

The Investigation of Peculiarities of Structure, Lattice Dynamics and Phase Transitions in Hydrogen-bonded Crystals by NQR Methods under hydrostatic pressure

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The investigated in this work hydrogen-bonded iodate crystals (AIO_3 and some mixed crystals obtained on their base, where $A = \text{H}^+, \text{K}^+, \text{NH}_4^+$) are very convenient for study of the symmetry hydrogen bonds problem. The main peculiarity of this crystals consist in possibility to pick out the rigid covalent-bonded iodate groups IO_3 , the oxygen atoms of which can form the hydrogen bonds of different energy. These facts are well known from numerous experimental data obtained by structure and vibrational spectroscopy studies. However to investigate the behavior of hydrogen bonds in these crystals at phase transition and under different outside effects (for instance, temperature and pressure) are difficult problems, it requires the complicated neutronographic investigations. The Raman and Infrared absorption spectra obtained in the wide temperature ranges give, as a rule, integrated information about the changes of structure and energy of hydrogen bonds in the critical temperature range.

Using the unique possibilities and simplicity of the NQR method as structure probe we try to solve this problem starting from the analysis of the temperature and pressure dependencies of the NQR spectra parameters.

First of all, the calculations of electronic structure of different iodate groups ($\text{H}_x(\text{IO}_3)$, where $x=0$ and 1) with different by MO LCAO method were made. This allows to obtain parameters of the ^{127}I NQR spectra: quadrupole coupling constant e^2Qq_{zz} and asymmetry parameter η including different states of hydrogen atoms which can form relative strong covalent $\text{O}-\text{H}$ part or weak $\text{O}\cdots\text{H}$ bond of hydrogen bond $\text{O}-\text{H}\cdots\text{O}$.

Then the obtained theoretical data were compared with experimental results. The analysis of the hydrogen bond structure for different crystals in the wide temperature range was made. The type of the phase transitions and changes of hydrogen bonds structure near the phase transition points was determined.

The analysis of the pressure dependencies of the NQR spectra parameters lead to detection of the symmetrization effect of "so called" interionic hydrogen bonds under hydrostatic pressure. It was shown, that this effect has a general character and is valid for both symmetric hydrogen bonds with disordered proton and asymmetric bonds. The main sense of the symmetrization effect consists in some moving of proton to geometrical center of the hydrogen bonds $\text{O}\cdots\text{H}\cdots\text{O}$ or $\text{O}-\text{H}\cdots\text{O}$ when hydrostatic pressure increase. In a pure appearance the symmetrization effect developers for $\alpha\text{-HIO}_3$ crystal for which the decreasing of asymmetry parameter on resonance nuclear ^{127}I with increasing hydrostatic pressure was observed.