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Assignment of the Even-Parity Excitons in Cu_2O

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This Letter presents for the first time a detailed two-photon spectrum of the even-parity excitons of the yellow series in Cu_2O. Contrary to one-photon data, it is possible to measure directly S and D exciton contributions without applying external perturbations. The two-photon spectrum gives evidence for a strong mixing between the yellow and the green series which is explained by exchange interaction and nondiagonal parts in the effective-mass Hamiltonian.

Cu_2O is by far the most extensively studied exciton system. For literature on this subject we refer to a recent review article by Agekyan[1] and the paper by Washington *et al.*[2] on resonant Raman scattering in Cu_2O. Despite many efforts there are still existing controversies concerning the assignments of the yellow series. The nP yellow series, which can be followed up to $n = 10$ directly in one-photon absorption, shows an almost perfect $1/n^2$ dependence. The parity-forbidden nS and nD members of the yellow series, however, can be detected in one-photon absorption only through their quadrupole interaction, their phonon interaction, and internal or external perturbations. The main experimental controversy is the location of the $2S$ state and following nS and nD states. Up to 1974 the $2S$ level was placed below the $2P$ level by Agekyan *et al.*[3] and Deiss, Daunois, and Nikitine.[4] Agekyan and Stepanov[5] were the first to raise doubts on the old assignment of the yellow nS series $n \geq 2$. From the exchange-strain splitting they concluded that the "old" $2S$ line of the yellow series (17 250 cm^{-1}) has to be interpreted as the $1S$ line of the green series and the main quantum number of the other nS lines of the yellow series have to be decreased by 1. In addition the same authors[5] assigned the lower lines of the doublet components as dipole-forbidden P levels $3P'$ and $4P'$. In a later paper, however, Agekyan and Braulova[6] go back to the old assignment, interpreting these states as $3D_1$ and $4D_1$. This assignment is also supported by the resonant Raman-scattering measurements of Washington *et al.*[7]

Despite considerable improvements of sensitivity, e.g., by application of modulation techniques,[8,9] there are inherent difficulties in interpreting the one-photon data for the following reasons[2]: (1) The perturbation-induced structures are rather small as compared with the dominant nP spectrum. (2) The spectrum is complicated by the overlapping exciton series of the lower valence band (green series), the indirect orthoexciton and paraexciton transitions,[10] and the indirect continuum. (3) Impurity absorption[9] confuses the interpretation by causing weak lines comparable to the parity-forbidden nS and nD lines.

In this Letter we will present results from a complementary method, namely two-photon absorption (TPA), which avoids the difficulties listed above resulting in a conclusive answer to the controversial assignment of the nS and nD states.

As pointed out very early by Loudon,[11] TPA is ideally suited to study the parity-forbidden exciton transitions in Cu_2O. The first experimental attempts[12] were rather unsuccessful in resolving any structure. By the use of a tunable dye laser (HITC, Oxazine 750 pumped by a krypton laser), we were able to improve the spectral resolution to about 0.1 meV. In addition, the high photon

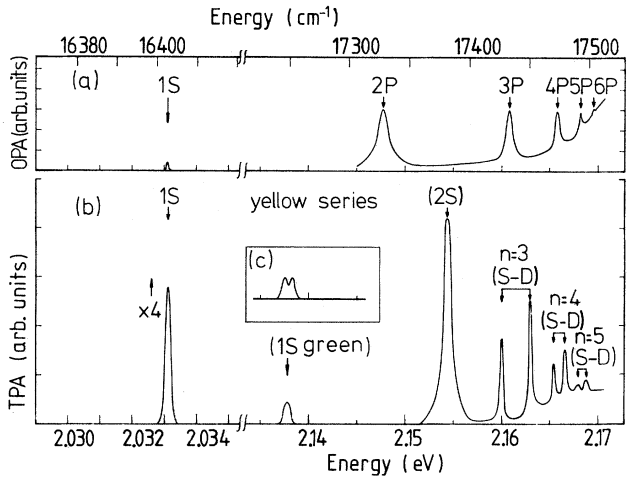

FIG. 1. One- and two-photon spectra of Cu_2O. (a) One-photon data at 4.2 K from Ref. 14. (b) Two-photon data at 4.5 K; the yellow 1S line was measured at 20 K. (c) Splitting of green 1S exciton in a magnetic field of 8.5 T (Voigt configuration). Note the enlarged energy scale for the yellow 1S region.

flux of the dye laser as compared with a flash lamp allows us to measure the rather small absorption signals ($\Delta I/I_0 \sim 10^{-2}$) with an accuracy of about 5%. 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). Details of the experimental setup are published by Fröhlich and Sondergeld.[13] Our measurements were performed on highly pure, arc-image-grown Cu_2O crystals.

