Excitonic Bands in the Optical Absorption Spectra of (Bu₄N)CuBr₂, (Et₄N)₂Cu₂Br₄, (Pr₄N)₂Cu₄Br₆, (Bu₄N)₂Cu₂I₄, (Me₄N)Cu₂I₃, (Pr₄N)₄Ag₄I₈, (Me₄N)Ag₄I₃, (Et₄N)Ag₂Br₃, and Similar Compounds

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The title compounds (natural low-dimensional semiconductor systems) exhibit strong excitonic optical absorption bands in the UV spectral region, because of the quantum confinement of excitons, as in the cases of bivalent-metal and trivalent-metal halide complexes. The excitonic bands are shifted to longer wavelengths, approaching those of the corresponding bulk materials, as the anion-size or the anion-dimensionality increases.

The excitonic bands in the optical absorption, luminescence and photoconductivity spectra of some natural low-dimensional (LD) semiconductor systems are characterized by enhanced excitonic binding energy, oscillator strength and optical nonlinearities with respect to the corresponding three-dimensional (3D) systems (for a review see [1]). The results are similar to those obtained from artificial systems based on conventional semiconductors [1, 2]. In references [3 - 10] (see also [1]), some recent results concerning the optical and related properties of natural LD systems based on trivalent metal [8 - 10] and bivalent metal [3 - 7] halide complexes are reported. There is only little information on the solid state spectra of monovalent metal halides [11, 12]. It has been found that the spectra of ZCuX₂ compounds (X = Cl, Br, I; Z = cation) show peaks at ca 230 nm and, after treatment with CuX, shifts to longer wavelengths because of the formation of larger species [11]. The spectra of compounds with Cu₄I₃ anions are also described in [12].

In this paper the room temperature excitonic optical absorption spectra of (Bu₄N)CuBr₂, (Et₄N)₂Cu₂Br₄, (Pr₄N)₂Cu₄Br₆, (Bu₄N)₂Cu₂I₄, (Me₄N)Cu₂I₃, (Pr₄N)₄Ag₄I₈, (Me₄N)Ag₄I₃, (Et₄N)Ag₂Br₃, and similar compounds (where Me = methyl, Et = ethyl, Pr = propyl and Bu = butyl) are described. The spectra are compared with those obtained for the corresponding conventional semiconductors, i.e., CuBr, CuI, AgI, AgBr (bulk or small particles).

Experimental

The preparations, crystals structures and electronic band structures of these compounds are described in [11 - 24]. To avoid oxidations of Cu(I) materials, a small amount of H₃PO₄ was added to the mother solutions before precipitation of crystals [19]. A modified method was applied for the precipitation of (Pr₄N)₂Cu₂Br₂, instead of (Pr₄N)₂CuIBr₂, using Pr₄NBr and CuBr in molar ratio 2:1 [19], instead of 1:1 [18]. (Me₄N)Cu₂I₃ and (Me₄N)Ag₂I₃ were prepared by using Me₄NI and MX (M=Cu, Ag) in a ratio 1:2 [19], instead of 1:1 [21, 24]. The structure of the crystals was identified by Weissenberg diagrams or by a complete X-ray-diffraction crystal structure solution. In the case of Me₄NAg₂I₃, the structure was found to be little different from that in the literature [23]. The space group Pmnn, a = 10.066, b = 7.426, c = 17.739 Å, V=1326 Å³ [19] was found. Thin deposits (of these compounds as well as of the corresponding conventional compounds) are mainly prepared by translational or rotational rubbing the crystals on quartz plates (see [9] and refs therein). The optical absorption spectra of these deposits were recorded on a Varian 2390 model UV-visible-near-IR and/or on a Perkin Elmer Lambda 19 spectrophotometer.

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Results and Discussion

(Bu₄N)CuBr₂ consists of discrete linear anions CuBr₂⁻ (4.45 Å long) with copper(I) at a centre of inversion [15, 16]. (Et₄N)₂Cu₂Br₄ contains discrete anions Cu₂Br₄²⁻ (7.5 Å long) as centrosymmetric dimers with a distorted trigonal-planar coordination of copper(I) [17]. (Pr₄N)₂Cu₄Br₆ features discrete anions Cu₄Br₆²~. Each anion consists of an aggregate composed of an octahedron with a square of trigonal-planar coordinated copper atoms [18, 19]. In all cases the 0-dimensional anions (clusters) are isolated by the cations, Me₄N, Et₄N or Pr₄N, and the Cu—Cu distances are large compared to that in the metal (which is 2.56 Å). Also, there are cluster imperfections (disorders) [12, 18, 20].

