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Optical spectra and structure of frozen aqueous electrolyte solutions with molecular anions

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The local surrounding influence on the structure of the vibrational and electron-vibration bands has been studied for SCN^- and NO_2^- impurite anions in frozen aqueous solutions of alkali metal halides. The relation between the nea-order positional structure of these impurities and nonuniform broadening of their spectra has been considered.

Изучено влияние локального окружения на структуру колебательных и электронно-колебательных полос примесных ионов SCN^- и NO_2^- в замороженных водных растворах щелочных галогенидов металлов. Рассмотрена связь между позиционной структурой ближнего порядка этих примесей и неоднородным уширением их спектров.

The local surrounding influence on the structure of the impurity molecular anions (MA) in solid (frozen) and liquid aqueous electrolyte solutions is rather difficult to study. The factors forming contours of such bands are to be taken into account. There are two most important groups of such factors. The first one determines anharmonic interactions of the local excitation of the impurity center with other local vibrations as well as with the matrix ones (uniform broadening of the spectrum). The second group is associated with fluctuations of the impurity local surrounding. It causes nonuniform broadening of the impurity energy levels. At low temperatures (in frozen solution) the uniform broadening decreases essentially while the non-uniform one increases as the solution becomes transformed into solid state. It is due to the destruction of solution homogeneity when local regions with variable relation between H_2O molecules and impurity ions arise.

We investigated the IR absorption spectra of the SCN^- impurity anion to analyze its local surrounding influence on the band structure of the intramolecular vibration ν_1 (Σ^+) (stretch vibration of C–N bond) as well as the luminescence band caused by $^1B_1 \rightarrow {}^1A_1$ transitions in the impurity $MANO_2^-$ in frozen aqueous solutions of alkalimetalhalides (AMH) MHal (M = Li, Na, K, Rb, Cs; Hal = Cl, Br). The corresponding salts MNCS and MNO_2 were used as activators. The infrared absorption spectra were recorded using an UR-20 IR spectrophotometer. The experimental technique for the low-temperature measurements was described in [1]. The luminescence spectra were excited by an LGI-21 laser (λ_{ex} = 337.1 nm, average power 2 mW) and were recorded using the DFS-12 spectrometer. The investigated solutions were frozen at a highrate (the standard cuvette with the sample was first dipped into liquid nitrogen and then into a He cryostat).The freezing rate v_f was 0.005 K/s and 20 K/s for solutions of SCN^- and NO_2^-, respectively (that was connected with the cryostats design).

As our previous investigations have shown [2], the non-uniform broadening of the low-temperature bands is more than that of liquid phase ones. At 300 K, in the SCN^- ion solutions the ν_1-vibration band has a smooth symmetric contour without singularities while at 77 K, this contour is asymmetric and may contain 2 or 3 weak maxima (Table 1). For example, there are