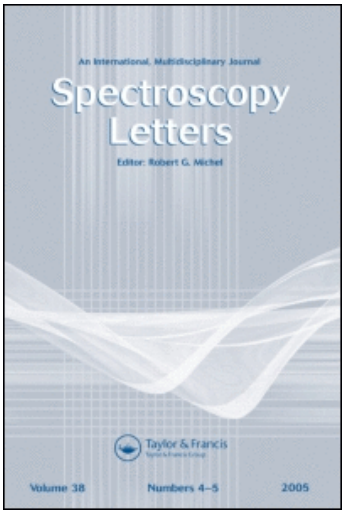

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Stress-Induced Changes in the Optical Parameters in Copper Chloride

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ABSTRACT We have calculated the stress-induced variations in refractive indices (of the index of refraction Δn and of the extinction coefficient Δk) of CuCl by the means of the Kramers–Kronig relationship from the piezoreflectance spectra of the 1s Z_3 and 1s Z_{12} excitons. In the two studied configurations corresponding with the applied stress $\boldsymbol{p}//[001]$ and $\boldsymbol{p}//[111]$ the spectrum of the differential parameters Δk consist of two principals absorption lines in the region of the Z_3 band. The corresponding energetic separation is comparable with the transverse-longitudinal splitting. The longitudinal Z_3 exciton Γ_{5L} is mixed with the transverse exciten Γ_{5T} by virtue of the stress-induced k-linear term and became optically active.

KEYWORDS CuCl, Piezoreflectance, Kramers-Kronig, Optical parameters, Splitting

INTRODUCTION

A great number of linear and non linear stress-optical experiments on copper halides CuCl, CuBr and CuI have been reported.[1–9] In unstressed crystals of copper chloride (CuCl), the theoretical fine structures of the 1s Z_3 excitons associated with Γ_6 (conduction band) and Γ_7 (valence band) and of the 1s Z_{12} excitons associated with Γ_6 and Γ_8 (valence band) are well-known. The electron-exchange interaction is particularly important because the excitonic Rydberg is relatively large ($R_{exc} = 189\,meV$) and the exciton radius is small ($a_{exc} \approx 0{,}7\,nm$).[10] Accordingly, the short-range part of the electron-hole exchange interaction splits the singlet state Γ_5 (dipole allowed) and the triplet state Γ_2 (Z_3 excitons) or $\Gamma_3 + \Gamma_4$ (Z_{12} excitons) (dipole forbidden), whereas the long range splits further the singlet state Γ_5 into transverse optically active states Γ_{5T} and longitudinal inactive states Γ_{5L}. The application of uniaxial stress to semiconductors produces changes in the lattice constant and symmetry of the crystal, and, as a consequence, these cause important changes in the electronic properties, which manifest themselves in the optical ones. The hydrostatic and shear components of the strain can produce shifts and splitting of the energy band, respectively. The piezoreflectance spectra (modulated reflectance spectra by dynamic uniaxial stress) of the 1s Z_3 and Z_{12} excitons in single crystals of copper chloride CuCl at 95 K with linearly polarized light are measured and reported in Ref. [9] From the stress-induced

shifts and splitting of the excitonic levels, the shear excitonic deformation potentials are deduced.

The aim of this paper is to investigate the measured piezoreflectance spectra of CuCl in the excitonic range by the means of the Kramers–Kronig relationship and to evaluate changes in optical parameters produced by applied stress to obtain more information in the stress-induced effect in the electronic properties of this material.

MATERIALS AND METHODS

To measure the piezoreflectance spectra of CuCl in the excitonic range, samples having a parallelepiped shape, of about $5 \times 3\,mm^2$ reflecting area and 0.5 mm thickness, were used. They were cut from single crystal blocks of CuCl grown by the melting zone method. The sample surfaces were oriented by X-ray Laue transmission measurements. The obtained cleavage planes were of high optical quality. The piezomodulation of the reflectivity spectrum of CuCl was performed by mounting it on a piezoelectric transducer of lead zirconate–titanate type. The transducer was driven by a sinusoidal electric field of 200 V/mm, and an alternating stress of about 1000 Hz (different to the resonance frequency) was respectively applied along the [001] and [111] crystal directions (scheme 1). The samples were fixed on the ceramic by means of vacuum grease and mounted in a cryostat evacuated to about 10^{-5} Pa and cooled by liquid nitrogen. The temperature of the sample recorded by a gallium arsenic sensor was 95 K. Because the transducer was maintained by an electrically insulating support (plastic matter) Scheme 1 and the sample in the cryostat was not in direct contact with the liquid nitrogen, its temperature is higher than 77 K.[8, 9]

