Displaying of local structural phase transitions in Raman spectra of alkali sulphates

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Ordinary polymorphous phase transitions are known to arise in reality due to "incidental" closeness of thermodynamic potentials of the certain compound in its different structures. This "incidental" closeness is not attributed to structural phase transitions leaded by lose of thermodynamic stability in crystal at certain temperature. At the such transitions the main role is assigned to soft mode frequency of which tend to zero when the temperature tend to T_c point of phase transition.

Transition into the lowtemperature phase with a lower lattice's symmetry can be observed in the spectra of vibration and electron-vibration transitions and, so, in the Raman spectra as a result of degeneration of some levels or changes of lines intensities due to cancellation restriction on some transitions. But, it must be noted the question about role of local phase transition that originates a volume segnetoelectric type phase transition is studied not enough from both theoretical and experimental points of view.

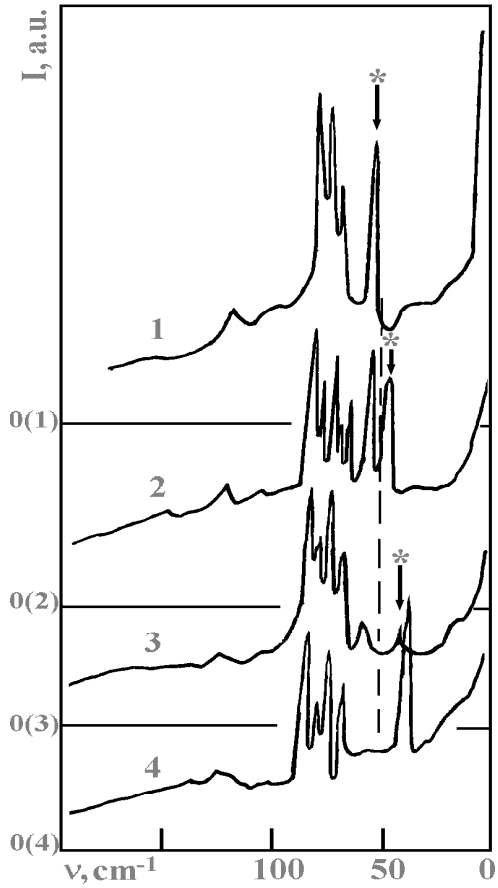

Fig. 1. Raman spectra of K_2SO_4 (S_2^-) crystals at T = 300 (1), 77 (2), 50 (3) and 4,2 K (4)

Obtained data on temperature dependencies of kinetic and intensity of luminescence of S_2^- local centers in alkali sulphate crystals have a distinctive character of a jumplike phase transition. The high sensitivity of kinetic processes in luminescence centers of sulphate crystals to structural transformation has to be considered as connected with interaction of electron subsystem with lattice's vibrations near the luminescence center: effective interaction of electron-vibration transition with lowfrequency pseudolocal vibrations and bonded electron-phonon modes.

Attempt to answer whether the S_2^- luminescence center have to be considered only as a probe sensible to phase transition or it oneself makes conditions for a local structural phase transition was made by investigation of temperature effects on Raman spectra of sulphate crystals (Fig.1). Obtained results have shown absence of jumping of Raman properties for inner modes of sulphate groups in a crystal. At the same time, the sharp changes were observed in the region of lowfrequency modes of impurity crystals caused by presence of S_2^- centers in a lattice. Intensity of the lines leaded by vibrations of pseudolocal type decreases with the temperature decreasing and wholly disappears at T < 30 K. Thus, observed phase transition can be characterized as a local phase transition.