NEW ASSIGNMENT OF THE BAND GAP IN THE ALKALI BROMIDES BY TWO-PHOTON SPECTROSCOPY

Dietmar Fröhlich and Bernd Staginnus
Physikalisches Institut der Universität, Frankfurt am Main, Germany
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Hopfield, Worlock, and Park[1,2] were the first to report two-photon spectroscopy experiments. They measured the two-photon spectrum of KI and CsI. With an improved experimental setup[3] we are able to extend the spectroscopic range to alkali bromides and to do for the first time a detailed study of the polarization dependence of the two-photon absorption. In this Letter we report measurements on RbI, RbBr, KBr[4] (Figs. 1 and 2)[5] and NaBr. These results lead in the case of KBr and RbBr to a new assignment of the band gap; for NaBr a determination of the band gap is made for the first time, since no identification has been possible from the one-photon spectrum. A detailed investigation of the polarization dependence of the two-photon absorption in RbI at an energy of 6.8 eV is shown in Fig. 3.

Since it is commonly assumed that the upper valence band in the alkali halides is constructed from atomic p functions and the lowest conduction band from s functions, direct band-to-band transitions are parity forbidden in the two-photon absorption at the Γ point. Because of this fact there are two possible approaches to assign the two-photon edge:

(1) The two-photon edge is due to a "forbidden"[6] transition at the Γ point. Then the two-photon absorption should start in the region of the "step" of the one-photon spectrum, which is commonly assigned as the band gap. Hopfield and Worlock[2] could explain their results as being due to such a transition at the Γ point. Our measurements on another iodide (RbI) seem to confirm their results. For the alkali bromides, however, the two-photon spectrum (Fig. 2) contradicts the adopted assignment of the band gap to the region of the "step" in KBr[7,8] and in RbBr, since the two-photon absorption starts already 0.6 eV before the "step." From our measurements we make the following new assignments for the band-to-band transitions: The first rise in the two-photon spectrum (7.2 eV in RbBr, 7.3 eV in KBr, and 7.0 eV in NaBr) reflects[9] the band gap ($\Gamma_8^- \rightarrow \Gamma_6^+$), which does not show up in the one-photon spectrum, since it is hidden underneath the second exciton peak.[5] The second rise in the two-photon spectrum (7.7 eV in RbBr and 7.8 eV in KBr) which is in the region of the "step" of the one-photon spectrum corresponds to the transition from

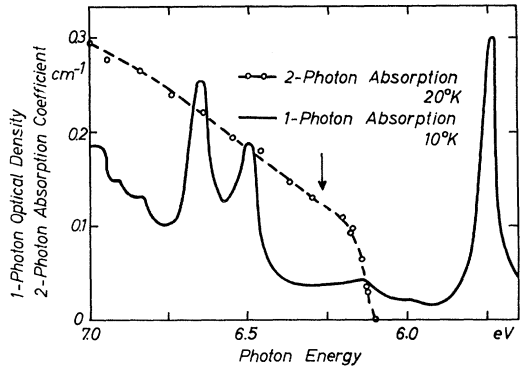

FIG. 1. One-photon (Ref. 5) and two-photon absorption spectra of RbI. Arrow indicates band gap energy. Laser flux: 5×10^{25} photons/cm^2 sec.

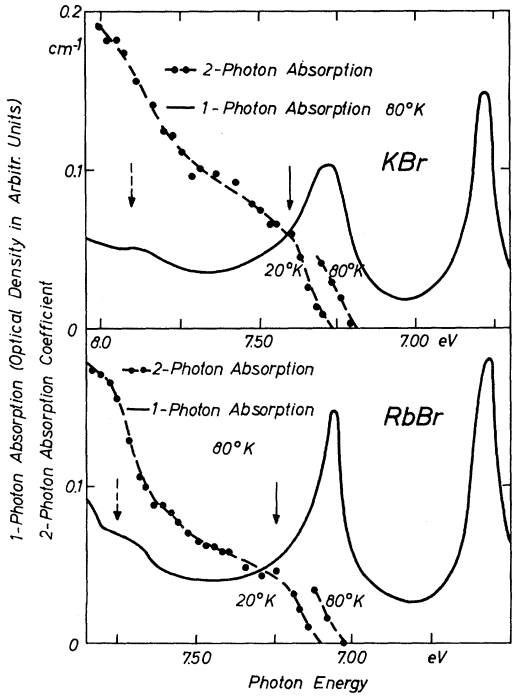

FIG. 2. One-photon (Ref. 5) and two-photon absorption of KBr and RbBr. Dotted arrow indicates old gap assignment; solid arrow indicates new gap energy. Laser flux: 5×10^{25} photons/cm^2 sec.

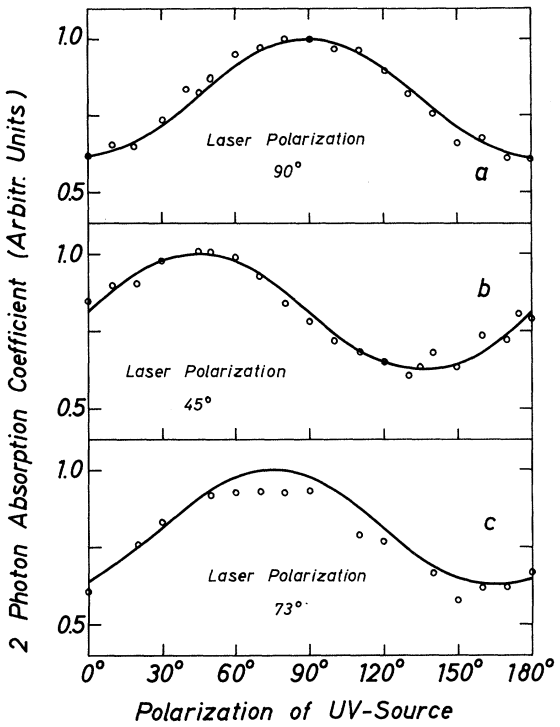

FIG. 3. Two-photon absorption in RbI at 6.8 eV and 20°K as a function of the uv-source polarization for indicated fixed laser polarization. (a), (b) Solid lines are the best fits to the experimental points. (c) Solid line is calculated from the results of graphs (a) and (b). The 0° direction of polarization is referred to the [100] crystal direction; the light beams are incident along [001]. Note the suppressed zero in the ordinate of the graphs.

