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Determination of deformation potentials by three-photon piezoabsorption of paraexcitons in KI

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Three-photon piezoabsorption of paraexcitons is introduced as a method for the determination of deformation potentials. The splitting of the fivefold paraexciton in KI is clearly resolved for uniaxial stress up to 800 bar. The hydrostatic, tetragonal, and trigonal deformation potentials are determined with much higher accuracy than is possible with the classical method of piezoreflection.

Deformation potentials are important fundamental parameters that are used to describe static as well as dynamic properties of solids. Although these parameters are introduced in the Hamiltonian to account for the effect of a static stress on the electronic eigenstates, the same parameters are also of great relevance for the description of dynamical properties, e.g., electron-phonon scattering. In a series of publications, Bir and co-workers[1] developed the theory of the effects of deformation on the energy spectra of semiconductors. In cubic crystals there are three deformation potentials, which are classified as hydrostatic, tetragonal, and trigonal according to the kind of strain in the crystal. Therefore the application of stress along different crystallographic directions is necessary in order to determine the three deformation potentials. There are, however, considerable difficulties in resolving stress-induced splittings and shifts of optical resonances such as band-to-band or exciton transitions by means of linear optical techniques. Because of strong absorption of these dipole-allowed transitions, in most cases one has to do reflectivity measurements, which lead to rather broad bands. Ingenious methods of modulation spectroscopy were invented in order to overcome these difficulties. For a detailed discussion of advantages and drawbacks of these methods we refer the reader to the classical monograph by Cardona.[2]

In this paper we introduce a nonlinear optical method for the determination of deformation potentials that does not show the deficiencies of linear optical methods. Our method of three-photon piezoabsorption is applied to the lowest paraexciton in KI but it should also be applicable to semiconductors and even molecular crystals. Up to now deformation potentials in alkali halides were mainly derived from piezoreflectivity measurements.[3-7] Gavini and Cardona[8] have determined deformation potentials of KI by stress-induced birefringence. There are large differences between the values obtained by these methods which can be explained by the influence of background oscillators. The comparison of the linear optical method of piezoreflectivity and our nonlinear optical method of three-photon piezoabsorption leads to the following points in favor of the new technique: (i) Due to the small linewidth of the paraexcitons ($\Delta E \sim 0.5$ meV) as compared to reflectivity spectra ($\Delta E \sim 80-100$ meV) we can observe directly the splitting of the exciton under static stress; this splitting can be measured very accurately. Absolute values of deformation potentials also can thus be determined very accurately. Because of the large linewidth, piezoreflectivity has to be measured by modulation of the stress. As discussed by Cardona,[2] it is often difficult to get accurate values for the amplitude of the stress. In many cases it is therefore only possible to determine relative values of deformation potentials. (ii) We certainly measure a bulk effect, while reflectivity data

