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THE PROPERTIES OF $Cs_2NaB^{3+}Cl_6$ SINGLE CRYSTALS NEAR THEIR CURIE POINTS

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The investigations of thermal expansion, elasticity and X-ray analysis of some elpasolite type crystals were carried out. The thermodynamical description of the structural phase transitions is discussed.

The elpasolite type crystals of $Cs_2NaB^{3+}Cl_6$ (B^{3+} - Bi, Nd, Pr) belong at the room temperature to the O_h^5 space group.[1] Recently optical study of the crystals was made and the ferroelastic phase transitions were found at low temperatures.[2] Here we will discuss some results on X-ray, thermal expansion and elasticity of the crystals in the phase transition regions. The thermodynamical description of the transitions will be given also.

X-ray analysis of $Cs_2NaPrCl_6$ powder samples was carried out at 123 K by means of the low temperature cryostat URNT-180 of diffractometer DRON-2.0. The measurements of thermal expansion were made with a quartz dilatometer.[3] The pulse ultrasonic method at 10 Mps[4] was used for elasticity study.

The optical observations under polarizing microscope revealed twin structure of the crystals at low temperatures.[2] The twins of $Cs_2NaB^{3+}Cl_6$ crystals are similar to the twin structure of $ABCl_3$ perovskites in tetragonal phases. A tetragonal distortion of $Cs_2Na \cdot B^{3+}Cl_6$ crystals below the transitions was suggested.[2]

A splitting of $Cs_2NaPrCl_6$ powder lines is in agreement with tetragonal distortion of the crystal lattice. The parameters of a tetragonal unit cell are a=10.808, c=10.850 Å. The powder and single crystal X-ray patterns show that translation symmetry of the crystal does not change at phase transition.

Linear thermal expansion coefficient was measured along [100] and [110] directions of $Cs_2NaBiCl_6$. Its values do not practically depend on temperature at the initial phase (Figure 1). The first order phase transition takes place at T_o=98.83±0.02 K. The coefficient along [110] is nearly equal to zero for the temperatures below 80 K. The volume jump at Curie point is estimated as $(6±2)\cdot10^{-5}$.

The velocity of longitudinal wave of $Cs_2NaBiCl_6$ increases linearly with temperature decreasing to 160 K (Figure 2). It decreases rapidly near Curie point. A tendency of the temperature dependence of transversal wave is similar (Figure 2).

The experiments show that $Cs_2NaB^{3+}Cl_6$ crystals undergo the phase transitions of the first order without changing of the unit cell. A group-theoretical analysis predicts two possible space groups D_{4h}^{17} and C_{4h}^5 for the low temperature phases. The elastic stiffness c_{44} must be softening for the $O_h^5 \rightarrow C_{4h}^5$ transition. Such behaviour does not agree with experiment (Figure 2).

Phase transition with the change of symmetry $O_h^5 \rightarrow D_{4h}^{17}$ can be described by the thermodynamical potential

$$F = a(T-T_c)(q_1^2+q_2^2) + bq_1^2q_2^2 + c(q_1^4+q_2^4) + d(q_1^3-3q_1^2q_2 +$$

$$q_2^3-3q_2^2q_1) + f(q_1(x_1+x_2-2x_3)+q_2(x_1-x_2)) + \frac{1}{2}c_{11}(x_1^2+x_2^2+ \qquad (1)$$

$$x_3^2) + c_{12}(x_1x_2+x_2x_3+x_1x_3) + \frac{1}{2}c_{44}(x_4^2+x_5^2+x_6^2) \ .$$