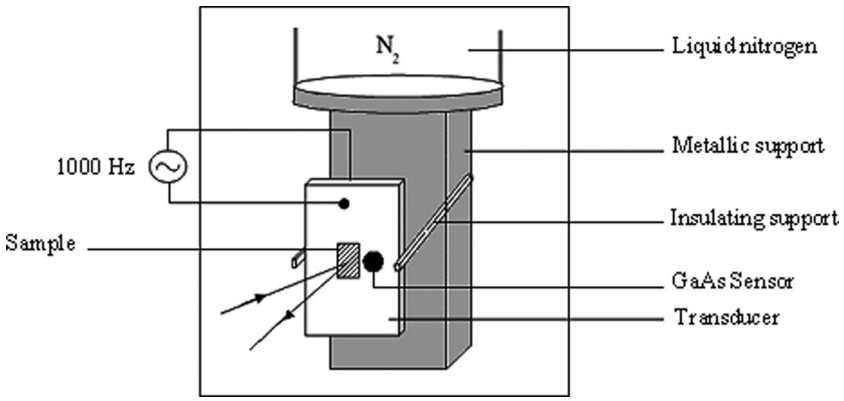
All measurements were made with wave vector $\boldsymbol{k}$ of the incident light perpendicular to (110) cleaved surface and the pressure $\boldsymbol{p}$ oriented parallel to one of the two meaning crystallographic axis. The electric field vector (polarization) ε of the incident electromagnetic wave was set either parallel (π component) or perpendicular (σ component) to the direction of the applied stress. A polarizer of GLAN type was used.

EXPERIMENTAL RESULTS

Figure 1 shows the reflectance power R of the unstressed crystal of copper chloride CuCl, measured in the region of exciton absorption at the temperature of 95 K without a polarizer. The spectrum shows two absorption lines (1s Z_3 and 1s Z_{12}), which are of main interest in this paper.

The real n and imaginary k parts of refractive indices of the unstressed crystal calculated from the reflectance power R at 95 K by the means of the Kramers–Kronig relationship are shown in Fig. 2.

Figures 3 and 4 contains the piezoreflectance spectra $\Delta R/R$ measured at the temperature of 95 K for the two completely independent configurations of the applied stress $\boldsymbol{p}$// [001] and $\boldsymbol{p}$// [111]. The lock-in amplifier is tuned to the fundamental frequency ω of the applied stress. The spectrum in polarization $\varepsilon//\boldsymbol{p}$ (polarization π) consists of a negative sharp peak Z_3 3232 meV and a positive broad structure Z_{12} 3314 meV. In the other polarization $\varepsilon\perp\boldsymbol{p}$ (polarization σ), the spectrum exhibits a positive sharp peak Z_3 and a negative broad structure Z_{12}. In each polarization $\varepsilon//\boldsymbol{p}$ or $\varepsilon\perp\boldsymbol{p}$, the amplitude



SCHEME 1 **Sample mounted on the piezoelectric transducer driven by a sinusoidal electric field about 1000 Hz.**

