:omplicated exciton-impurity complexes in tin ioxide

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When SnO_2 is doped with indium or antimony, complex centers are produced, to which excitons start to be bound. The ground state of the exciton-impurity complex yields an absorption line whose energy does not depend on the type of introduced impurity, whereas the excited states have different spectra.

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1. In some not-specially-doped SnO_2 crystals, lines of exciton-impurity com-exes (EIC) with low exciton-impurity binding energy are observed on the long-ave side of the absorption line of the free exciton. These lines are located -15 cm^{-1} away from the 1*S* line and probably correspond to the shallow donors pical of SnO_2 (the Rydberg constant of the exciton series is equal to 270 cm^{-1}). he spectra of the doped crystals contain EIC absorption lines with much larger nding energy and with specific distinguishing properties.

2. Whereas the 1*S* state of the free excitons is quadrupole,[1] all the EIC nes adjacent to it, even the shallowest, are dipole. The relative intensity of e EIC lines in SnO_2 are determined both by the giant oscillator strength[2] and r the allowed type of the optical transition. Consequently, the EIC lines at the ›ping level 10^{17} cm^{-3} are more intense than the 1*S*-state lines of the free exci-n. The dipole character of the EIC lines manifests itself in their identical tensity for any position of the wave vector **k** of the light in a plane perpendicu-r to the fourfold axis C_4, whereas the quadrupole 1*S* line oscillates in the case rotation in this plane (Fig. 1).

3. After "pure" SnO_2 crystals are doped by the thermal diffusion method, an IC line 0′ appears in their spectrum, shifted 70 cm^{-1} away from 1*S*, as well s a group of narrow absorption lines on the long-wave side of $2P_{\pm 1}$—the lines

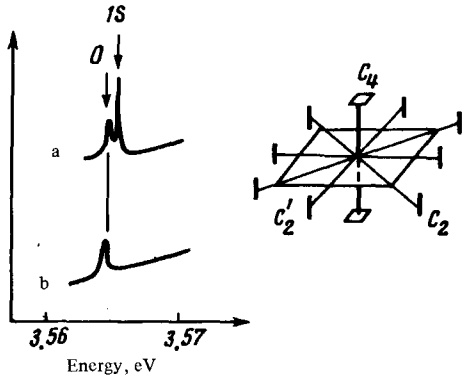

FIG. 1. Free exciton 1*S* and shallow bound exciton (0) in the absorption spectrum of SnO_2 when observed along the twofold axes $C_2(a)$ and $C_2'(b)$. $T = 4$ °K. Right—scheme of the symmetry axes of SnO_2.

1—6 of the free exciton. These lines correspond to excited EIC states.[1)] It would be of interest to analyze these states for the construction of a molecular model of the EIC, since the ground state has only one level and does not afford such an opportunity. However, the lines 1—6 may correspond, first, to $nP_{\pm 1}$ excitons, where n need not necessarily be equal to 2, and second, they can correspond to states nP_0, nS, nD, etc., since forbidden transitions to the free exciton levels correspond to dipole transitions to EIC levels. If the binding of the exciton to the impurity can be regarded as a perturbation, then for a more detailed analysis of the EIC it is necessary to know the dependence of the energy of EIC production on the exciton quanta numbers n and l, a dependence which apparently has not been calculated. For a correct analysis it is necessary also to estimate the ratio of the exchange forces and the Coulomb forces leading to the formation of the EIC in the case of neutral and charged defects, and the Coulomb forces in the exciton. We note that the distance of lines 1 and 2 (Fig. 2) from the longest-wavelength $2P_{\pm 1}$ line[2)] of the free exciton is larger than the distance between the $0'$ and $1S$ lines, and these energy distances exceed the binding energy of the $2P_{\pm 1}$ state of the free exciton.

4. Doping of identical "pure" SnO_2 crystals with indium or antimony yields identical lines of the ground state of EIC. The energies and relative intensities of lines 5 and 6 of the excited states are equal, and those of the remaining lines are not. The indium and antimony replacing the tin become respectively an acceptor and donor, and therefore the EIC spectra should differ strongly. The fact that in both cases the ground-state lines of the EIC are exactly identical indicates that the doping produces not a simple substitution but the formation of a more complex center, consisting of an atom of the introduced impurity and of a previously existing defect. Identical EIC are produced in crystals grown by different methods, and therefore the initial is apparently an intrinsic one. The reason why the EIC spectrum appears only after doping may lie both in the very nature of the complex center produced in this case, and in the consolation of the intrinsic defect, which decreases the lattice distortion near it.

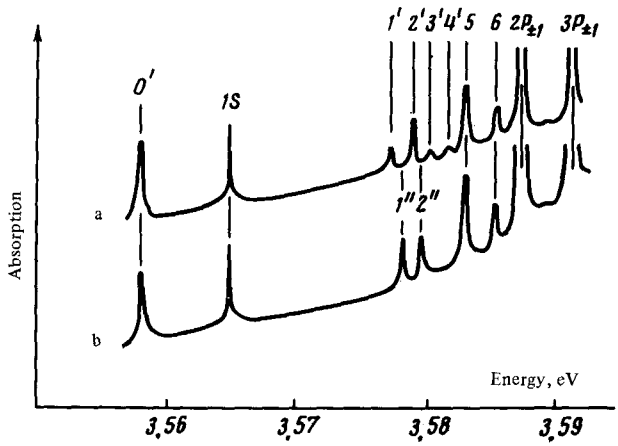

FIG. 2. Absorption spectra of free excitons $1S$, $2P_{\pm 1}$, $3P_{\pm 1}$, and EIC in the crystals SnO_2: Sb (a) and SnO_2: In (b). $T = 4\,^\circ K$.

Thus, a characteristic property of the exciton bound with a complex center is e fact that the binding energy of the ground state of the EIC is determined only the initial defect, whereas the spectrum of the excited states of the EIC de- nds on the type of introduced impurity. It is this which offers evidence of the mplexity of the center binding the exciton.

5. In a magnetic field H, numerous very narrow lines appear in the spectrum tin dioxide, some of which do not pertain to the states of the free exciton. hese lines can be interpreted as an EIC spectrum corresponding to free exci- ns with large values of n, which become stabilized in the magnetic field, that , the magnetic-absorption spectrum of semiconducting crystals with EIC con- in, besides the series of the diamagnetic excitons adjacent to different andaua levels, also EIC lines. With increasing H, the energy difference be- veen the EIC lines and the free-exciton lines should decrease, since the xternal perturbation predominates in a strong field, and the influence of the nding of the exciton to the impurity becomes negligible.

Lines 1—6 cannot be phonon replicas of the ground state of an EIC, since the phonons interacting with it have a much higher energy.[3]
The $2S$ line in SnO_2 has a higher energy than $2P_{\pm 1}$.

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