In Fig. 1 we compare the two-photon spectrum with the well-known one-photon data for the P series and the 1S quadrupole line[14] of the same series. As expected, the two-photon spectrum shows very clearly the even-parity excitons. When the two spectra are compared, the assignment of the yellow 1S exciton and the lines for $n \geq 3$ is obvious. The appearance of doublets (S-D) for $n \geq 3$ clearly supports the assignment. The remaining two lines, at 2.1378 eV (weak line) and at 2.1544 eV (strong line), are interesting because of their relative oscillator strength and their position as compared with the 2P exciton. The rather large shift (7 meV) of the strong line (2S) towards higher energies is surprising since it is too large to be explained solely by exchange interaction for the yellow series, which would yield 1.5 meV as derived from the known exchange splitting of the yellow 1S exciton.[10] The other very puzzling result is the small oscillator strength of the structure at 2.1378 eV, which should be comparable to that of the 1S yellow exciton, if it is to be assigned solely to the 1S green exciton. Both results can be explained by the exchange interaction between the even-parity members of the yellow series and the 1S exciton

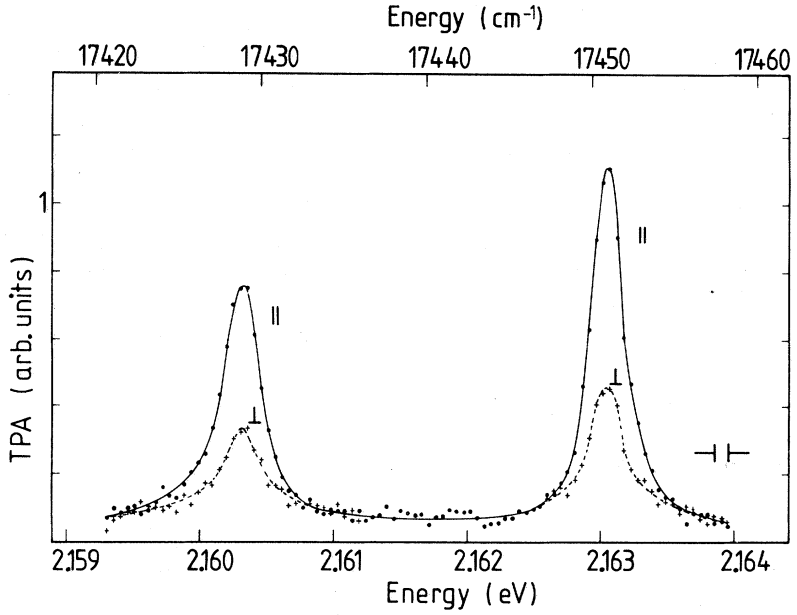

FIG. 2. Two-photon spectra of the $n = 3$ excitons for different polarization configurations at 4.5 K (resolution 0.1 meV). In ∥ configuration, both polarization vectors $\vec{\epsilon}_1$ and $\vec{\epsilon}_2$ are parallel to $[\bar{1}11]$; in ⊥ configuration, $\vec{\epsilon}_1$ in $[\bar{1}11]$ and $\vec{\epsilon}_2$ in $[1\bar{1}2]$ directions.

TABLE I. Excitation energies of the even-parity excitons in Cu_2O.

State[a]		E_{exp} (eV)[b]	E_{calc} (eV)[c]
1S Y	(Γ_2^+)	2.0212[d]	2.0212
1S Y	(Γ_5^+)	2.0330	2.0330
1S G	(Γ_3^+, Γ_4^+)	2.1269[e]	2.1260
1S G	(Γ_5^+)	2.1378	2.1386
2S Y	(Γ_5^+)	2.1544	2.1564
3(S,D) Y	(Γ_5^+)	2.1603	2.1597
	(Γ_5^+)	2.1630	2.1629
4(S,D) Y	(Γ_5^+)	2.1653	2.1651
	(Γ_5^+)	2.1666	2.1663
5(S,D) Y	(Γ_5^+)	2.1678	2.1676
	(Γ_5^+)	2.1685	2.1682

[a] Symmetry assignment; Y and G refer to the yellow and green series, respectively; (S,D) denotes states with mixed symmetry.

[b] Energies of the Γ_5^+ excitons as obtained by TPA.

[c] Energies calculated within the spherical model (Ref. 16) taking into account the split-off Γ_8 valence band and exchange interaction.

[d] Triplet exciton energy according to Ref. 10.

