

## Electronic Structure Measurements in KI at High Pressure Using Three-Photon Spectroscopy

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This work is the first report of the use of nonlinear optics techniques to probe the pressure dependence of electronic energy levels in a solid. An advantage which may be significant is that for the multiphoton processes involved, relatively low-energy photons that are not absorbed by the cell windows can probe states having energies which would be strongly absorbed by the windows in a one-photon excitation. The measurements follow the pressure dependence of the energetically lowest polariton in KI using the three-photon-spectroscopy method.

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Currently, most of the experimental work on electronic energy levels of solids at high pressure is based either on one-photon reflectivity [1] or on absorption measurements [2]. While very versatile, these have some limitations, caused mainly by limited spectral transmission of cell windows [3], usually diamond or sapphire, as well as sample geometry and surface problems [4]. This paper represents an attempt to mitigate some of the problems by using nonlinear optical (multiphoton) excitation of a solid at high pressure. We report direct measurements of the pressure dependence of the energetically lowest polariton in KI via the three-photon-spectroscopy (TPS) method recently introduced and extensively used by Fröhlich and co-workers in a series of detailed investigations of alkali halides [5-7].

This method can directly determine the dispersion relation of the upper polariton branch [5,6]. Three polaritons can fuse nonlinearly to form a polariton of total energy  $E$  and a total wave vector of either  $3k$  or  $k$  where the latter arises through the reflection of one  $E/3$  polariton at the far side of the KI crystal [6] or the rear window of the pressure cell. We report measurements of the pressure dependence of energy, linewidth, and curvature parameter of the upper polariton branch for wave vectors  $k$  near the center of the Brillouin zone.

For pressurizing our samples we used a two-stage pressure intensifier system which was capable of generating pressures up to 10 kbar in helium. Standard techniques were used to measure the pressure at low temperature [8]. The sample crystals (size approximately  $5 \times 1 \times 1$  mm) obtained from Dr. R. B. Murray were originally purchased from Harshaw Chemical Company [9]. They were freshly cleaved and mounted in a sapphire-ball cell (SBC) [10] which was flushed several times with helium and sealed. The cell was coupled to a closed-cycle cryorefrigerator and cooled to 10 K.

The laser system consisted of a short pulse nitrogen-laser [11] pumping a tunable dye laser [11]. Most of the scans ran over a wavelength range from 604 to 630 nm. The pulses had a spectral FWHM of about  $1.5 \text{ cm}^{-1}$  and a temporal FWHM of 0.5 ns. Wavelength calibration was performed by a temperature-controlled monochroma-

tor. A collimating lens of focal length 50 cm or more focused the laser light pulses onto the sample generating an estimated intensity of  $200 \text{ MW/cm}^2$  in the focal plane.

As described by Beerwerth and Fröhlich [5,6] three photons can cause a valence electron in KI to undergo a transition to excitonic states just below the conduction band. After such a transition KI emits light mostly at 300 and 370 nm. The intrinsic luminescence is due to the formation of self-trapped excitons ( $V_k$  centers in the crystal) [12]. The luminescence was collected by a lens and detected by a photomultiplier. Several appropriate filters or a monochromator blocked the pump light. For each pressure a full excitation spectrum was taken and each wavelength data point was averaged over at least 40 shots.

Throughout the pressure range (0 to 7 kbar) the excitation spectrum showed the same two peaks due to the transverse polaritons (TP) at wave vectors  $k$  and  $3k$  (cf. Fig. 1). It was found that the pair of polaritons could be well fitted by two Lorentzians throughout the pressure range. The peak energies  $E(k)$  and  $E(3k)$  experienced a linear blueshift with increasing pressure  $p$ . For the TP( $k$ ) the relation was  $48004 \text{ cm}^{-1} + (124 \text{ cm}^{-1}/\text{kbar})p$  (kbar), for the TP( $3k$ ) we measured  $48715 \text{ cm}^{-1} + (108$

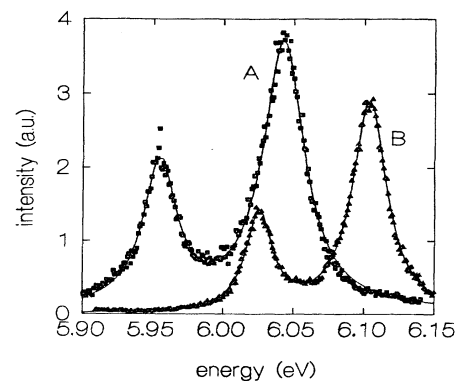


FIG. 1. Three-photon excitation spectra of KI at pressures of 100 bars (A) and 4828 bars (B);  $T=10 \text{ K}$ . The solid lines represent the nonlinear least-squares best fit.