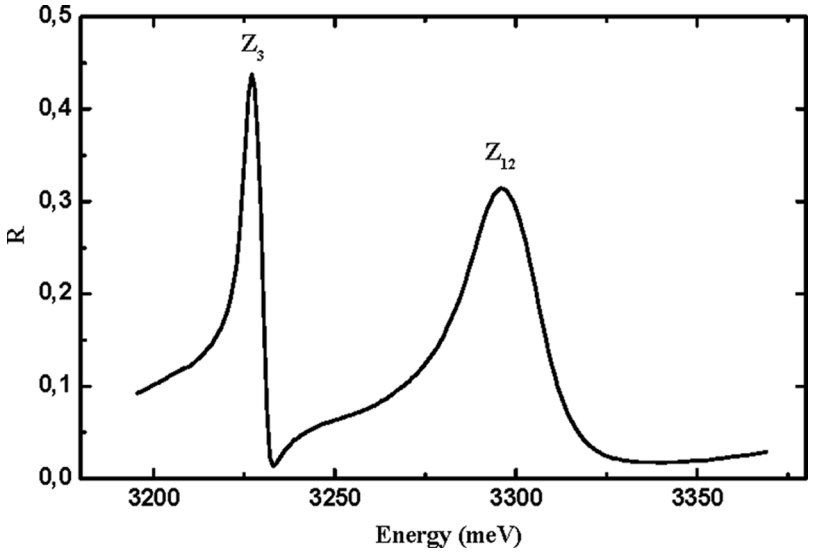


FIGURE 1 Reflectance power *R* at 95 K in the region of the excitonic absorption of CuCl.

of the sharp peak is stronger than the broad one. The magnitude of the applied pressure $\boldsymbol{p}$ was estimated from transducer characteristics and elastic properties of CuCl. In this case, the estimated values in [001] and [111] crystal directions are respectively $p_{001} = 1\,\text{MPa}$ and $p_{111} = 0.75\,\text{MPa}$.

PROCEDURE FOR TREATING THE DATA

It is well-known that the real and imaginary parts n and k of the refractive indices are not completely independent. If one of the two functions is completely specified as a function of energy E, the other one can be determined by the Kramers–Kronig relationship. This statement is equally true for both the unstrained case and the strained one. It follows that changes in optical parameters induced by stress also must satisfy a Kramers–Kronig relationship. This relationship may be derived directly from the usual Kramers–Kronig relation between the phase angle θ of the reflected wave and the reflectance power R of the material.[10]

$$\theta(E_0) = \frac{1}{2\pi}\int_0^\infty \frac{d}{dE}(\ln R)\ln\left|\frac{E+E_0}{E-E_0}\right| dE \qquad (1)$$

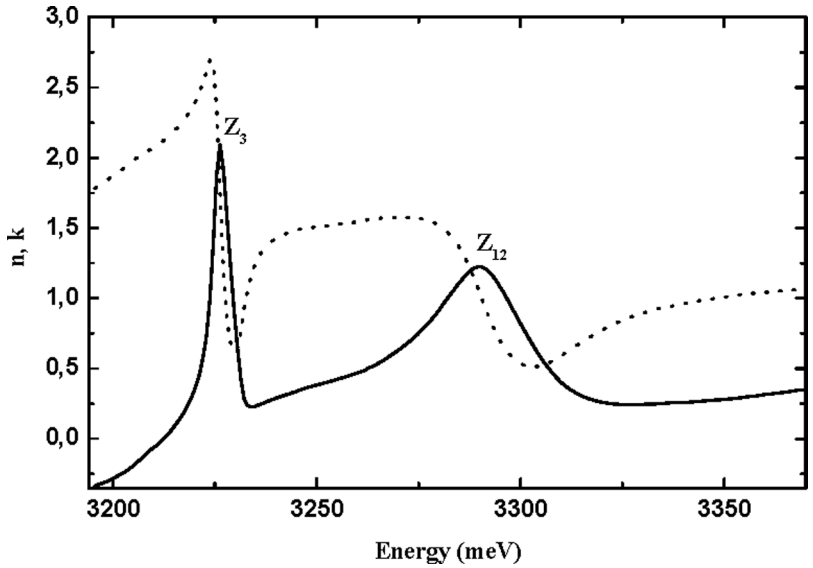


FIGURE 2 Index of refraction n (.....) and extinction coefficient k (—) of CuCl calculated from reflectance power *R* at 95 K.