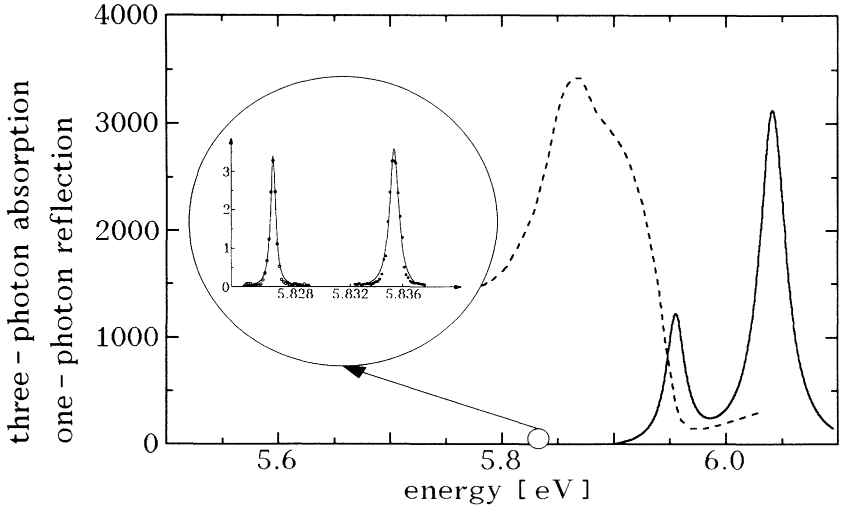

FIG. 1. Three-photon spectra (in arbitrary units) and one-photon reflection (dashed line) of lowest exciton structure in KI at 7 K. The two solid curves around 6 eV refer to resonances on the upper polariton branch. The inset shows two components of the paraexciton under uniaxial stress of 633 bars in [110] direction. The lower and higher energy resonances are measured with laser polarization perpendicular and parallel to the stress direction, respectively. Note the enlarged scale of the inset.

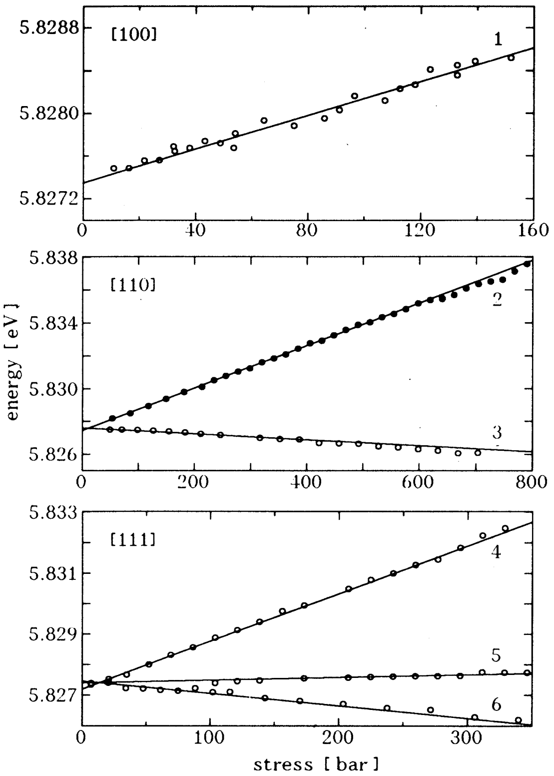

FIG. 2. Stress-dependent splitting and shift of components of paraexciton in KI for orientation of stress as indicated. Open and solid circles refer to measurements with laser polarization perpendicular and parallel to stress direction, respectively. The solid lines represent a fit with the use of the Pikus-Bir Hamiltonian [Eq. (1)]. Note different scales for stress and energy.

depend critically on the quality of the surface. (iii) In the case of the paraexciton, we deal with a pure and isolated exciton. The analysis of the experimental data is therefore straightforward, since the exciton wave functions are known. In the case of piezoreflection, however, one has considerable complications due to the fact that one measures a polariton resonance which cannot be strictly isolated from background oscillators. For the analysis of reflectance spectra information on the dispersion and line shape is necessary. In many cases it is more desirable to do a Kramers-Kronig analysis. For a detailed discussion of this point we again refer the reader to Cardona.[2]

For our experiments we used ultrapure single crystals of KI with a size of about $3\times3\times12$ mm^3. They were cleaved ([100] orientation) or cut and polished ([110] and [111] orientation). The stress apparatus is described in detail by Forchel *et al.*[9] A dye laser (Radiant RDP) pumped by a Nd:YAG laser (Quanta Ray GCR 3 where Nd:YAG means neodymium-doped yttrium-aluminum-garnet) was used for the excitation of the paraexciton resonances. The three-photon absorption was monitored by the subsequent emission from the self-trapped exciton at 300 nm. In order to detect the very weak transition to the paraexciton (10^{15} incoming laser photons lead to about one photon count in the detection channel) it is of great importance to suppress background signals which might stem from nonlinear optical effects of the crystal surface or optical components. Details of the experimental setup are given in a previous publication.[10]