$\text{cm}^{-1}/\text{kbar})p$  (kbar) with an estimated error of  $3 \text{ cm}^{-1}/\text{kbar}$  for the pressure shift and about  $12 \text{ cm}^{-1}$  for the energies at  $p=0$  (see Fig. 2). Figure 3 shows our data for the linewidth of the polaritons. Even though they are quite scattered, it is obvious that the linewidth of the TP( $k$ ) is always smaller than that of the TP( $3k$ ). The scatter is believed to be due to local inhomogeneities in the crystal. Nevertheless, we observe that the linewidth decreases significantly with increasing pressure. A linear fit to the data gives us  $286 \text{ cm}^{-1} - (10 \text{ cm}^{-1}/\text{kbar})p$  (kbar) for the FWHM of the TP( $3k$ ) and  $236 \text{ cm}^{-1} - (11 \text{ cm}^{-1}/\text{kbar})p$  (kbar) for the TP( $k$ ). The error is estimated to be  $14 \text{ cm}^{-1}$  for the values at  $p=0$  and  $4 \text{ cm}^{-1}/\text{kbar}$  for the pressure shift.

The pressure-dependent index of refraction  $n$  of KI is needed to evaluate the wave vector  $k$  (because of the proportionality of  $k$  to  $n$ ). This index has been measured at room temperature for pressures up to 14 kbar at 589 nm [13] and at liquid helium and room temperature for several wavelengths [14]. We fitted both data sets with second-degree polynomials and combined them linearly to obtain  $n$  as a function of wavelength and pressure at a temperature of 10 K.

This procedure gives us two value pairs [ $k_1, E(k_1)$  and  $k_3, E(k_3)$ ] at each pressure. A two-oscillator formula with five parameters normally used in connection with KI [5,6] cannot be taken here to fit our data since we only have two value pairs, but  $E(k)$  can be expanded in powers of  $k^2$  for the first transverse polariton on the upper branch near  $k=0$ . In this way it is still possible to find the energy of the first longitudinal exciton  $E_{1L}$  for  $k=0$  and the curvature parameter  $A$  [defined by Eq. (2)] of the upper TP branch at  $k=0$ . One obtains the following equations:

$$E(k) = E_{1L} + Ak^2 + \frac{A^2}{\Delta} k^4, \quad (1)$$

$$A = \frac{E_{1L}^2 - E_{1T}^2}{2E_{1L}} \frac{E_{2T}^2 - E_{2L}^2}{E_{2L}^2 - E_{1L}^2} \frac{\hbar^2 C^2}{\epsilon_b}, \quad (2)$$

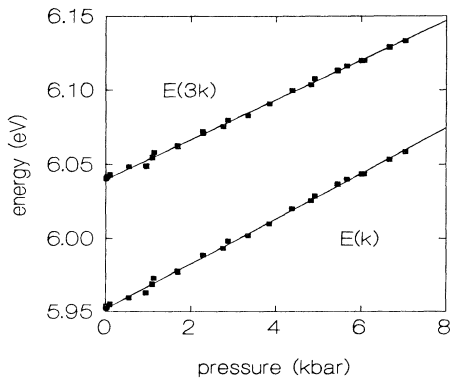


FIG. 2. Pressure dependence of the lowest transverse polaritons of wave vector  $k$  and  $3k$  in KI. The solid lines represent the linear best fit.

