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Band-Gap Assignment in SnO₂ by Two-Photon Spectroscopy

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We present for the first time two-photon measurements on rutile SnO₂. The detailed polarization analysis yields Γ_3^+ symmetry for the direct forbidden 1S exciton and the upper valence band. Our results clear up the long-standing controversy concerning the symmetry of the upper valence band.

As proposed by Loudon,¹ the direct forbidden transitions are specially suited to be studied by two-photon spectroscopy. Loudon calculated the two-photon absorption for Cu₂O, which was later studied by Pradère and co-workers.² Because of experimental difficulties these authors found only a weak structure, which they attribute to the 1S exciton. They were not able to measure the polarization dependence. We present for the first time a detailed polarization analysis of such a direct forbidden transition. Using this technique we are able to resolve the long-standing puzzle on the band-gap assignment in SnO₂ (D_{4h}^{14}).

Though the early indication of SnO₂ being an indirect material^{3,4} could no longer be maintained after the excellent work of Nagasawa and Shionoya,⁵ the symmetry assignment of the direct gap remained as a controversy. Nagasawa and Shionoya were able to show that the band gap is direct forbidden at $\bar{K} = 0$. They offer three possibilities for the highest valence band (Γ_2^+ , Γ_3^+ , Γ_4^+) assuming a Γ_1^+ lowest conduction band, which is agreed on in later experimental^{6,7} as well as theoretical investigations.^{8,9} Agekyan¹⁰ analyzed the quadrupole transition to the 1S exciton and determined Γ_3^+ symmetry for the top valence band. There are two band-structure calculations^{8,9} published which contradict each other as well as the assignment of Agekyan. Arlinghaus⁸ assigns the top valence band to be of Γ_1^+ symmetry whereas Jacquemin⁹ comes up with a Γ_5^+ valence band. Jacquemin states that his assignment is compatible with the experimental results of Agekyan.¹⁰

A third band-structure calculation was very recently presented by Robertson,¹¹ who calculated the highest valence band to be of Γ_3^+ symmetry. In order to clear up this controversy, we present two-photon data on the lowest exciton. A complete polarization analysis of this transition allows an unambiguous assignment of the upper valence band to Γ_3^+ symmetry.

Our basic experimental setup is described in detail by Fröhlich and Sondergeld.¹² To improve

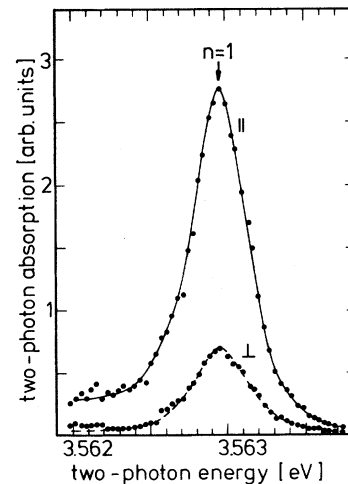


FIG. 1. Two-photon spectra of 1S exciton in rutile SnO₂ at 4.5 K (resolution 0.15 meV). || configuration (0°/0°), both polarization vectors $\vec{\epsilon}_1$ and $\vec{\epsilon}_2$ parallel to [100]; ⊥ configuration (0°/90°), $\vec{\epsilon}_1$ in [100] and $\vec{\epsilon}_2$ in [010] directions.

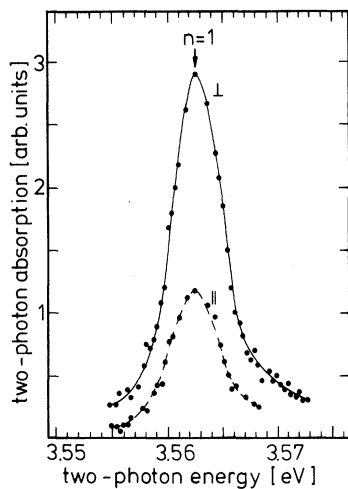


FIG. 2. Two-photon spectra of 1S exciton in rutile SnO_2 at 4.5 K (resolution 5 meV). \parallel configuration ($45^\circ/45^\circ$), both polarization vectors $\vec{\epsilon}_1$ and $\vec{\epsilon}_2$ parallel to [110]; \perp configuration ($45^\circ/135^\circ$), $\vec{\epsilon}_1$ in [110] and $\vec{\epsilon}_2$ in $[\bar{1}10]$ directions.

the signal-to-noise ratio and the spectral resolution we used for most of the measurements a stilben dye laser (0.15 meV resolution) pumped by a krypton laser instead of the standard xenon flash-lamp plus monochromator (5 meV resolution). As a high-power laser we used a Raman-shifted (H_2 gas at 40 bars) Nd-doped yttrium-aluminum-garnet laser (0.6496 eV). The crystals¹³ were of high quality as indicated by the narrow linewidth of the 1S exciton.

In Figs. 1 and 2 we present two examples of experimental spectra. All data presented here were taken with \vec{K} vectors parallel to the tetragonal axis. The high-resolution (0.15 meV) results of Fig. 1 were gained with the dye-laser setup whereas for the measurements in Fig. 2 we used the standard flash-lamp setup (5 meV resolution). From the high-resolution data of Fig. 1 we deduce for the position of the 1S exciton an energy of $(3.5630 \pm 3) \times 10^{-4}$ eV, which is in agreement with one-photon data.^{5,10} The polarization analysis using the standard formalism¹⁴ allows an unambiguous assignment: From Fig. 1 we deduce the two possibilities of Γ_1^+ and Γ_3^+ as final state. The result of Fig. 2 excludes Γ_1^+ , thus leading to the assignment of Γ_3^+ symmetry to the lowest exciton. Since the lowest conduction band is of Γ_1^+ symmetry we deduce for the upper valence

band Γ_3^+ symmetry. The rather small absorption in the perpendicular configuration ($0^\circ/90^\circ$) in Fig. 1 and in the parallel configuration ($45^\circ/45^\circ$) in Fig. 2 can be explained by the depolarization of the crystal. Additional measurements with circular polarized light confirm the above assignment.

Other compounds with a direct forbidden band gap like GeO_2 , TiO_2 , and Cu_2O are good candidates to be studied with this technique. The polarization analysis should help to clear up still existing uncertainties concerning the symmetry assignments not only of the uppermost valence band and lowest conduction band but of higher-energy transitions as well. Using this technique one should, e.g., be able to locate the second conduction band in SnO_2 , which is supposedly of Γ_4^+ symmetry.

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