CHAPTER 3 The sequence of phase transitions in compounds A_2BX_4 (X = J).

In this chapter we provide experimental data (the study of phase transitions in the compounds of Cs_2CdJ_4 (CCJ); Cs_2ZnJ_4 (CZJ) and $(NH_4)_2ZnJ_4$; involving mutually complementary methods, the main of which is the NQR try organize and discuss these data.

NQR study sequence phase transitions in Cs_2CdJ_4.

Initially, the synthesis and study NQR [127]J compound Cs_2CdJ_4 were taken in 1983.laboratory IP SB AS USSR diplomnitsey Skripichnikova V.V. [76] under the leadership of A.K. Moskalyov In the available samples revealed the presence of two phase states, which were attributed to crystalline hydrates Cs_2CdJ_2-H_2O and the mixed state of Cs_2CdJ_4 + Cs_2CdJ_4-nH_2O. Get resilience nonhydrating connection failed, therefore the studies were limited supervision absorption signals NQR [127]J at 77 K and the temperature dependence of the dielectric constant e(T) and conductance G(T). By anomalies in the temperature dependence was assumed the existence of phase transitions at T^+_1 = 187K, T^+_2 = 207 K, T^+_3 = 231K with a temperature hysteresis ΔT »14K.

In 1986 year studies were continued in [139]. Crystals Cs_2CdJ_4 were grown from an aqueous solution by the Bridgman method. In studies of NQR [127]J for the transition (1/2« 3/2) at a temperature of 77 K, we observed three NQR signal from the samples grown from solution. After annealing the samples at temperatures above 400K, was observed in all samples (at 77 K) 16 lines in the spectrum of the quadrupole resonance.

Studies have shown that under various conditions are realized two different crystal modifications of a substance Cs_2CdJ_4 - α and β. Modification of α - Cs_2CdJ_4 is stable in conditions of high humidity and changes in modification -Cs_2CdJ_4 under forced drying of samples, for example, after warming the crystal above 420K. When the thermally induced in the α-β transition was not observed decrease in the weight of the sample (within 2%) [77], and the NMR dataindicated the absence of crystalline bound water in the - modification (within 2%). On this basis it was concluded that the α-phase is a structural modification of the polymorphous compound Cd_2CsJ_4. β-modification is metastable and the storage of samples under conditions of high atmospheric humidity (h ³ 55%), during the hours £1-20 goes into α-form.

NQR studies were performed in the temperature range 77--450K using the optimal matching [78-81].

To a temperature of 130K were measured in liquid thermal chamber with temperature stabilization 0.1K. From the α-form was not observed any anomalies in the NQR temperature range studied. Temperature dependence of the frequency of β-Cs_2CdJ_4 presented in Figure 3.1. The data clearly indicate the existence of three phase transitions at T_{C1} = 335K; T_{C2} = 260 K and T_{C3} = 184K. In the high-temperature phase observed three spectral lines that usually characterizes the connection β-K_2SO_4-type structure and phase symmetry $D^{16}2h$ (Pnma). However, above T_{C1} signals are detected only by the decay of free precession. At T_{C1} NQR signals disappear and reappear only in the vicinity of T_{C2}, where their spectral form is typical of the incommensurate structure. On this basis it was concluded that in the temperature range 335-260K has incommensurate phase. In the G1

phase observed four NQR signal approximately equal intensity. Phase transition from the phase Jc in the G1 phase accompanied by a slight temperature hysteresis 2K (see inset in Figure 3.1). When approaching T_{C3} intensity NQR lines from the G1 phase and decreases sharply below 184K appears 16 spectral lines, the intensity of which increases with decreasing temperature. At 77K all 16 lines have equal intensity. Thermal hysteresis in the transition G1 « G2 is absent and there is coexistence of phases G1 and G2 in the temperature range 2K.

