PHYSICAL REVIEW B VOLUME 44, NUMBER 12 15 SEPTEMBER 1991-II

Two-photon spectroscopy in KCl using synchrotron radiation

M. Casalboni, C. Cianci, R. Francini, and U.M. Grassano
Dipartimento di Fisica, Università di Roma, "Tor Vergata," Via Orazio Raimondo, 00173 Roma, Italy

M. Piacentini
Dipartimento di Energetica, Università di Roma, "La Sapienza," Via Antonio Scarpa 14, 00161 Roma, Italy

N. Zema
Istituto di Struttura della Materia del Consiglio Nazionale delle Ricerche, Via Enrico Fermi 38, 00044 Frascati, Italy

(Received 26 March 1991)

Two-photon absorption spectra in the excitonic region of KCl up to 8.65 eV are reported. The sources employed in the two-photon experiment are the synchrotron radiation together with a neodymium-doped yttrium aluminum garnet laser. The measured absorption spectra show structures attributed to the $2p$ and $3p$ exciton levels associated with the direct gap of KCl. These optical data give a direct measurement of the energy gap and an estimation of the exciton mass of KCl.

I. INTRODUCTION

Two-photon spectroscopy is a widely used experimental technique in atomic and solid-state physics. Two-photon absorption (TPA) consists in the measurement of the absorption coefficient of a *probe beam* in the presence of a powerful laser beam. The interest in this kind of spectroscopy lies in the possibility of determining the energy position of those states with the same parity as the ground state.

The two-photon absorption spectra in many families of compounds have been measured in the past years, using, as a probe beam, conventional light sources or tunable lasers.[1,2] For this reason the spectral interval accessible to measurement was limited to energies lower than 8 eV and, for example, in the alkali halides the investigations were limited to the iodides and bromides.[3]

The tunable vacuum-ultraviolet (VUV) synchrotron radiation allows for the extension of the available TPA spectral range up to the band-to-band transitions in the large-gap insulators including alkali-metal and alkaline-earth fluorides. Some of the present authors have already shown[4,5] the feasibility of such an experiment, detecting, in several alkali halides, the depletion of the VUV synchrotron radiation in the presence of a powerful neodymium-doped yttrium aluminum garnet (Nd:YAG) laser beam. In this work we report on several improvements of our previous results and we present additional data on two-photon absorption in KCl over a wider energy range and with a better energy resolution.

The improved experimental setup made it possible to resolve absorption structures that we assign to the two-photon allowed $2p$ and $3p$ excitonic transitions. Improved values for the two-photon absorption coefficient and for the direct energy-gap value of KCl are also derived, which take care of some inaccurate estimations made in a previous paper.[4]

II. EXPERIMENT

Nominally pure potassium chloride single crystals were purchased from three sources: Harshaw Chemical Co., Physics Department of the University of Rome–"La Sapienza," and Crystal Growth Laboratory of the University of Utah (Salt Lake City). One crystal from the latter source was grown from powders processed in a Cl_2 atmosphere. This sample, characterized by very low OH^- ion concentration and high transparency in the region from the ultraviolet up to the intrinsic absorption, could not be used in our experiment because of the unexpected low value of the dielectric breakdown threshold: sample damage occurred at a laser energy flux (< 1 GW/cm^2) too low for detecting any TPA signal.

Freshly cleaved samples ($\sim 0.5 \times 1 \times 1$ cm^3) were mounted on the cold finger of a variable-temperature cryostat (10–300 K). The experiment was performed at the Adone storage ring of the Frascati National Laboratories using a modified version of the apparatus described in detail in Ref. 5.

The synchrotron-radiation (SR) beam is dispersed by a 1-m normal-incidence monochromator and it is then focused inside the sample by means of a concave mirror. The emerging beam is collected on a window coated with sodium salycilate, whose visible luminescence is detected by a 14-stage fast photomultiplier. The signal appears as a train of pulses (3-ns duration, 8.57-MHz repetition rate), their intensity being proportional to the number of the electrons stored inside the ring and to the crystal transmission.

The laser beam (photon energy = 1.17 eV, peak power $\sim$ 10 MW, pulse duration 12 ns, and repetition rate $\sim$ 10 Hz), focused with a 700-mm lens, intercepts at right angles the VUV beam inside the sample. Spatial and temporal overlapping of the two beams is crucial and particular care was used to minimize the laser radiation scattered towards the detector in the measurement chamber. The best compromise between the necessity of a large photon flux and still avoiding sample damage was found with a laser beam diameter of ~ 1 mm inside the crystal.

The main changes with respect to the previous experimental apparatus concern the coincidence unit and the acquisition and signal processing system. The coincidence unit triggers the laser Pockel cell in such a way to produce a laser pulse that arrives on the sample at the same time of one VUV pulse with a maximum jitter of less than 1 ns. The same coincidence unit supplies also the timing for the completely digital acquisition system: two subsequent gates trigger a fast analog to digital converter (LeCroy 2249 SG) to acquire the integrated intensities of the SR pulse coincident with the laser and that of the next arriving SR pulse (117 ns after the first pulse), the latter providing the reference intensity.