the lower valence band to the conduction band ($\Gamma_6^- \rightarrow \Gamma_6^+$). This interpretation does not contradict the photoconductivity measurements of Huggett and Teegarden,[8] and reproduces very well the known spin-orbit splitting of about 0.5 eV.[10] In addition, the new gap assignment lowers the s-exciton binding energy of the bromides from 1.2 to 0.6 eV, which is now close to the 0.5 eV for the iodides[11] and 0.7 eV for the chlorides.[11]

(2) The two-photon spectrum is due to an "allowed"[6] band-to-band transition. This case has been explicitly studied by Inoue and Toyozawa.[12] They show that symmetry assignments of the excited state can be obtained by two-photon measurements with polarized light. Each of the three graphs of Fig. 3 shows the two-photon absorption as a function of the polarization of the uv source with the indicated fixed polarization of the laser. Using Inoue and Toyozawa's analysis we determine from Figs. 3(a) and 3(b) the coefficients for their three independent angular functions. These coefficients enable us to calculate the solid line in Fig. 3(c), which is in good agreement with the experimental points, showing the internal consistency of the analysis. The values of these coefficients indicate that the transition takes place either on the Σ line or at the K point in the Brillouin zone. These polarization properties do not change throughout the whole spectrum. In RbBr the polarization dependence was studied at two energies (7.2 and 7.8 eV); the same behavior was found as in RbI. As a consequence of this analysis the difference between the upper valence band and the conduction band on Σ or at K may be obtained from the onset of the two-photon absorption.

Both proposed explanations lead to a new assignment for the band gap of the bromides. This result is especially important for band calculations, since the experimentally determined band gap is mostly used as a fitting parameter.[13] Our investigations will be extended to a detailed comparison of the one- and two-photon spectra in other alkali halides including chlorides.

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HELICON-GANTMAKHER-WAVE INTERACTIONS IN COPPER

G. Weisbuch and A. Libchaber
Groupe de Physique des Solides de l'Ecole Normale Supérieure,* Paris, France
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This Letter is concerned with the propagation of low-frequency electromagnetic waves through monocrystalline plates of copper, in the presence of a strong dc magnetic field perpendicular to the plate. It is well known[1] that helicons can propagate under these conditions. Gantmakher and Kaner[2] (GK) have shown the existence of a different type of wave, related to the spiral motion of the electrons along the magnetic field. In this Letter we report the observation of interaction between these two waves and we propose a theoretical explanation for the observed phenomena.

Let us first recall that according to GK, two types of waves may be excited at the surface of a metal plate placed perpendicular to the magnetic field. The first type, including helicon, corresponds to the roots of the dispersion equation

$$q^2 - i\mu\sigma(q)\omega = 0,$$

where q is the wave vector, $\omega/2\pi$ the frequency, μ the permeability, and $\sigma(q)$ the q dependent conductivity.

The second type, which we call Gantmakher waves, corresponds to the branch points of $\sigma(q)$. They have a wave vector k depending only on the spatial periodicity u of the electronic orbit (displacement of the orbit center along magnetic field during one cyclotron period):

$$k = \frac{2\pi}{u} = \frac{2\pi}{\hbar} eB\left(\frac{\partial S}{\partial K_z}\right)^{-1},$$

where $2\pi\hbar$ is Planck's constant, e the electronic charge, B the magnetic field along z axis, and S is the area of the orbit in K space. These quantities have to be taken at the orbits of extremal u. For a spherical Fermi surface, u is extremal at the limiting point $p_z = p_F$ and $k = \omega_c/v_F$ ($\omega_c/2\pi$ is the cyclotron frequency and v_F the Fermi velocity). In this Letter we shall always refer to the wave-vector solution of the dispersion equation as q and to the Gantmakher wave vector as k.

The domains of existence of these waves are limited. For a spherical Fermi surface, helicons propagate with low attenuation outside of the Doppler-shifted cyclotron resonance region, i.e., $\omega_c > qv_F$. Gantmakher waves, on the other hand, are typically excited by strongly attenuated electromagnetic waves. We thus expect to see the propagation of the two waves in their respective domains, and a region of interaction near $\omega_c = qv_F$ where both waves have the same wave vector.

Experimental procedure.-We use copper single crystals in the form of plates, the thickness of which varies from 3 to 0.3 mm. We start from 99.999% pure materials[3] and use a Bridgman technique to obtain single crystals. The plates are spark cut and planed, and are finally electropolished in phosphoric acid (at least 0.2 mm removed). After annealing for 48 h in 2×10^{-4} mm Hg oxygen, we obtain a 6000 resistivity ratio with good reproducibility.[4]

For the experimental set up we use the low-frequency transmission technique developed by Grimes.[5] A coil excites a wave on one side of the plate, which is then detected on the other side by a second coil placed parallel to the first. The transmitted signal interferes with a leakage signal and the resulting wave is analyzed by a HR 8 lock-in amplifier,[6] and recorded as a function of the dc magnetic field on an X-Y recorder. The magnet is a 9-in. Varian.

Experimental results.-Two geometries gave