From a modification in the temperature range from 390K to TCA-observed three NQR lines [127]J, marked on Figure 3.1 in broken lines. The ratio of the intensities of these lines 1:2:1. Stroke frequency (T) is linear with $\P n_I/\P T = 1,5*10^{-2}$ MHz /К, $\P n_{II}/\P T = 1,18-10^{-2}$ MHz /К, $\P n_{III}/\P T = 5,4*10^{-3}$ MHz /К. Relaxation measurements β-Cs_2CdJ_4 showed that phase P spin relaxation times are at the limit of time resolution and equipment up for T_{Q1} <50μs and T_{Q2}<10μs this phase NQR signals are recorded only by induction. NQR signals in the absence of phase Jc can be explained by a decrease in time T_{Q1} and T_{Q2} abroad temporal range of the spectrometer. In the G1 phase of the value of the spin-spin relaxation time T_{Q2}^3 10μs.
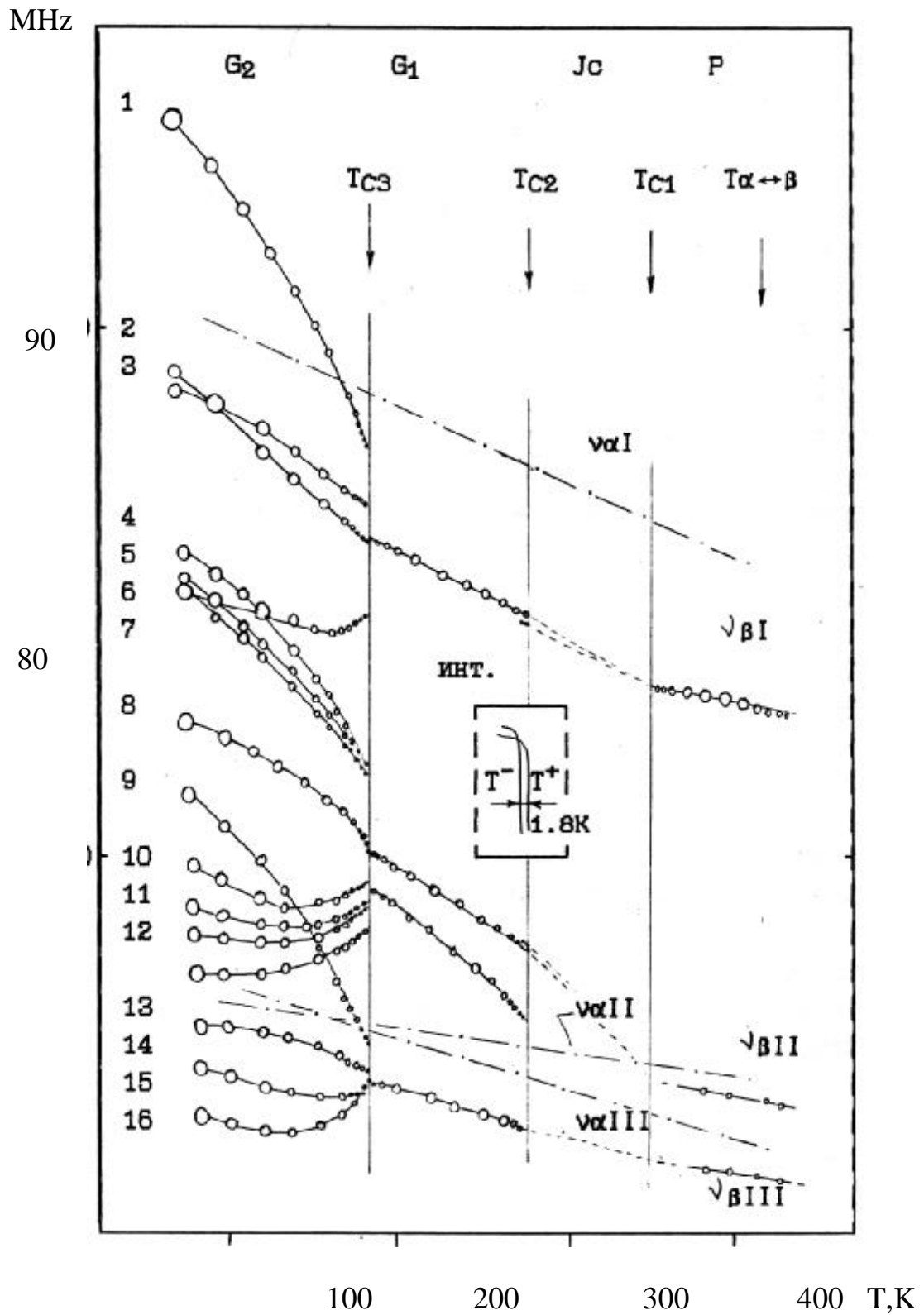
Figure 3.1.The temperature dependence of the NQR frequencies ^{127}J in Cs_2CdJ_4

This, along with a uniform contribution irregularities present contribution to NQR signals. However, the spin-lattice relaxation time is still below the threshold of measurement $T_{Q1}<50\mu s$. Figure the temperature dependence of the time T_{Q1} and T_{Q2} near T_{C3}. With increasing temperature of the G2 phase is observed critical shortening of these times. In the absence of thermal hysteresis G2 « G3 and observation of phase coexistence in a narrow neighborhood of $T-T_{C3} \approx > 2K$, it was assumed that the phase transition T_{C3} is close to the tricritical point. Phase transitions of β-modification were also investigated methods us colorimetry, electro-optics [78.139].