Here q_1, q_2 - the order parameter components, x_i (i=1,...,6) - strain components. Eliminating from (1) x_i by the usual way we get for the stress free conditions:

$$F = a(T-T_c^*)(q_1^2+q_2^2)+d(q_1^3-3q_1^2q_2+q_2^3-3q_2^2q_1)+bq_1^2q_2^2+c(q_1^4+q_2^4) \ , \qquad (2)$$
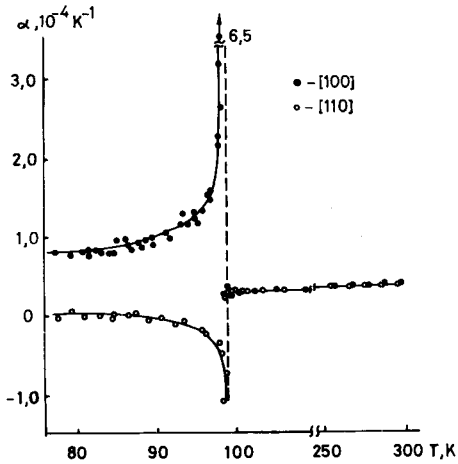
FIGURE 1. The thermal expansi-
on of Bi-elpasolite along [100]
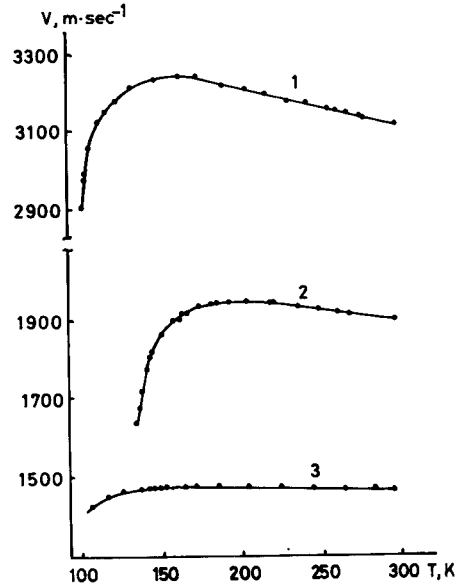and [110] directions.

FIGURE 2. The velocities of
longitudinal and transversal wa-
ves in directions: [100] [100](1),
[100] [010](3) - Bi-elpasolite;
[110] [1$\bar{1}$0](2) - Nd-elpasolite.

where $T_c^* = T_c + f^2/a(c_{11}-c_{12})$. By minimizing of (2) one can find three
solutions:

$$q_1 = q_2 = 0; \quad q_1 = q_2 \neq 0; \quad q_1 \neq 0, \quad q_2 = 0 . \qquad (3)$$

The last solution corresponds to the transition of the crystal into
D_{4h}^{17} group.

    The potential (1) contains the term with linear combinations of
order parameter and strain components. Therefore the temperature de-
pendence of elastic stiffness at cubic phase follows to

$$C_c = (c_{11}-c_{12})/2 = c_c^0(T-T_c^*)/(T-T_c) . \qquad (4)$$

The dependence is really observed for the transversal wave of $Cs_2Na \cdot NdCl_6$ in direction $[110][1\bar{1}0]$ (Figure 2).

The phase transitions of the first order in $Cs_2NaB^{3+}Cl_6$ crystals are determined by the cubic invariant in (2). The jump of order parameter and transition point can be found as

$$q_o = -3d/2c, \quad T_o = T_c^* + 9d^2/4ac \ . \tag{5}$$

The $Cs_2NaB^{3+}Cl_6$ crystals are structurally related to $ABCl_3$ perovskites. Many phase transitions in $ABCl_3$ crystals are due to M_3 and R_{25} soft modes.[6] It is reasonably to suppose that the transitions in the elpasolites are associated with tilts of $NaCl_6$ and $B^{3+}Cl_6$ octahedra. The estimation of mean tilt angle with help of formulas [7] gives 4,5° for $Cs_2NaPrCl_6$. A thorough study of the lattice vibrations near Curie point by neutron and Raman scattering methods would be useful for elucidation of origin of the transitions. It could be suggested that a variety of structural phase transitions due to octahedral tilts exist in $A_2B^+B^{3+}X_6$ and A_3BX_6 crystals.

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