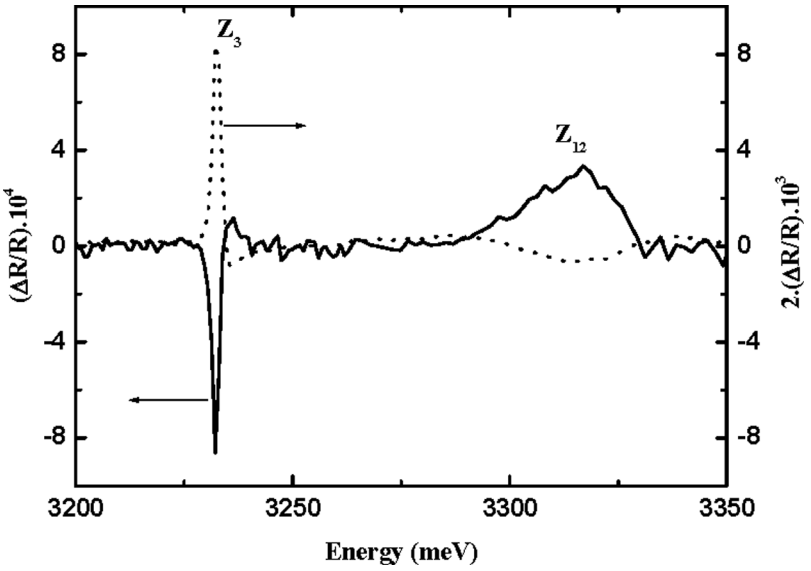


FIGURE 3 Piezoreflectance spectra of 1s Z_3 and 1s Z_{12} excitons in CuCl at 95 K: (—) p// [001], ε//[001] and (. . ..) p// [001], $\varepsilon\perp$[001].

where $r = |r|e^{i\theta}$ is the complex reflection coefficient and $R = |r|^2$.

For the strained material,

$$\theta(E_0) + \Delta\theta = \frac{1}{2\pi}\int_0^\infty \frac{d}{dE}[\ln(R + \Delta R)]\ln\left|\frac{E + E_0}{E - E_0}\right| dE. \tag{2}$$

Subtracting equation (2) from (1) yields the desired relationship.

$$\Delta\theta(E_0) = \frac{1}{2\pi}\int_0^\infty \frac{d}{dE}\left(\frac{\Delta R}{R}\right)\ln\left|\frac{E + E_0}{E - E_0}\right| dE. \tag{3}$$

with both $\Delta R/R$ and $\Delta\theta$ known, changes in n and k produced by the applied stress can be calculated from the piezoreflectance spectrum in a manner similar to that used in analyzing conventional reflectivity spectra. The changes Δn and Δk are obtained from the expressions:

$$\Delta n = \frac{1}{4}[n^2 - k^2 - 1]\frac{\Delta R}{R} + [nk]\Delta\theta \tag{4}$$

$$\Delta k = \frac{1}{2}[nk]\frac{\Delta R}{R} - \frac{1}{2}[n^2 - k^2 - 1]\Delta\theta. \tag{5}$$

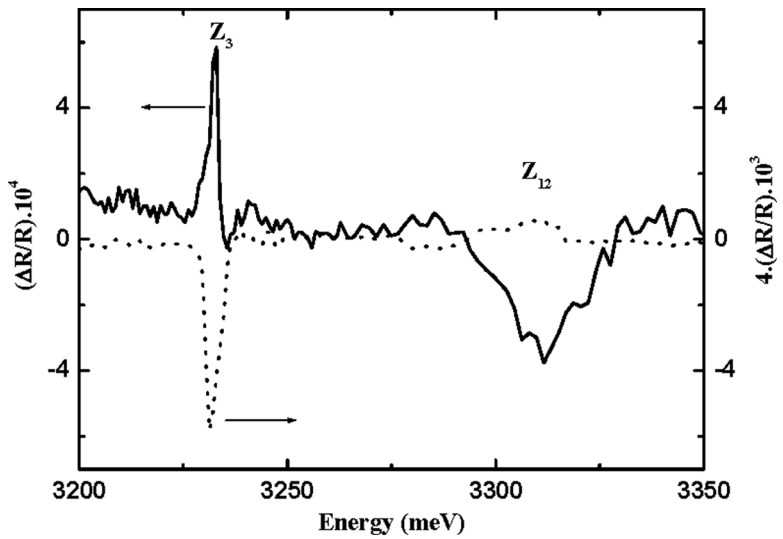


FIGURE 4 Piezoreflectance spectra of 1s Z_3 and 1s Z_{12} excitons in CuCl at 95 K: (—) p// [111], ε//[111] and (. . ..) p// [111], $\varepsilon\perp$[111].

