, B, and D.

E_A (eV)	E_B (eV)	E_D (eV)
6.994±0.003	7.100±0.003	7.194±0.003
α_A (meV/kbar)	α_B (meV/kbar)	α_D (meV/kbar)
19.5±0.3	−6.2±0.1	−6.8±0.1
β_{AB} (meV)	β_{BD} (meV)	β_{AD}
46±3	0.8±12	55±1

2. Band gap and binding energy

Some sources listing substance specific electronic band structure parameters still give a value of 6.37 eV for the band gap in CsI as reported by Fischer and Hilsch on the basis of absorption measurements published in 1959.[38] This value caused problems for Onodera about 10 years later when he calculated the band structure of CsI and found that in his calculations the Γ_6^+ band was 0.11 eV higher in energy than the Γ_8^+ band despite experimental evidence that the Γ_6^+ band should have been the lowest.[39] He noted that the band gap energy would have to be substantially lower than 6.37 eV in order for Γ_6^+ to be the lowest band.[39]

Fröhlich *et al.* interpreted the onset of a featureless continuum of two-photon transitions at 6.05 eV as the band gap energy for Γ_8^--Γ_6^+.[40] Generally, one would expect two photons to excite transitions to p-type exciton-polaritons below the band gap, as for example observed for KI.[41] However, those were not observed by them.[40]

When Nosenzo and Reguzzoni analyzed the electronic structure in Cs halides based on thermo-reflectance studies they listed 5.82 eV for the $n=1$ exciton of the Γ_8^--Γ_6^+ transition and 6.06 eV for the corresponding $n=2$ exciton.[42] In the Wannier exciton picture this would have indicated a bandgap energy of 6.14 eV and a binding energy of 0.32 eV.

Our own measurements based on direct observations of the $n=2$ and $n=3$ (longitudinal) exciton-polaritons now unambiguously identify the energy gap as 6.135 eV and the binding energy as 263 meV.

B. CsBr

1. Fermi resonance

Table II summarizes the results for the Γ_4^- excitations in CsBr. The Fermi resonance in CsBr has thus been experimentally confirmed and the levels are closest in energy for a pressure of ∼5 kbar. The exact resonances occur at 4 kbar (levels A and B) and 7.5 kbar (A and D). In agreement with theoretical calculations by Satpathy[3] the anticrossing and/or spin-flip region for CsBr happens at a higher pressure than that for CsI.

2. Band gap and binding energy

Fröhlich *et al.* also measured the two-photon absorption spectrum of CsBr and again interpreted the first rise of the

signal at 7.18 eV as the Γ_8^--Γ_6^+ band gap.[40] Unfortunately so far nobody has been able to directly observe the $n=2$ transition to establish a direct measurement of the band gap. If the situation is similar to the one in CsI one would expect the $n=2$ transition of the A peak at energies higher than the D peak (7.19 eV) which would establish 7.20 eV as a lower bound for the Γ_8^--Γ_6^+ band gap.

3. CsI and CsBr: Linewidth dependence on pressure

A thorough quantitative analysis of the linewidth dependence on pressure is beyond the scope of this paper since it would have to take the pressure dependence of the exciton states, the phonon density of states as well as the exciton-phonon coupling coefficients into consideration, maybe similar to a treatment presented by Iwamoto and Onaka.[4] In their work, however, the existence of the paraexciton band C below the first singlet polariton band A as a target state for scattering was not considered. Also, the polariton nature of the excitations would have to be taken into account explicitly as previously calculated by Tait and Weiher for the case of CdS.[43]

It has been assumed for the case of[28] CsI that the most likely reason for the dramatic line narrowing of the A peak might be the decrease in the LT splitting making it increasingly difficult to relax to the lower polariton branch via phonon emission. This might not need to be the situation for CsBr. In fact, the less dramatic change in the spectral linewidth for CsBr (Fig. 7) could also be interpreted as evidence for the existence of a lower energy triplet state which is shifting upward into the pressure-induced Fermi resonance region, removing it as a possible final state for scattering from higher energy states.

VI. CONCLUSION

The reported measurements provide very detailed information about the electronic and excitonic structure of the two simple cubic cesium halides CsI and CsBr over a pressure range of up to 7 kbar at low temperature (9 K). For both of them a Fermi induced resonance of the three Γ_4^- levels is realized via hydrostatic compression. The Fermi resonance region of closest approach in CsI occurs at 1–4 kbar: At 1 kbar for the exact resonance of A and B and at 4 kbar for B and D. A similar behavior was found for CsBr, however, the Fermi resonance in CsBr happens to occur at a higher pressure than in CsI, in keeping with theoretical predictions: The exact resonances occur at 4 kbar (A and B) and 7.5 kbar (A and D). The Fermi resonance of the two Γ_5^- states in CsI with an anticrossing at 5 kbar is also observed through direct measurements of the lower level.

The direct observation of the $n=2$ and 3 (exciton)-polaritons of the Γ_8^--Γ_6^+ transition (levels E and F) establishes the band gap of CsI unambiguously at 6.135 eV and allows determination of its pressure dependence up to 6 kbar. They also allow the determination of the binding energy at 263 meV, which stays constant within the experimental uncertainty over this pressure range. With this value for the binding energy and an LT splitting of 38 ± 10 meV for the $n=1$ (exciton)-polariton the hydrogenic defect is therefore on the order of 14%.

Our measurements establish that the Γ_8^--Γ_6^+ bandgap in CsBr must be somewhat higher than 7.20 eV. Similarly to CsI the lowest level in CsBr also exhibits significant line narrowing with increasing pressure, however not as dramatic.

It is hoped that the highly resolved experimental observations made in these two Cs halides will stimulate further calculations and experiments.

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