with  $\Delta = E_{1L} - E_{1T}$  being the longitudinal-transverse splitting,  $E_{1T}$  is the energy of the first transverse exciton,  $E_{2L}$  and  $E_{2T}$  are other parameters used in the two-oscillator formula incorporating higher energies, and  $\epsilon_b$  is a "background" dielectric constant due to the contribution of higher electronic states [5]. The expansion is only exact to order  $k^2$ .  $A^2/\Delta$  is an approximation retaining only the dominant part of the coefficient for the  $k^4$  term and exploiting the fact that  $\Delta \ll E_{1L}$ .  $\Delta$  can be expressed as [15]

$$\Delta = E_{1T} [(1 + 4\pi\alpha/\epsilon_b)^{1/2} - 1], \quad (3)$$

which can be approximated by  $\Delta/E_{1T} = 2\pi\alpha/\epsilon_b$  because  $\Delta \ll E_{1T}$  for KI ( $\alpha$  represents the electronic polarizability).  $\Delta$  has the value  $887 \text{ cm}^{-1}$  for ambient pressure [5]. Equation (3) shows that  $\Delta$  itself depends on pressure through  $E_{1T}$  and  $\alpha$  assuming that the background dielectric constant does not change within the pressure range of our experiment. Taking this into account, however, does not alter the values of  $E_{1L}$  and  $A$  obtained through the fitting of the data with Eq. (1) by more than the stated accuracy. For the energy of the first longitudinal exciton we found  $E_{1L} = 47951 \text{ cm}^{-1} + (125 \pm 3 \text{ cm}^{-1}/\text{kbar})p$  (kbar).

The value of  $E_{1L}$  at  $p=0$  is  $8 \text{ cm}^{-1}$  (1 meV) smaller than the value stated in Ref. [5], but still within their and our stated experimental error. This is not caused by neglecting terms higher than  $k^4$  in our expansion of  $E(k)$  of the first transverse polariton near  $k=0$ . Estimated error for  $E_{1L}(p=0)$  is again about  $12 \text{ cm}^{-1}$ .

The curvature parameter  $A$  was found to decrease linearly with pressure:

$$A = (1.874 - 0.047p/\text{kbar}) \times 10^{-13} \text{ cm}^{-1} \text{ m}^2.$$

For comparison, the unapproximated value of  $A$  at  $p=0$  is  $1.815 \times 10^{-13} \text{ cm}^{-1} \text{ m}^2$  using the values of Ref. [5]. The error in the pressure coefficient of  $A$  is estimated to be less than 6%.

$E_{1T}$  is the energy at  $k=0$  of an electron-hole pair

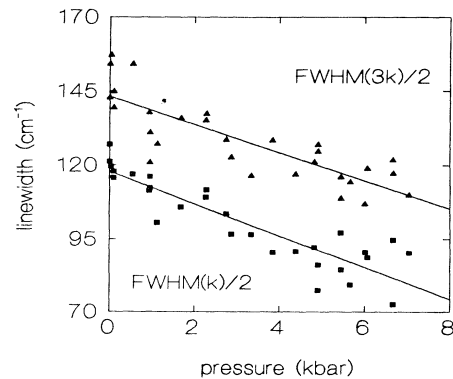


FIG. 3. Pressure dependence of the FWHM/2 of the transverse polaritons in KI. The solid lines represent the linear best fit.

without coupling to the electromagnetic field of the incident light. It is lower in energy than  $E_{1L}$  by the longitudinal-transverse splitting  $\Delta$ . If  $\Delta$  depends on pressure only through  $\alpha$  and  $E_{1T}$  one can exploit the above given pressure dependence of  $E_{1L}$  and the fact that  $\alpha$  is in good approximation proportional to the ionic volume for alkali halides. Rearranging  $E_{1L}(p) = E_{1T}(p) + \Delta(p)$  one finds that  $E_{1T}(p) = 47070 \text{ cm}^{-1} + (130 \text{ cm}^{-1}/\text{kbar})p$ , where the value of Ref. [5] was used for the energy at  $p=0$  (the bulk modulus of KI at 10 K is about 130 kbar [16]). The difference from the  $125 \text{ cm}^{-1}/\text{kbar}$  shift of the longitudinal exciton  $E_{1L}$  is almost negligible. This value should be compared with recent measurements of the exciton-absorption tail at room temperature versus pressure, which gave a value of  $201 \text{ cm}^{-1}/\text{kbar}$  [17] and a shift of  $136 \text{ cm}^{-1}/\text{kbar}$  found through piezoreflectivity spectra at 120 K [18].