[e] Triplet exciton energy according to Ref. 5.

state of the green series. The 1S exciton of the green series and the nearby 2S exciton of the yellow series are mixed by exchange interaction in such a way that nearly all oscillator strength is transferred to the high-energy component of the interacting states and the 2S line is shifted appreciably towards higher energy. This also explains the anomalous large exchange splitting (9 meV) of the 2S exciton as measured by Agekyan and Braulova.[6]

A detailed analysis using the standard formalism[15] shows that the polarization dependence of both components of the doublets (Fig. 2) is that of a direct two-photon allowed S state of Γ_5^+ symmetry. This can only be explained by the assumption of strong S-D mixing. An interaction between S and D states is caused by d-like contributions to the effective-mass Hamiltonian[16] which lead to a coupling between the Γ_7^+ and Γ_8^+ valence-band components. This interaction is strong in Cu_2O because the 1S exciton of the green series is close to the higher states of the yellow series.

A first calculation taking into account exchange interaction and the spherical H_d term confirms that the anomalous behavior of the even-parity excitons can be explained within the discussed concept. In Table I we present numerical results which were obtained by an exact diagonalization of the effective-mass Hamiltonian within the spherical approximation including both valence bands (Γ_7^+ and Γ_8^+). Parameters of the theory are fitted to the 1S-triplet energies of both series.[5,10] The exchange interaction is chosen to yield the experimental exchange splitting of the 1S state of the yellow series. Our calculations confirm also that the upper valence band is of Γ_7^+ symmetry as proposed by Elliott.[17] Additional evidence for the weak line at 2.1378 eV to result from the split-off valence band (Γ_8^+) is supported by magneto-optic measurements. Contrary to the other excitons, the 1S green exciton shows a pronounced splitting in a magnetic field of 8.5 T [Fig. 1(c)]. The two-photon data thus confirm the new assignment of the S exciton series by Agekyan and Stepanov.[5] The doublets are assigned to result from S and D states which are considerably mixed. The quantum numbers S and D are for this reason no longer too useful. Even the main quantum numbers 1S green and 2S yellow should be quoted with care, since both states are strongly mixed.

We have demonstrated experimentally that TPA is superior to other methods in studying even-parity excitons. Since the experimental difficulties are solved, a new field of interesting experiments is now feasable. Applying, e.g., an electric field one should be able to detect the P excitons and some of their components which are one-photon forbidden. Two-photon magneto-optics, and experiments with uniaxial stress and possibly in connection with an electric field, will certainty yield further detailed information on the exciton system. The theoretical analysis demonstrates that both valence bands contribute simultaneously to the detailed exciton structure. The commonly used concept of assigning quantum numbers to the different series of even-parity exciton transitions in Cu_2O has to be revised to take these interactions into account, which then leads to a quantitative understanding of the anomalous experimental results such as, e.g., oscillator strengths and exchange splitting.

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Disorder and Superconductivity in *A*-15 Compounds

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The universal depression of the superconducting transition temperature T_c in disordered A-15 compounds is examined. Existing energy-band calculations are used to calculate the density of electron states, which is possibly enhanced by disorder in some cases such as Nb_3Ge. The dramatic drop in T_c in Nb_3Ge at a critical value of the resistivity is attributed to overdamping of acoustic plasmons which decreases the electron pairing interaction despite small changes in the density of states.

Disorder induced by crystal growth conditions, α-particle irradiation, and neutron damage yields a remarkable depression of the superconducting transition temperature T_c for the high-temperature superconducting A-15 compounds Nb_3Ge, V_3Si, and similar materials. Testardi, Poate, and Levinstein[1] have pointed out the universal nature of the depression of T_c by correlating it with the residual resistance ratio for various types of damage. A thorough investigation of neutron irradiation by Sweedler, Cox, and Moehlecke[2] demonstrated that the relative decrease of T_c in many A-15 compounds followed a similar pattern as a function of the neutron flux. The measured transition temperatures of disordered V_3Si samples are plotted versus the residual resistance $R(T = 25\,^{\circ}\mathrm{K})$ in Fig. 1. The drop in T_c from 18 to 4 °K is characteristic of the general trend for Nb_3Ge, Nb_3Al, and similar materials. Also the

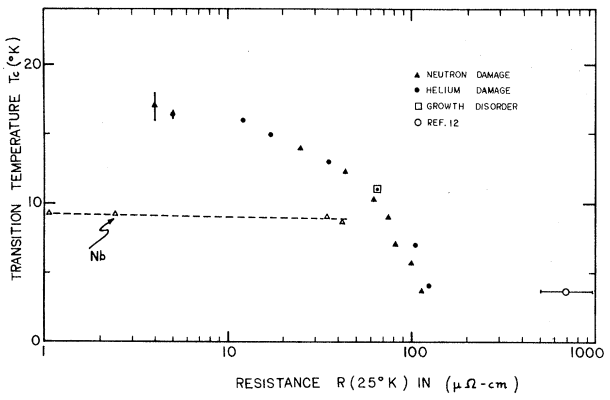

FIG. 1. Superconducting transition temperature of V_3Si subjected to various types of damage as a function of residual resistivity. The universal drop in T_c is common to other A-15 compounds, and is in sharp contrast to the behavior of Nb shown by the dotted curve.

