

INVESTIGATION OF THE RAMAN SPECTRA OF SINGLE CRYSTAL NaClO_3 IN A WIDE TEMPERATURE INTERVAL

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The theory of Ginzburg and Levanyuk [1,2] relates second-order phase transitions in crystals with the dynamics of the crystal lattice. According to this theory, the frequency of one or several lines observed in the Raman spectrum drops to zero on approaching the transition point, and the line intensity increases strongly. Similar results are obtained in the semiphenomenological theory of ferroelectricity developed by Cochran [3].

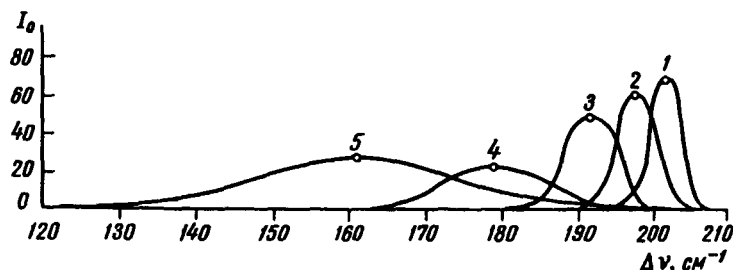
The present study is a continuation of investigations [4-7] devoted to searches for these effects. These investigations did not yield convincing results to confirm the theories of [1-3].

In the present study we investigated the Raman spectrum of single-crystal NaClO_3 , whose temperature dependence of the static dielectric constant is typical of that of a ferroelectric, with a Curie point $\theta = 593^\circ\text{K}$. The investigated samples were small cubes measuring $10 \times 10 \times 10$ mm. The procedure used to record the Raman spectra was described in detail in [6]. The investigations were made in the temperature interval $83 - 483^\circ\text{K}$. It is difficult to come closer to the ferroelectric transition point, since the melting temperature of the crystal is 537°K .

The Raman spectrum of single-crystal NaClO_3 at room temperature was investigated in a number of works [8,9]. The lines observed by us agree essentially with the published data. The entire spectrum can be subdivided into three line groups: 1 - weak lines with lowest frequencies $\Delta\nu_1 = 72 \text{ cm}^{-1}$, $\Delta\nu_2 = 81 \text{ cm}^{-1}$, and $\Delta\nu_3 = 107 \text{ cm}^{-1}$ corresponding to translational vibrations; 2 - lines with $\Delta\nu_4 = 123 \text{ cm}^{-1}$, $\Delta\nu_5 = 131 \text{ cm}^{-1}$, and $\Delta\nu_6 = 179 \text{ cm}^{-1}$ corresponding to orientational vibrations; 3 - lines with higher frequencies corresponding to internal vibrations of the NaClO_3 molecule (the values of the frequencies are given at a temperature $t = 45^\circ\text{C}$). All the vibrations are active in the Raman spectra.

We investigated all three groups of lines. It turns out that with increasing temperature all the lines except $\Delta\nu_6$ shift only slightly in frequency (by $3 - 5 \text{ cm}^{-1}$) and broaden. Significant temperature variations are observed for the line $\Delta\nu_6$. The measurement results for this line are shown in the table and in the figure. When the temperature rises from 83 to 483°K , the line $\Delta\nu_6$ shifts by $\sim 45 \text{ cm}^{-1}$ toward the exciting line and its width increases from 5 to 44 cm^{-1} . The quantity $I_{0\gamma}$ characterizes approximately the integral intensity of this line; we see that this quantity increases with temperature. Thus, all the effects predicted by the theory [1-3] are qualitatively confirmed. A new experimentally observed effect is the appreciable broadening of the line in question. At high temperatures, this line spreads so much that apparently the harmonic approximation of the crystal-lattice vibrations becomes incorrect. The failures of the earlier attempts to observe the effects predicted by the theory [1-3] are apparently due to the fact that the line in question became

so broad near the transition point, that it merged with the background and therefore escaped observation.