In Fig. 1 we present the spectrum of paraexcitons of KI for a uniaxial stress of 633 bars which is applied along a [110] direction. The two components are selectively excited with polarized light parallel ([110]) or perpendicular ($[1\bar{1}0]$) to the stress direction. Because of the small linewidth (about 0.5 meV) the splitting can be well resolved down to a stress of about 30 bar. For comparison the three-photon resonances on the upper polariton branch of the orthoexciton are also shown in the figure. The two resonances refer to different total k vectors ($k_{\max}$ and $\frac{1}{3}k_{\max}$) as discussed in Ref. 10. We also show a reflection spectrum of Baldini *et al.*[11] Due to the large linewidth of about 100 meV a splitting under static uniaxial stress cannot be resolved.

In Fig. 2 we present the detailed stress dependence of the paraexciton components for three orientations of the applied stress. The maximum stress which could be applied before destroying the sample depends on preparation and mounting of the crystal and also on the stress orientation. The experimental results for the slopes were reproducible within 3% for different runs.

For the analysis of our experimental data we have to consider only excitons which stem from the uppermost valence band (Γ_8^- symmetry, $j_v=\frac{3}{2}$) and the lowest conduction band (Γ_6^+ symmetry, $j_c=\frac{1}{2}$). Because of the large spin-orbit splitting of about 1 eV the stress-induced coupling to excitons of the lower valence band (Γ_6^- symmetry, $j_v=\frac{1}{2}$) can be neglected. As discussed in detail by Onodera and Toyozawa[12] the coupling of $j_v=\frac{3}{2}$ and $j_c=\frac{1}{2}$ leads to a threefold dipole-allowed orthoexciton

TABLE I. Expressions for slopes as deduced from diagonalization of H_s [Eq. (1)] and corresponding experimental values, which are taken from Fig. 2 as indicated by numbers 1–6.

Orientation		Theoretical expressions for slopes $\frac{dE}{d\tau}$	Expt. slopes (μeV/bar)
[100]	1	$a(s_{11}+2s_{12})+\frac{1}{2}b(s_{11}-s_{12})$	6.03±0.07
[110]	2	$a(s_{11}+2s_{12})-\frac{1}{4}b(s_{11}-s_{12})-(\sqrt{3}/4)d\,s_{44}$	12.9±0.1
	3	$a(s_{11}+2s_{12})-\frac{1}{4}b(s_{11}-s_{12})+(\sqrt{3}/4)d\,s_{44}$	−2.32±0.05
[111]	4	$a(s_{11}+2s_{12})-(\sqrt{3}/3)d\,s_{44}$	15.9±0.2
	5	$a(s_{11}+2s_{12})+(\sqrt{3}/6)d\,s_{44}$	1.1±0.2
	6	$a(s_{11}+2s_{12})+(\sqrt{3}/3)d\,s_{44}$	−3.6±0.1

(Γ_4^- symmetry, $F=1$) and a threefold (Γ_5^- symmetry) and a twofold (Γ_3^- symmetry) paraexciton, which correspond to a fivefold-degenerate state ($F=2$) in the spherical limit. The paraexcitons are pure triplet states and are thus not affected by the exchange interaction. The strong coupling of the Γ_4^- exciton to light leads to the well-known polariton structure.[10] The stress-induced mixing of the paraexcitons and orthoexcitons is very weak as can be deduced from the small oscillator strength of the paraexcitons (Fig. 1). For the analysis of the energy shift and splitting caused by the applied stress we can thus neglect this mixing and diagonalize the stress Hamiltonian within the subspace of the paraexcitons. A consequence of this mixing is nevertheless a small singlet part of the paraexciton states which is necessary for the excitation of these resonances. The splitting between the Γ_5^- and Γ_3^- paraexcitons due to the anisotropic exchange interaction is of the order of 0.1 meV (Ref. 10) and can thus also be neglected. The stress Hamiltonian H_s was first derived by Pikus and Bir.[1] We use the definition of the deformation potentials a,b,d as in Ref. 2 and in a more recent publication by Waters *et al.*,[13]

$$H_s = a\,\mathrm{Tr}(e) - 3b[(L_x^2 - \tfrac{1}{3}L^2)e_{xx} + \text{c.p.}] - 2\sqrt{3}d[(L_xL_y + L_yL_x)e_{xy} + \text{c.p.}]\ . \tag{1}$$

