Dipole and quadrupole bound excitons in Cu$_2$O crystals doped with cadmium

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New narrow lines have been observed in the absorption spectrum of Cu$_2$O:Cd crystals near $1S$ excitons. It is shown that the observed lines are due to dipole and quadrupole transitions to bound-exciton levels.

The absorption and luminescence spectra of excitons of pure Cu$_2$O crystals were investigated in great detail.[1,2] At the same time, the effect of impurities on the optical properties of these crystals have hardly been studied. One of us[3] has established that

doping of Cu_2O crystals with cadmium leads to the appearance of a number of narrow lines in the luminescence spectrum. These lines are apparently due to annihilation of bound excitons. No bound excitons, however, were observed in the absorption spectra.

In this paper we consider the influence of cadmium impurities on the absorption spectrum of excitons in Cu_2O crystals. We investigated polycrystalline samples prepared by oxidation of copper-cadmium alloys, and single crystals of cuprous alloys doped by heating in cadmium vapor.

When cadmium is doped, the higher members of the yellow and green exciton series ($n \geqslant 2$) shift towards the longer wavelengths. The spin-orbit splitting of the valence band is preserved in this case. The level shift is proportional to the concentration[1] of the cadmium and amounts to $\Delta \nu \approx -15$ cm^{-1} at a concentration of 1%. We observed no level shifts of the azure and blue exciton series.

The absorption spectrum undergoes qualitative changes near the edge of the excitons of the $1S$ state of the yellow series. The penetration of the cadmium makes the $n = 1$ line much weaker, and new narrow absorption lines A, B, C, and D appear next to it. Narrow absorption lines appear also ahead of the edge (A', B', and C') and are due to indirect transition to the $1S$ state, with production of a Γ_{12}^- phonon. The new lines are particularly distinct at $T = 4.2$ K (see Fig. 1).
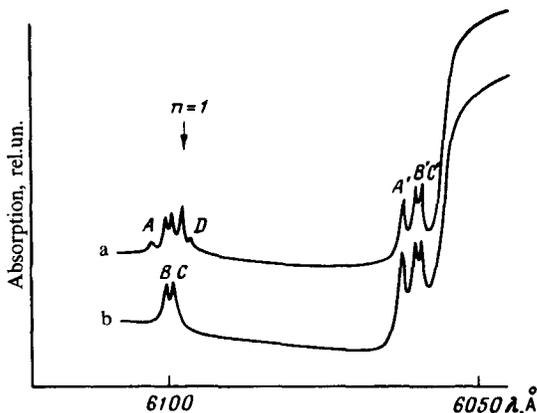

FIG. 1. Microphotograph of the absorption spectrum of the crystal Cu_2O: Cd, $k\|C_2$, $T = 4.2$ K. a—$E\|C_4$, b—$E \perp C_4$.

The distances between the lines located near $n = 1$ and corresponding to the lines ahead of the edge coincide with the energy of the Γ_{12}^- phonon. It is therefore natural to assume that the lines A', B', and C' are phonon replicas of the lines A, B, and C. This interpretation is confirmed by the behavior of the new lines under uniaxial compression. Detailed results of the investigation will be published later, and we note here the following: 1) Under deformation alone the split components of the lines A, B, and C are displaced in such a way that the distances between them and the corresponding components with $n = 1$ are preserved. 2) The character of the splitting of the lines A, B, and C is similar to the character of the splitting of the lines A', B', and C'. The

distances between the corresponding components always remains equal to the energy of the Γ_{12}^- phonon ($\hbar\omega = 109$ cm^{-1}). Since the splitting of the $n = 1$ line is due to lifting of the degeneracy of the 1S-excitonic state, and not as a result of the band splitting, item (1) points to a genetic connection between the lines A, B, and C with the 1S exciton. The fact that the phonon replicas appear in the form of lines (A ', B ', and C ') rather than steps indicates that these states are localized. Thus, doping cuprous oxide with cadmium produces bound excitons with exceedingly low binding energies, $E_b = 3.5$, 6.5, and 12 cm^{-1} for the lines C, B, and A, respectively.

The relatively intense doublet D, C is optically isotropic and is apparently of dipole origin. The absorption lines A and D behave in analogy with the quadrupole line of the $n = 1$ exciton. They are also fully polarized (polarization $\mathbf{E}\|C_4$) when observed along a twofold axis and unpolarized when observed along other crystallographic axes of Cu$_2$O. Since the electric and magnetic dipole transitions in anisotropic centers which are possible in a cubic crystal lead to complete optical isotropy,[4] the anisotropy of the absorption can be attributed only to the quadrupole character of the transition into these states. It appears that this is the first observation of quadrupole absorption by bound excitons in a cubic crystal.

A fact worthy of attention is that the binding energy of the produced localized excitons is much less than expected. For excitons bound to impurity centers, the relation $E_b > 0.055E_D$ should be satisfied.[6] In our case, the binding energy does not exceed one-hundredth of the impurity dissociation energy.[1] To explain this discrepancy, we must assume that bound small-radius excitons can be produced. Then a local change of the lattice parameters (for example, deformation) can be accompanied by a splitting of local states from the 1S-exciton band. The absorption line D, which is located on the short-wave side of $n = 1$, can be attributed to the onset of a pseudolocal excitonic state. If it is recognized that the radius of the 1S excitons of the yellow series in Cu$_2$O is comparable with the dimension of the unit cell, this assumption seems likely.

Within the framework of this model one can understand the observed decrease of the 1S-exciton absorption-line intensity. We note that anisotropy of the absorption of the bound exciton, which is analogous to the anisotropy of the absorption of the 1S exciton, can occur when the exciton is localized in a region with cubic symmetry as well as in a region with lowered (say, tetragonal) symmetry.

[1]The concentration was determined from the cadmium content in the alloy.
[2]Very shallow bound excitons were observed also in SnO$_2$ crystals.

[1]E.F. Gross, Usp. Fiz. Nauk **76**, 433 (1962) [Sov. Phys. Usp. **5**, 195 (1962)].
[2]F.I. Kreĭngol'd and B.S. Kulinkin, Opt. Spektrosk. **33**, 706 (1972).
[3]F.I. Kreĭngol'd, Opt. Spektrosk. **30**, 286 (1971).
[4]A.A. Kaplyanskiĭ and P.P. Feofilov, Usp. Fiz. Nauk **76**, 201 (1962) [Sov. Phys. Usp. **5**, 79 (1962)].
[5]V.T. Agekyan, Pis'ma Zh. Eksp. Teor. Fiz. **23**, 574 (1976) [JETP Lett. **23**, 526 (1976)].
[6]J.J. Hoffield, Proc. Seventh Intern. Conf. on Physics of Semiconductors, Paris, 1964, publ. by Dunod, Paris; Academic Press, New York (1965), p. 725.