Size Effect Caused by Incommensurate Superstructure in \([\text{N(CH}_3\text{)}_4]_2\text{Zn}_{0.58}\text{Cu}_{0.42}\text{Cl}_4\) Crystals

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Surfaces in the crystal physics is considered as a two-dimensional defect, in particular, as a special state of a crystal where the crystallography and the energy structure differs from those in a bulk crystal.

A distorted surface structure cannot jump to the ordered structure of the bulk crystal, so there is some transition zone. Therefore the surface is considered as the surface phase, which physicochemical properties differ from the bulk part of the crystal. Such surface makes influence on the lattice and electronic subsystem of the crystal. It changes spectra of elementary excitations that are sensitive to changes in symmetry and boundary conditions.

It is suggested that the thickness of the surface defect layer in the direction of the incommensurate modulation axis for crystals with incommensurate phase is about a wavelength of incommensurate modulation. Superstructure period increases with decreasing temperature of the crystal increasing the impact of surface energy on the crystal volume.

In this work, an influence of the surface layer on the crystal volume when the wavelength of the incommensurate modulation increases was studied.

The period modulated superstructure in \([\text{N(CH}_3\text{)}_4]_2\text{MeCl}_4\) (Me=Cu, Co, Zn, Mn) crystals is about 100 unit cells, namely 1500-800 angstroms. Hence the size effect related to the size of the crystal of proportion to the wavelength of incommensurate modulation in micron diapason be expected, crystal size is commensurate to the incommensurate wavelength.

Based on the obtained temperature dependences of optical birefringence of \([\text{N(CH}_3\text{)}_4]_2\text{Zn}_{0.58}\text{Cu}_{0.42}\text{Cl}_4\) crystal the shift of phase transition temperature parent-incommensurate phase \((T_i)\) toward low temperatures is observed, the thickness of the crystal measured along the axis of incommensurate modulation is \(d_c = 35 \div 40\) microns. Under the same conditions a similar bias value phase transition temperature incommensurate-commensurate phase of long-seen in the \(d_c = 75 \div 80\) microns, and the phase transition to the incommensurate-commensurate ferroelectric phase \((T_c)\) at \(d_c = 95 \div 100\) microns.

So increasing the thicknesses of the crystal in which there is a size effect caused by increasing wavelength incommensurate modulation. Note, the incommensurate modulation wavelength increasing with crystal temperature growing from \(T_i\) to \(T_c\).