Variation of $\Delta\nu_e$ line with temperature. I_0 - intensity at maximum (arbitrary units), $\Delta\nu$ - frequency; the lines are plotted with allowance for their half-widths; 1 - $T = 83^\circ\text{K}$, 2 - $T = 113^\circ\text{K}$, 3 - $T = 203^\circ\text{K}$, 4 - $T = 318^\circ\text{K}$, 5 - $T = 423^\circ\text{K}$.

T a b l e *

T°, K	$\Delta\nu, \text{cm}^{-1}$	δ, cm^{-1}	Δ, cm^{-1}	γ, cm^{-1}	I_0	$I_0 \gamma$
83	202	0	1	5	70	350
113	198	4	1	6	62	370
203	192	10	1	8	49	392
318	179	23	2	16	25	400
373	172	30	4	26	-	-
423	161	41	6	32	28	900
483	157	45	8	44	-	-

* $T^\circ\text{K}$ - temperature, $\Delta\nu$ - frequency, δ - shift, Δ - error in measurement of shift, γ - half-width, I_0 - intensity at maximum in arbitrary units.

It is natural to assume that the observed changes in the vibration parameters of $\Delta\nu_e$ are the cause of the ferroelectric properties of NaClO_3 . However, the temperature shifts of the frequency of this vibration turn out to be much smaller than required by the theory [1-3] and can explain the temperature dependence of the dielectric constant [10] only qualitatively.

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EFFECT OF LATTICE-DISTORTING IMPURITIES ON PROTON MAGNETIC RESONANCE SPECTRA

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It was observed in proton magnetic resonance (PMR) investigations of laboratory-synthesized potassium hexacyanoosmiate $K_4Os(CN)_6 \cdot 3H_2O$ that the spectra of polycrystalline samples registered at room temperature (Fig. 1), differ greatly from the spectra of the previously investigated isomorphous potassium ferrocyanide $K_4Fe(CN)_6 \cdot 3H_2O$. A study of the central peak in the spectrum has shown that its width does not exceed several hundredths of an Oersted and can therefore be attributed only to the diffusion of the water molecule in the crystal lattice. (The large width of the central maximum on Fig. 1 is due to the large modulation used here to register the weak "wings" of the spectrum.) This diffusion could presumably be due to the presence of free or weakly bound water adsorbed by the sample, but thorough drying of the samples did not change the form of the spectra.

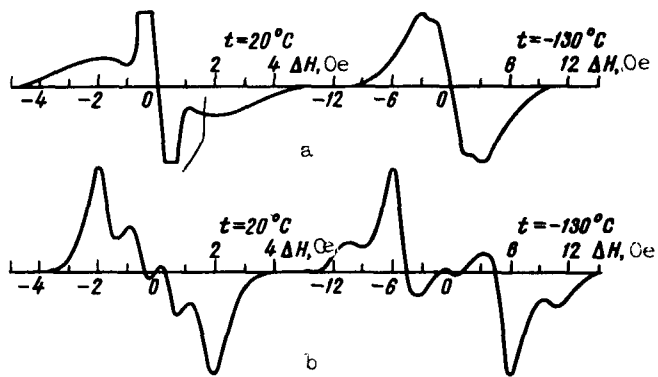


Fig. 1. PMR spectra (derivatives of absorption lines) of polycrystalline $K_4Os(CN)_6 \cdot 3H_2O$ at different temperatures as indicated in the figure; a - before purification, b - after purification.

Cooling the samples to "freeze" the water-molecule mobility changed the intensity of the narrow central peak little, down to $\sim -59^\circ C$, where the peak vanished within a temperature interval of several degrees. But even below this temperature, a noticeable central maximum remained in the spectra and the spectrum, as seen from Fig. 1, differs appreciably from the characteristic spectra of hydrates with "rigid lattice" (see [1]) even at $-130^\circ C$. The temperature variation of the second moments (S_2) also offers evidence that the mobility of the water