With both R and θ known, the values of the optical constants n and k can be determined from the follow expressions:

$$n = \frac{1 - R}{1 + R - 2\sqrt{R}.\cos\theta}. \quad (6)$$

$$k = \frac{2\sqrt{R}\sin\theta}{1 + R - 2\sqrt{R}.\cos\theta}. \quad (7)$$

The reflectance power R is given by the Fresnel equation for the normal incidence:

$$R = \left|\frac{n + jk - 1}{n + jk + 1}\right|^2. \quad (8)$$

We have measured reflectance power R and piezoreflectance $\Delta R/R$ only in the excitonic range. For the Kramers–Kronig transformation, the reflectance power and piezoreflectance values for lower energies and higher ones are assumed to be constants. For the numerical calculation of θ (E) or Δθ (E), we are use the following relation[10]:

$$\theta(E) = -\pi^{-1}\sum_{k=1}^{n} p_k \left\{ \begin{array}{l} [(E - E_k)\ln|E - E_k| \\ +(E + E_k)\ln|E + E_k|] \end{array} \right., \quad (9)$$

with

$$p_k = u_{k+1} - u_k \text{ and } u_k = \frac{\ln R^{\frac{1}{2}}(E_k) - \ln R^{\frac{1}{2}}(E_{k-1})}{E_k - E_{k-1}}.$$

Equation (9) is used in numerical calculation on digital computers using FORTRAN language.

RESULTS AND DISCUSSION

The stress-induced changes in optical parameters Δn and Δk as obtained from $\Delta R/R$ and Δθ using equations (4) and (5) for the two configurations $\boldsymbol{p}$// [001] and $\boldsymbol{p}$// [111] are presented in Figs. 5 and 6. n and k used in calculations of Δn and Δk are obtained from R and θ using equations (6) and (7). In the two configurations, the spectrum of the differential extinction coefficient Δk, which is proportional to the absorption coefficient, consists of two principal absorption lines A (3225.00 meV) and B (3232.31 meV) in the region of the Z_3 band and two lines C (3288.21 meV) and D (3317.46 meV) in the region of the Z_{12} band.

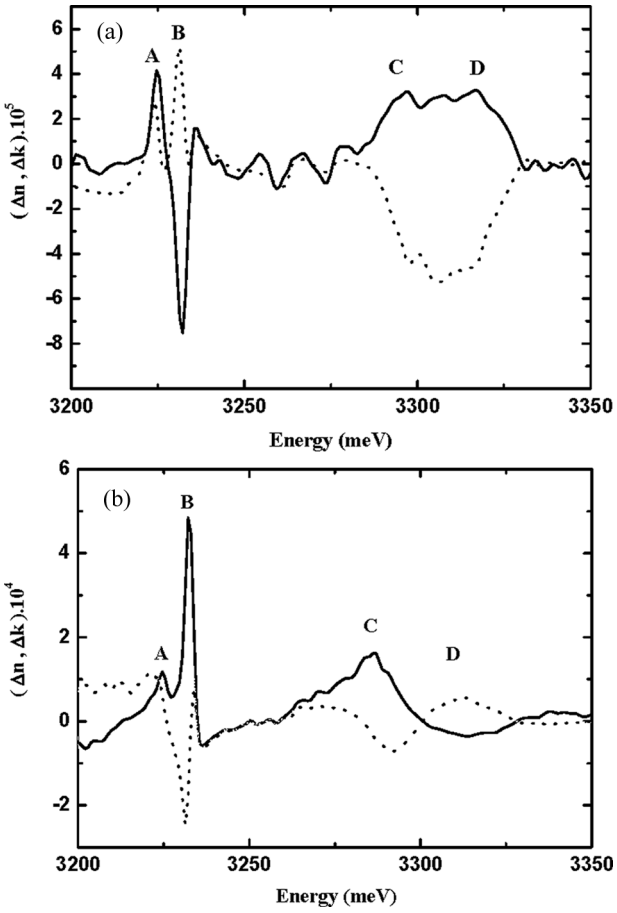


FIGURE 5 **The strain-induced changes in the index of refraction Δn (.....) and the extinction coefficient Δk (—) calculated at 95 K: (a) p// [001], ε//[001] and (b) p// [001], ε⊥[001].**