L ($l=1$) is the angular momentum operator for the hole, e_{ij} ($i,j=x,y,z$) are the components of the strain tensor, and c.p. denotes cyclic permutation with respect to x,y,z. With the use of the tables of Koster *et al.*[14] one can easily determine the eigenvalues E of H_s in the fivefold subspace of the paraexciton. In Table I we list the slopes $dE/d\tau$ for all experimental configurations. The uniaxial stress τ is negative for compressive stress and the elastic compliance constants $s_{11}=(0.298\pm0.006)\times10^{-5}$ bar^{-1}, $s_{12}=(-0.018\pm0.006)\times10^{-5}$ bar^{-1}, and $s_{44}=(2.72\pm0.06)\times10^{-5}$ bar^{-1} are calculated from the data of Ref. 15. We thus get six equations, which are then used to determine the three deformation potentials. From the experimental slopes we derive the deformation potentials by a least-squares fit, taking the errors of the compliance constants into account:

$$a=(-2.2\pm0.1)\ \text{eV},\quad b=(-0.3\pm0.1)\ \text{eV}\ ,$$
$$d=(0.63\pm0.02)\ \text{eV}\ .$$

The hydrostatic and trigonal values a and d are determined with high accuracy. For the tetragonal deformation potential b, however, the relative error is about 30%. For comparison we present in Table II experimental results of other authors. With the exception of Miyabe *et al.*,[6] there are no error bars quoted in the literature for the deformation potentials, which are determined by linear optical methods.[3–5,7,8] For the tetragonal deformation potential b there are even different signs cited. As stated above we are convinced that there are inherent difficulties in determining deformation potentials from piezoreflectivity data. Very recently, Lipp and Daniels[16] measured the shift of resonances on the upper polariton branch in KI under hydrostatic stress by three-photon spectroscopy. In this case the polariton character has to be taken into account. From their shift of the transverse exciton energy we derive a hydrostatic deformation potential of $a=-2.05$ eV. The analysis of these data encounters similar difficulties as in linear optics since even close to a specific resonance the influence of other dipole-allowed levels cannot be neglected. From measurements of the splitting of the lower polariton branch by uniaxial stress we have clear evidence for this point. First results which are gained by three-photon difference-frequency generation show a wave-vector-dependent splitting and shift of the lower polariton branch. Although the splitting is well resolved, the analysis does not yield the deformation potentials in a straightforward way as in the case of the paraexcitons. Again, for the analysis of the stress-induced effects on the lower polariton branch the contributions of higher dipole-allowed transitions cannot be disregarded.

TABLE II. Values for the deformation potentials a, b, and d obtained by piezoreflection (Refs. 3–7), piezobirefringence (Ref. 8), and three-photon piezoabsorption.

Reference	a (eV)	b (eV)	d (eV)
3	−2.3	0.16	0.57
8		−0.44	0.22
4		−0.06	0.76
6	−2.16±0.4	0.32±0.08	0.73±0.12
7	−2.05	0.02	0.76
This work	−2.2±0.1	−0.3±0.1	0.63±0.02

It would certainly be interesting to study the stress dependence of the oscillator strength of the paraexciton components (Γ_3^- and Γ_5^- symmetry) for different wave vectors and polarization directions. For a quantitative interpretation the stress-induced mixing with the orthoexciton (Γ_4^- symmetry), the anisotropic exchange interaction, and possibly stress-induced k-dependent terms have to be taken into account.

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