SPECTROSCOPIC STUDIES OF THE CHARGE LOCALIZATION IN ONE-DIMENSIONAL ORGANIC CONDUCTORS BASED ON TTF DERIVATIVES

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ABSTRACT

Infrared and Raman spectroscopy was used to study the charge localization in quasi-one-dimensional organic conductors based on TTF derivatives.

Firstly, [*o*-DMTTF]$_2$X salts with different halide anions (X = Cl, Br and I) were measured. In these salts organic donors are arranged in strictly regular stacks. Organic conductors with such uniform conducting stacks, which preserve their uniformity down to the lowest temperatures, are very rare. Therefore, these crystals offer a unique possibility for investigation of electron – electron correlations in one dimension i. e. the problem of Mott localization in one – dimensional, ¼ filled band (in terms of holes). The salts are isostructural and crystallize in the tetragonal system, space group $I-\bar{4}2\mathrm{d}$. A characteristics structural feature is an existence of hydrogen bonds between methyl groups and halide anions. The compounds undergo a metal – insulator phase transition at about T_{MI}= 50 K, moreover, the electrical conductivity data show a weak charge localization below 215 K. In slats with Cl or Br anions are obserwed spin Peierls transition (in 50 K) and Mott insulator dimer (in 80 K). The spin Peierls transition and formation of the Mott insulator dimer are visible in temperature dependence of C–S and C=C bands, also in transport parameters obtained from the Lorentz model. From the infrared studies it results that the metal-insulator transition is not related with any drastic modification of the electronic structure. The Raman investigations show that charge distribution in conducting

organic stacks is uniform in the whole temperature range, i.e. there is no charge ordering effect in these salts. On the other hand, the infrared spectra show that the weak charge localization below 215 K is connected with a small reorganization of weak C–H•••X hydrogen bonds.

The next group of studied matertials were semiconducting $[tTTF]_2Y$ salts with halide anions Y = Br and I. These salts are isostructural and crystallize in the triclinic system, with space group P – 1; the conducting stacks are dimerized. A characteristic structural feature of these compounds is an existence of two different weak hydrogen bonds between carbon atoms and halide anions. At room temperature charge carriers are already localized in these salts. Raman studies showed existence of the charge ordering effect in the whole temperature range in conducting organic stacks. Similarly as for previous compounds, the infrared studies showed no important modification of the electronic structures.

Subsequently, $[DMtTTF]_2Z$ slalts with tetrahedral anions (Z = ClO_4 and ReO_4) were inwestigated. In these salts conducting organic stacks are also uniform in the whole temperature range and the band is filled in ¼. These salts are isostructural and crystallize in the monoclinic system with space group C2/c. They undergo a broad metal – insulator phase transition in the temperature range 100 - 150 K. The infrared investigations show no change of electronic structure on temperature lowering. On the other hand, Raman studies provided a proof that charge distribution in conducting organics stacks is uniform down to the lowest temperatures (no charge ordering effect). Additionally, a salt of 1:1 stoichiometr, [DMtTTF]Br salt was investigated. This salt crystallize in the monoclinic system, with the space group $P2_1/c$, and the organic stacks are dimerized.

Finally, the salt $[TCE–TTF]_3[ClO_4]_2$ was measured. It crystallizies in the heksagonal system, with space group $P\overline{3}$ and exhibits semiconducting properties. The conducting TCE–TTF stacks are uniform down to the lowest temperatues. On temperature lowering the compound undergoes a semiconductor – semiconductor phase transition at about 200 K. The infrared investigations gave an evidence of a disorder – order phase transition in the anion sublattice. On the other hand, the Raman spectra show that the charge is distributed uniformly in the conducting organic stacks.