In order to minimize signal fluctuations due mainly to the small number of photons per SR pulse collected by the detector, we average about 1000 laser pulses for each wavelength. The signal-to-noise ratio thus obtained, allows us to measure TPA spectra with a much better energy resolution compared to those previously published.[4]

A CAMAC-standard microcomputer drives the acquisition and control system. During the measurement it is then possible to directly monitor the behavior of the two-photon absorption coefficient β, defined as

$$\beta \equiv -\left(\frac{1}{dI_{\mathrm{las}}}\right)\ln\left(\frac{I_{\mathrm{sig}}}{I_{\mathrm{ref}}}\right), \tag{1}$$

where d is the laser beam diameter, I_{las} is the average laser flux expressed in MW/cm^2, and I_{sig} and I_{ref} are the intensities of the single SR pulse in coincidence and out of coincidence with the laser pulse, respectively.

For a laser-photon energy of 1.17 eV, the TPA spectra have an upper energy limit of ~ 1.1 eV beyond the onset of the first exciton linear absorption. At higher energies the VUV photons begin to be resonantly absorbed via the normal one-photon process. An attempt to extend the investigated range was made using more energetic laser photons, namely, the second harmonic of the Nd:YAG at 2.34 eV, produced by means of a potassium dihydrogen phosphate crystal. However, the intensity of the so obtained beam (peak energy flux ~ 100 MW/cm^2) was too weak to induce any detectable TPA signal.

III. RESULTS AND DISCUSSION

The two-photon absorption coefficient of KCl measured at $T = 10$ K is plotted in Fig. 1 (continuous line) together with the one-photon absorption coefficient (dashed line) obtained by Teegarden and Baldini[6] on evaporated films. The main differences of the present data with respect to the previous report are the resolved structures around 8.6 eV and the shift of the energy scale of the two-photon signal (that refers to the sum of the energies of the two photons). This shift derives from a more accurate recalibration of the vacuum monochromator on the synchrotron radiation beam line.

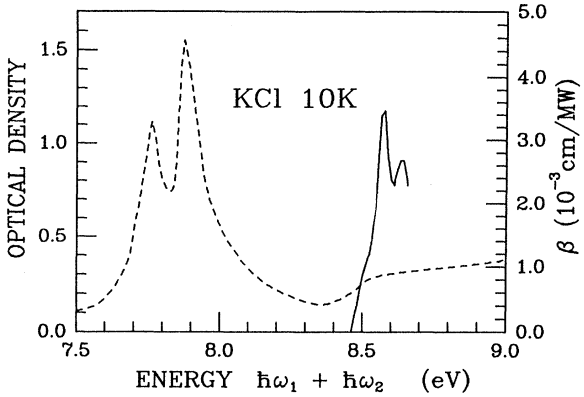

FIG. 1. Two-photon absorption spectrum (continuous line) of KCl at 10 K, compared with the one-photon absorption spectrum (dashed line) from Ref. 6.

The onset of the two-photon absorption coefficient occurs at 8.46 eV (at 10 K). The two-photon absorption spectra are plotted in Fig. 2 on an expanded energy scale for two different temperatures, at 10 K and 110 K. The presence of two peaks is clearly visible at both temperatures.

At 10 K the two peaks are found at 8.57 eV and 8.64 eV. At higher temperature (110 K) they shift to lower energies; the structures becomes broader and the relative intensity of two peaks is reversed. This last result may, however, derive from a rise of the absorption background that seems to occur at higher temperature.

The simple hydrogenic approximation for the exciton energy E_n gives

$$E_n = E_{\mathrm{gap}} - \frac{R^*}{n^2}, \tag{2}$$

where n is the principal quantum number and R^* the exciton binding energy

$$R^* = \frac{\mu}{\epsilon^2}R \tag{3}$$

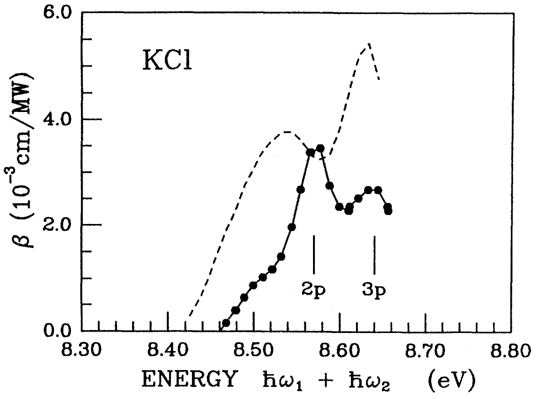

FIG. 2. Two-photon absorption spectra of KCl for two different temperatures: continuous line $T = 10$ K; dashed line $T = 110$ K.

related to the exciton mass μ, to the dielectric constant ϵ, and to the Rydberg constant $R = 13.54$ eV.