Fig. 1 shows the room temperature optical absorption spectra of (Bu₄N)CuBr₂, (Et₄N)₂Cu₂Br₄, and (Pr₄N)₂Cu₄Br₆, as well as the spectrum of CuBr observed under the same conditions, for comparison (see also [25, 26]). One can see that the low-frequency absorption peaks are shifted to longer wavelengths as the aggregation (size) of the clusters increases and approaches the peak positions of small CuBr - particles (ca. 396 nm) [26] and bulk CuBr (414 nm) [25, 26]. The spectra of solid (Bu₄N)CuBr₂ (with a peak at 231 nm) and solid (Et₄N)₂Cu₂Br₄ (a peak at 276 nm) are almost the same as those of CuBr²⁻ species and Cu₁Br₂⁺ anion species (x = 2.3) in solutions (see [20] and references cited therein). However, there have not been observed spectra of Cu₁Br₂⁺ anion species in solutions with peaks at longer wavelengths than 300 nm.

(Bu₄N)CuI₂ is isostructural with (Bu₄N)CuBr₂ [14-16] and its optical absorption spectrum exhibits a narrow band at 230 nm. Crystals of (Bu₄N)₂Cu₂I₄ consist of discrete cations and Cu₂I₄²⁻ anions similar to Cu₂Br₂⁻ [12, 16]. Crystals of (Me₄N)Cu₂I₃ consist of infinite polymeric anions (Cu₂I₃⁻)₁/₁ (1-dimensional system) [21]. In the anions there are Cu—Cu distances of 2.45 Å, i.e. smaller than in Cu metal [21].

Fig. 2 shows the optical absorption spectra of (Bu₄N)₂Cu₂I₄ and (Me₄N)Cu₂I₃ as well as the spectrum of CuI, for comparison. The spectrum of (Bu₄N)₂Cu₂I₄ exhibits a narrow band at 279 nm, the spectrum of (Me₄N)Cu₂I₃ a broad band at 323 nm, and the spectrum of CuI a shoulder at 400 nm.

Similar results were obtained for AgX based compounds, the crystal structures of which are reported in [14, 23 - 25 and refs therein]. Crystals of (Pr₄N)₄Ag₄I₈ contains discrete Ag₄I₈¹⁺ anions with a cubane-type core (0-dimensional) [23]. Crystals of (Me₄N)Ag₂I₃ contain infinite polymeric anions (Ag₂I₃⁻)₁/₁ (1-dimensional system) [19, 24]. In both cases, the Ag—Ag distances are large com-
pared to that in the metal (which is 2.88 Å), and the anions are isolated by the cations Pr$_4$N$^+$ and Me$_4$N$^+$ respectively.

Fig. 3 shows the room temperature optical absorption spectra of (Pr$_4$N)$_4$Ag$_4$I$_8$ (0-dimensional) and (Me$_4$N)Ag$_2$I$_3$ (1-dimensional) as well as the spectrum of AgI (3-dimensional) obtained under the same conditions, for comparison (see also [26 - 28]). The low frequency absorption peaks are shifted to longer wavelengths as the dimensionality (0 D $\rightarrow$ 1 D $\rightarrow$ 3D) or the size of the particles increases.

(Et$_4$N)Ag$_2$Br$_3$ is isostructural with (Me$_4$N)Ag$_2$I$_3$ [19, 24].

Fig. 4 shows the optical absorption spectrum of (Et$_4$N)Ag$_2$Br$_3$ and the spectrum of AgBr for comparison. The spectrum of (Et$_4$N)Ag$_2$Br$_3$ exhibits an intense band at 270 nm, while the spectrum of AgBr exhibits a weak band at 318nm (see also [25, 28]).

The results described herein for Cu(I)X and Ag(I)X crystalline solids are similar to those obtained for Pb(II)X$_2$, Sn(II)X$_2$, Bi(III)X$_3$ and Sb(III)X$_3$ analogs [1, 3 - 10]. The (low) frequency peaks in the optical absorption spectra are attributed to excitons, which are Frenkel-type for small clusters, and Wannier type for large clusters, chains and other lattices. The exciton Bohr diameter for CuBr, CuI, AgI is ca 25, 16, and 22 Å, respectively [25]. This means that for small particles (e.g., CuBr of 18 Å) the quantum confinement of excitons is weak (a weak blue shift of peaks [26 - 28]). However, for clusters of 5 - 7 Å the confinement is strong as it is observed in the spectra of complexes (Figs 1 - 4). Also, the values of electronic binding energy are small in conventional systems CuBr, CuI, and AgI (100, 58, 84 meV), while the estimated values from the spectra of CuX and AgX clusters and chains were found to be much larger (270 - 500 meV).

As in the case of BiX$_3$ and SbX$_3$ based systems, the photoluminescence excitonic peaks are weak at room temperature. Some Stokes-shifted intense photoluminescence bands were observed instead, which could be attributed to self-trapped excitons, because of the cluster imperfections.

Similar results are expected for the optical absorption spectra of other Cu(I) and Ag(I) halide compounds (natural low dimensional systems). If Cu—Cu and Ag—Ag separations in the anions are larger than the corresponding distances in the metals (M), the bands are narrow and strong. Otherwise, if there are M—M interactions (for such compounds see [21, 22]), the electron-electron correlation effects lead to a broadening of the excitonic bands [1].