Under normal conditions, CuCl crystallizes in the zincblende structure (point group T_d) and its band structure is well-known. The lowest conduction band is due to Cu^+ 4s states, which lead to a band Γ_6 symmetry in the notation of Koster et al.[11] The uppermost valence bands are composed of a melange of Cu^+ 3d and Cl^- 3p orbitals and are characterized by Γ_7 (upper) and Γ_8 (lowest).[12, 13] In CuCl, the spin-orbit is small and inverted. The direct exciton states associated with the Γ_7 and Γ_8 valence bands are called the Z_3 and Z_{12} excitons, respectively, by Cardona.[12] The separation between the 1s Z_3 and 1s Z_{12} excitons from our measurements at 95 K is $\Delta_{so} = 84$ meV.

The Z_{12} exciton is built up with Γ_6 electron and Γ_8 hole. This excitonic state is eightfold degenerate and has a total symmetry

$$\Gamma_1 \times \Gamma_6 \times \Gamma_8 = \Gamma_3 + \Gamma_4 + \Gamma_5. \quad (10)$$

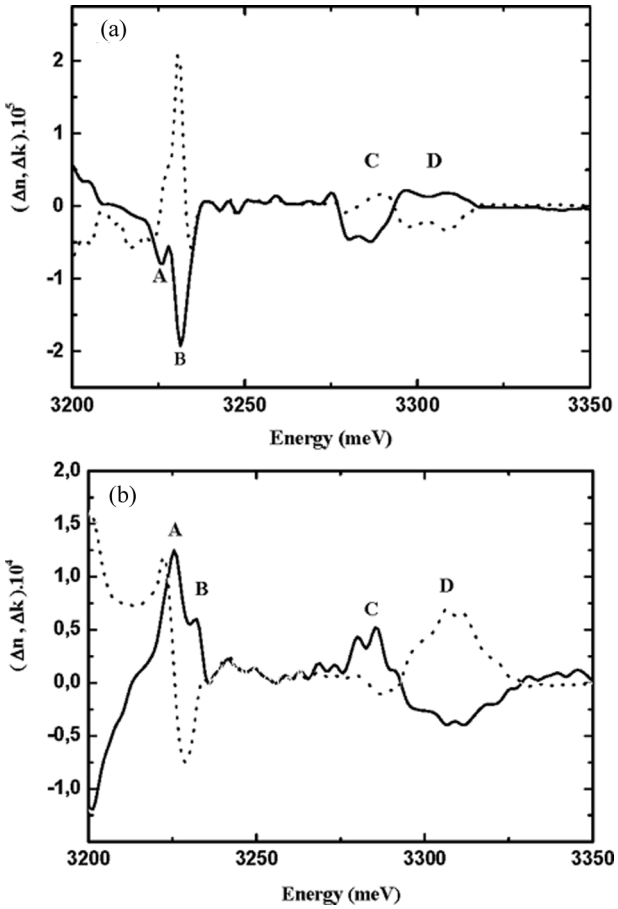


FIGURE 6 **The strain-induced changes in the index of refraction Δn (.....) and the extinction coefficient Δk (—) calculated at 95 K: (a) p// [111], ε//[111] and (b) p// [111], $\varepsilon\perp$[111].**

As indicated previously, the electron-hole exchange interactions are responsible for the singlet–triplet separation (Δ_{st}) between the $(\Gamma_3 + \Gamma_4)$ forbidden optical transition and the (Γ_5) dipole allowed exciton states and of the transverse–longitudinal separation (Δ_{lt}) between (Γ_{5T}) and (Γ_{5L}) exciton states.