The identification of the two structures with the $2p$ and $3p$ excitons leads to the determination of the energy-gap value for KCl. The obtained value, $E_{\text{gap}} = 8.70$ eV, is in agreement with several previous data based on one-photon measurements (Refs. 7–11). From the same equations we obtain the binding energy $R^* = 0.504$ eV. This value depends upon the ratio μ/ϵ^2 so that, using for the dielectric constant the static value $\epsilon_0 = 4.84$, we can estimate an exciton mass $\mu = 0.87\ m_e$, where m_e is the free-electron mass.

The exciton mass is related to the electron polaron (m_e^*) and to the hole polaron (m_h^*) mass by the relation

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}. \tag{4}$$

Using our value $\mu = 0.87 m_e$ for the exciton mass and the value $m_e^* = 1.25 m_e$ for the electron-polaron mass, determined via cyclotron resonance,[12] we derive the hole-polaron mass $m_h^* = 2.85 m_e$. The fairly large value is in agreement with the low dispersion of the valence band.

The use of the static dielectric constant in the screening of the Coulomb energy may be questionable for a Frenkel exciton and several authors[12,13] have indeed suggested that the high-frequency dielectric constant is more appropriate in the treatment of a problem for which the Franck-Condon principle is valid, i.e., the lattice does not relax during the optical absorption.

By using $\epsilon_\infty = 2.19$ instead of ϵ_0, one obtains $\mu = 0.18 m_e$. This value is, however, too low: with the electron polaron mass quoted above, or even with the effective electron mass $m_e^* \sim 0.45 m_e$,[13] one obtains for the effective hole mass $m_h^* = (0.2\text{–}0.3) m_e$. This value is unreasonably small in view of the valence band characteristic of the alkali halides. The same inconsistency was already pointed out by Knox and Teegarden,[13] who quote the results of Hopfield and Worlock[14] in KI for the exciton mass, $\mu = 0.2 m_e$, obtained using the high-frequency dielectric constant. It seems therefore that the Wannier excitonic model with the static dielectric constant ϵ_0 is a more accurate approximation in the description of the excitons in alkali halides, at least for the $2p$ and $3p$ excitonic levels.

We would like also to point out that the absolute value of the TPA coefficient β shown on the ordinate scale of Figs. 1 and 2 has been reevaluated through a more accurate measurement of the photon flux on the crystal surface. The order of magnitude of β is in good agreement with the value found by Liu *et al.*[15] for KCl with a single source (laser with $\hbar\omega = 4.66$ eV): they estimated $\beta = (1.7\text{–}2.7) \times 10^{-3}$ cm/MW, at a fixed energy of 9.32 eV.

In summary we have reported more accurate data of TPA in KCl that confirm the importance of this type of experiment in the study of the fundamental parameters such as energy-gap value and effective mass in wide energy-gap materials.

ACKNOWLEDGMENTS

The authors thank Professor A. Scacco of Dipartimento di Fisica, Università di Roma–"La Sapienza" for the KCl samples and Dr. R. Pizzoferrato for the valuable help in the starting up of the experimental apparatus. Thanks are due to C. Barchesi of Istituto di Struttura della Materia del CNR for the development of the coincidence unit.

---

[1] H. Mahr, in *Quantum Electronics*, edited by H. Rabin and C.L. Tang (Academic, New York, 1975), Vol. 1, Part A, p. 285.

[2] I.M. Catalano, A. Cingolani, and M. Lepore, Phys. Rev. B **33**, 7270 (1986); Solid State Commun. **60**, 385 (1986).

[3] D. Fröhlich, Festkörperprobleme **10**, 227 (1970).

[4] R. Pizzoferrato, M. Casalboni, R. Francini, U.M. Grassano, F. Antonangeli, M. Piacentini, N. Zema, and F. Bassani, Europhys. Lett. **2**, 571 (1986).

[5] R. Pizzoferrato and M. Casalboni, J. Phys. E **20**, 897 (1987).

[6] K.J. Teegarden and G. Baldini, Phys. Rev. **155**, 896 (1967).

[7] T. Miyata and T. Tomiki, J. Phys. Soc. Jpn. **24**, 1286 (1968).

[8] T. Tomiki, J. Phys. Soc. Jpn. **22**, 463 (1967).

[9] D.M. Roessler and W.C. Walker, J. Phys. Chem. Solids **28**, 1507 (1967).

[10] G. Baldini and B. Bosacchi, Phys. Rev. **166**, 863 (1968).

[11] R. Huggett and K.J. Teegarden, Phys. Rev. **141**, 797 (1967).

[12] J.W. Hodby, J.A. Borders, F.C. Brown, and S. Foner, Phys. Rev. Lett. **19**, 952 (1967).

[13] R.S. Knox and K.J. Teegarden, in *Physics of Color Centers*, edited by W.B. Fowler (Academic, New York, 1968), p. 1.

[14] J.J. Hopfield and J.M. Worlock, Phys. Rev. **137**, 1455 (1965).

[15] P. Liu, W.L. Smith, H. Lotem, J.H. Bechtel, N. Bloembergen, and R.S. Adhav, Phys. Rev. B **17**, 4620 (1978).