Among models, the phenomenological model of Hilsch and Pohl [19] seems to best describe the pressure shift. They found that the energy of the first excitation in alkali halides can be accurately described by  $E = E_A - E_I + \alpha_M e^2/a$ , with  $E_A$  the electron affinity of the halogen,  $E_I$  the ionization energy of the alkali atom,  $\alpha_M$  the Madelung constant (1.748 for the sodium chloride structure), and  $a$  as the nearest-neighbor distance (3.51 Å for KI). Assuming that  $E_A$  and  $E_I$  do not change with pressure one obtains a pressure shift of about  $148 \text{ cm}^{-1}/\text{kbar}$ , which is close to the experimental value of  $130 \text{ cm}^{-1}/\text{kbar}$ .

The supposedly better Wolff-Herzfeld model [20], which already fails in predicting the lowest excitation energy accurately, also provides a less good value of  $211 \text{ cm}^{-1}/\text{kbar}$  for the pressure shift.

Reference [21] contains a band-structure calculation of KI for two different lattice parameters from which a pressure shift of the direct band gap at  $k=0$  is derived. Substituting 130 kbar for  $B$  instead of the about 110 kbar used originally one finds  $470 \text{ cm}^{-1}/\text{kbar}$  as the expected shift of the gap.

Preliminary measurements of the  $n=2$  exciton indicate no significant change in the binding energy with pressure, whereas a substantial increase of the binding energy has been observed in recent experiments with the semiconductor GaAs [22]. Therefore one might conclude that the pressure shift of the exciton in KI is caused almost completely by the pressure shift of the band gap at  $k=0$  and that their values are very close.

Polaritons are stationary states of the coupled exciton-photon field [23]. Once the polariton is created (in our case, on the upper transverse branch) it has several decay channels. Scattering mechanisms include longitudinal-acoustical and -optical phonons as well as impurities. Toyozawa derived the interaction Hamiltonian coupling excitons and phonons [24]. Tait and Weiher were the first to evaluate this matrix element in the polariton picture for the case of CdS by expressing the excitonic creation and annihilation operators through polariton

ones [25]. We repeated their calculation for the cases of coupling with longitudinal-optical and -acoustical phonons at  $T=0$  K. It was found that scattering within the upper polariton branch was negligible. The dominant decay channel was to the lower branch. Here the calculated scattering due to emission of LO phonons was about 10 times stronger than that due to LA phonons and accounted for more than 50% of the observed linewidth.

The calculations were quite sensitive to changes of  $m_e$  when  $\mu$  was held constant. For  $m_e$  we used a value of  $0.33m$  [26] ( $m$  is the electron mass) and for the reduced excitonic mass  $\mu$  a value of  $0.26m$  [27], which determines the effective hole mass. In order to see a pressure dependence in the linewidth  $m_e$  was assumed to be proportional to the energy gap as done in the  $kp$  perturbation method for semiconductors [28]. Whether the hole mass changes in the same way or stays constant ( $\mu$  is not held constant) did not affect the results considerably. Changes in the LO-phonon energy  $E_{LO}$  and the dielectric constants with pressure were neglected which might not be justified. All other changes with pressure in the quantities  $E(k)$ ,  $E_{1T}$ , and so on were implemented. It was found that the calculated half-width was decreasing, but not as strongly as observed. One reason might be that the model is using a parabolic exciton dispersion which is only justified for small  $k$ . A polariton on the upper branch emitting a phonon generates a polariton on the lower branch at about half the distance to the edge of the Brillouin zone and the excitonic mass there is probably not independent of the wave vector.

We assume that the rest of the linewidth is caused by impurities and inhomogeneities. Possibly the crystals used in Refs. [5,6] were of higher quality because their linewidth is generally less than ours.

In conclusion, we have measured the behavior of the upper polariton branch in KI near the center of the Brillouin zone under hydrostatic pressure by using the technique of three-photon spectroscopy recently introduced by Beerwerth and Fröhlich [5,6]. The result for the pressure shift is in good agreement with a value obtained by piezoreflectivity spectra [18]. We also found that the curvature of the upper branch near  $k=0$  decreases with pressure. There still seems to be no better model to explain the pressure shift of the first electronic excitation in KI than that of Hilsch and Pohl from the year 1929 [19]. We tried to explain the observed decrease in the polariton linewidth with pressure using a method developed by Tait and Weiher [25], but the calculated decrease is smaller than the one we observe.

We hope this may introduce a powerful new tool to study the electronic states of crystals such as xenon and hydrogen under pressure in which the band gaps are greater than the transmission range of the cell windows.

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