Exchange interaction in exciton excited *S* states

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The simultaneous application of an electric field and uniaxial compression has made it possible to observe the exchange-deformation splitting of the excited *S* states in the absorption spectrum of cuprous oxide. It is established that the exchange splitting of the excited states is large and its ratio to the splitting of the ground state differs from the theoretical value.

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Short-range exchange interaction was first investigated experimentally and theoretically in the ground state (1*S*) of the exciton of the yellow series in cuprous oxide.[1–3] Later on similar investigations were made on other semiconducting crystals,[4–8] but all were confined to the ground states, since general considerations indicate that exchange effects weaken rapidly with increasing exciton radius.

The valence band of cuprous oxide is split by spin-orbit interaction into an orbitally nondegenerate band ${}^2\Gamma_7^+$ and a doubly-degenerate band ${}^4\Gamma_8^+$. The yellow-series *S* excitons are due to excitation of an electron from the upper valence band ${}^2\Gamma_7^+$ to the conduction band ${}^2\Gamma_6^+$ (both bands have only Kramers degeneracy). The exchange interaction causes splitting of the *S*-exciton levels into a nondegenerate level ${}^1\Gamma_2^+$ (paraexciton) and a triply degenerate level ${}^3\Gamma_5^+$ (orthoexciton). The exchange splitting of *nS* states is

$$\Delta_0^n \sim I_0 \quad |\Phi^{(n)}(0)|^2\Omega$$

where I_0 is an exchange integral made up of Bloch functions of both bands, $|\Phi^{(n)}(0)|$ is the modulus of the exciton wave function, *nS* are states at the point $r_e = 0$ (r_e is the exciton radius), and Ω is the volume of the unit cell.

The quadrupole level ${}^3\Gamma_5^+$ of the 1*S* state can be easily observed in the absorption spectrum, whereas the level ${}^1\Gamma_2^+$ corresponding to higher multipolarity appears only in luminescence[9] because it lies 100 cm^{-1} lower than the ${}^3\Gamma_5^+$ level ($\Delta_0^{(1)} = 100$ cm^{-1}). For *nS* excitons with $n > 1$, the positions of the ${}^3\Gamma_5^+$ levels can be determined from the dipole excitation in an electric field, whereas the ${}^1\Gamma_2^+$ levels are not observed experimentally at all. Thus, exchange splitting is known only for $n = 1$.

The exchange-interaction anisotropy that is produced by uniaxial compression of the crystal gives rise to additional lifting of the degeneracy—to the splitting of the ${}^3\Gamma_5$ level, principally because of the appearance of an energy term that depends linearly on the deformation and on the exchange. According to[10], this splitting is given by

$$\Delta_{\text{ed}}^{(n)} = \frac{\Delta_0^{(n)} \; l_\epsilon}{\Delta_{\text{so}}},$$

where *l* is a combination of the deformation constants of

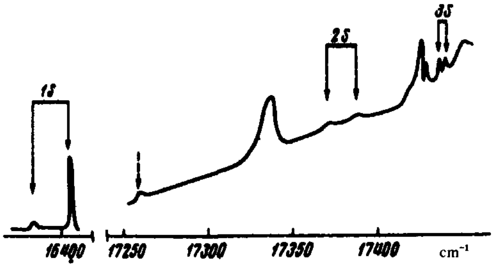

FIG. 1. Absorption spectrum of uniaxially compressed Cu_2O crystal in electric field, $p=8$ kg/mm^2, $E=3$ kV/cm. Dashed arrow-weakly split $^3\Gamma_5^+$ state of yellow-series 1S exciton. $T=4.2$°K.

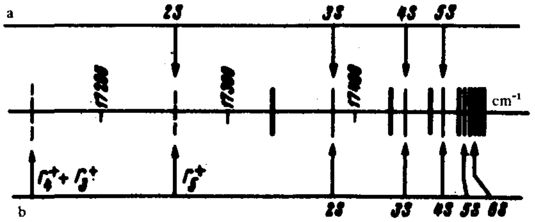

FIG. 2. Classification of the nS states of the yellow-series exciton: a—according to[12,13], b—according to the present paper. Thick lines-exciton nP states with $n \geq 2$, dashed—1S yellow-series exciton.

the valence bands, ϵ is the deformation tensor, Δ_{so} is the spin-orbit splitting of the valence band. The second energy term $\Delta_0^{(n)}\epsilon$, which takes into account the anisotropy of the exchange interaction proper due to the deformation-induced change of the band functions, is smaller than $\Delta_{ed}^{(n)}$ by one order of magnitude.

It is seen from (2) that measurement of the exchange-deformation splitting of the excited S states makes it possible to determine experimentally the dependence of $\Delta_0^{(n)}$ on the principal quantum number of the electron.

We applied simultaneously to the cuprous-oxide crystal an electric field and uniaxial compression up to 20 kg/mm^2. The field leads to excitation of exciton nS lines[1] with symmetry $^3\Gamma_5^+$ in the absorption spectrum, while the compression causes exchange-deformation line splitting whose magnitude is practically independent of the electric field intensity.

It was established that the ratio of the energies of the exchange-deformation splitting $\Delta_{ed}^{(n)}$ of the levels classified by Haken and Nikitin[12,13] as 1S, 3S, and 4S is 1 : 0.8 : 0.2 (Fig. 1), with $\Delta_{ed}^{(1)}$ equal to approximately 2.5 cm^{-1} at a pressure $p=1$ kg/mm^2. As to the level classified in[13] as 2S (the 17260 cm^{-1} line), its splitting is very weak and amounts merely to line broadening. In the case of strongly split 1S and 3S levels, the 2S level cannot remain unsplit, therefore the S levels should be classified differently. The new classification is given in Fig. 2.

In our opinion the 17260 cm^{-1} line is a transition of a yellow-series 1S exciton to the $^3\Gamma_5^+$ level. The closely located 17150 cm^{-1} line was already determined earlier to be a transition to the $^3\Gamma_4^+ + {}^2\Gamma_3^+$ level of the 1S exciton of the yellow series. These three states account for the entire set of levels of the yellow-series 1S exciton. The exchange-deformation splitting of the green series, which is weaker than that of the yellow series, should be investigated for a concrete combination of the deformation constants l in (2).

Let us turn to the comparison of the exchange splittings $\Delta_0^{(n)}$ of the levels that we classify as 1S, 2S, and 3S. First, according to (2), the values of $\Delta_{ed}^{(n)}$ should be related to one another as $\Delta_0^{(n)}$, and second, $|\Phi^{(n)}(0)|^2$ in (1) is equal to $(\pi n^3 a_e)^{-1}$, where a_e is the exciton Bohr radius. The ratios 1 : 0.8 : 0.2 experimentally obtained for $\Delta_0^{(n)}$ disagree with the theoretical dependence (like n^{-3}), and the probable cause is that the large-radius exciton approximation is not applicable to the yellow-series 1S exciton. This is indicated also by the large deviation of the binding energy of the 1S exciton from the calculated value, and the new classification of the nS levels make this discrepancy larger. At the same time, the ratio $\Delta_0^{(2)}/\Delta_0^{(3)}$ agrees with the theory, although $\Delta_0^{(2)}$ and $\Delta_0^{(3)}$ themselves are larger than predicted by the theory.

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[1] It was established in[11] that all the excited lines interpreted as exciton states have the symmetry $^3\Gamma_5^+$.

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