The Z_3 exciton is built up with Γ_6 electron and Γ_7 hole. The total symmetry of this fourfold degenerated exciton is

$$\Gamma_1 \times \Gamma_6 \times \Gamma_7 = \Gamma_2 + \Gamma_5. \qquad (11)$$

Taking into account both the short- and the long-range parts of the electron-hole exchange interactions, the degeneracy of the Z_3 exciton is partially lifted. The singlet–triplet separation $(\Gamma_2 - \Gamma_5)$ is due to the short (analytic) exchange interaction and the transverse-longitudinal splitting $(\Gamma_{5T} - \Gamma_{5L})$ is due to the long (nonanlytic) exchange interaction.[14]

Stress applied in the [001] direction lowers the symmetry of the crystal from T_d to D_{2v}. In the other case, stress parallel to [111] axis lowers the symmetry to C_{3v}. Consequently, the anisotropic nature of the strain produces stress-induced splitting and shifts of the energy levels and changes in the oscillator strengths, which can be related to the properties of the unstressed crystal. From a preliminary analysis of piezoreflectance spectra, we have obtained the new values of deformation potentials of CuCl in the excitonic range at 95 K.[9] To obtain more information on the stress-induced effect in CuCl, we have calculated the induced changes in the optical constant, Δn and Δk for the two configurations $\boldsymbol{p}//$ [001] and $\boldsymbol{p}//$ [111] of the applied stress. In this paper we restrict our discussion only to Z_3 band. The Z_{12} band is relatively broad, and the positions of the lines C and D cannot be noted with great precision.

In Table 1 are listed the positions of the maxima or minima of the two remarkable features A and B in the Z_3 band and the corresponding energetic separation $\Delta E_{AB} = E_B - E_A$. It is very interesting to note that the average of the energetic separation Δ_{AB} between the features A and B is equal to 7.31 meV. This value coincides within experimental accuracy with the transverse–longitudinal splitting $(\Gamma_{5T} - \Gamma_{5L})$. However, the two principal lines A and B in the calculated induced changes in the imaginary part of the refractive indices Δk can be attributed respectively to the longitudinal and transverse components of Z_3 band. Theoretically in cubic zincblende CuCl, the Γ_6- conduction and the

TABLE 1 **Positions of lines A and B in stress-induced change of extinction coefficient Δk and their energetic separation ΔE_{AB}**

Stress axis	Polarization	$E_A(meV)$	$E_B(meV)$	$\Delta E_{AB} = (E_B - E_A)(meV)$
[001]	π	3224.59	3231.31	6.72
	σ	3224.59	3232.15	7.56
[111]	π	3225.42	3231.31	5.89
	σ	3225.42	3232.15	7.73

Γ_7-valence bands for Z_3 exciton possess no *k*-linear term: the external applied uniaxial stress split them at the off Γ-points, giving rise to the stress-induced *k*-linear terms. In this paper for the two studied configurations $\boldsymbol{p}$// [001] and $\boldsymbol{p}$// [111], the two features A and B can be interpreted by considering that the longitudinal Z_3 exciton, which is optically inactive in unstressed crystals, is mixed with the transverse one by virtue of the stress-induced *k*-linear term. Therefore, the mixed mode became optically active. This obtained result is in good agreement with that obtained by Koda et al.[1,2] They observed in uniaxial static stress measurements on reflection spectra of CuCl crystals at 1.8 K that with small stress, a sharp reflection peak appears at the high-energy side of the Z_3 exciton. Its position coincides with the energy of the longitudinal exciton Γ_{5L}. They concluded in their study that the stress-induced *k*-linear term is playing an important role in the anomalous transverse–longitudinal mode mixing observed in configuration of $\boldsymbol{p}$// [001] and $\boldsymbol{k}$// [110].

CONCLUSION

The stress-induced variations in the optical parameters Δn and Δk of CuCl were calculated using the Kramers–Kronig relationship from the modulated reflectance spectra of the 1s Z_3 and 1s Z_{12} excitons measured at the temperature of 95 K. In the two studied configurations corresponding with the applied stress $\boldsymbol{p}$//[001] and $\boldsymbol{p}$//[111], the spectrum of the extinction coefficient Δk, which is proportional to the absorption, consists of two principal absorption lines in the region of the Z_3 band. However, the longitudinal Z_3 exciton Γ_{5L}, which is optically inactive in unstressed crystals, is mixed with the transverse exciton Γ_{5T} by virtue of the stress-induced *k*-linear term and became optically active in stressed crystals. This result confirms well that the stress-induced *k*-linear term is playing an important role in the splitting of the excitonic Z_3 energy band in CuCl.

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