According to X-ray diffraction data given NQR sequence was established as follows symmetry transformation [79]:

$$Pnma\ (Z=4)\ \text{«}\quad Jc\ \text{«}\quad P2_1/n\ (Z=4)\ \text{«}\quad P\bar{1}\ (Z=8)$$

In the phase system was found Jc incommensurate satellite reflections with $\mathbf{q}_d$ varying from 0,25* to 0,24* with decreasing temperature [78].

α -modification of the Cs_2CdJ_4 was identitsirovana Center structure $P2_1/m$ (Z=2). Thus NQR relaxation measurements indicate its dynamic stability ($T_{Q1}=>1ms$, $T_{Q2}>200s$) compared to -form.

§ 3.2 Study the sequence of phase transitions in Cs_2ZnJ_4 NQR [127]J.

Initial data on the study compound Cs_2ZnJ_4 NQR presented in [45]. Continuous method at room temperature observed three rezonananyh absorption signal from the nucleus of [127]J and only one absorption line at temperature of 77K.

In 1988, the compound Cs_2ZnJ_4 originally synthesized and studied by NQR author, and then were held and more comprehensive studies [78-82,138].

Cs_2ZnJ_4 crystals grown from ZnJ_4 aqueous solution at 313K. According to our diffraction studies, at this temperature, the compound has an orthorhombic structure with space group symmetry Pnma-Dah[16]. NQR spectra were recorded by the optimal matching in gas-liquid heat chamber in the temperature range 77 400 K. At room temperature (RT) at the transition 1/2 « 3/2 nucleus [127]J observed three absorption lines at the frequencies8.87; 75.50; and 72.75 MHz with an intensity ratio other than the ratio of 1:1:2 (the latter position should reflect symmetry nucleus [127]J at positions I, II, III and (III ') structure Pnma). Fixed ratio of intensities and frequencies, but different from that registered by super regenerative NQR [45]. At 77, we observed eight singlet spin-echo signals and three NQR signal decay of free precession (MTP). One of the precession signal whose intensity was greatest, was close to a single frequency signal is observed at TCA [45].

In a wide range from 120 to 400 K the temperature dependence of high-frequency components of the spectrum is linear with $d\nu_I/dT = 5,87*10^{-2}$; $d\nu_{II}/d\nu = 1,51*10^{-2}$ $d\nu_{III}/dT = 1,19*10^{-2}$ MHz/K. Below 120 K the temperature dependence of the NQR frequency spectrum and its multiplicity change (Figure 3.3, 3.4). At a temperature $T_i = 118K$ the first phase transition is observed, which is fixed on the anomalous behavior of the spectra shape Figure 3.4 and 3.5, and the spin-spin T_{Q2} and the spin-lattice relaxation time T_{Q1} nucleus iodine Figure 3.7.
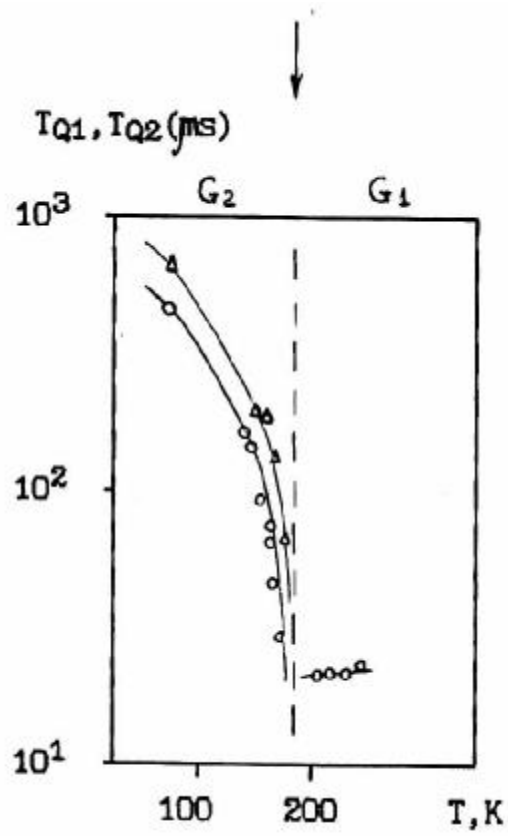
Fig. 3.2. Temperature dependence of the time T_{Q1} and T_{Q2} of the quadrupole relaxation of ^{127}J in Cs_2ZnJ_4
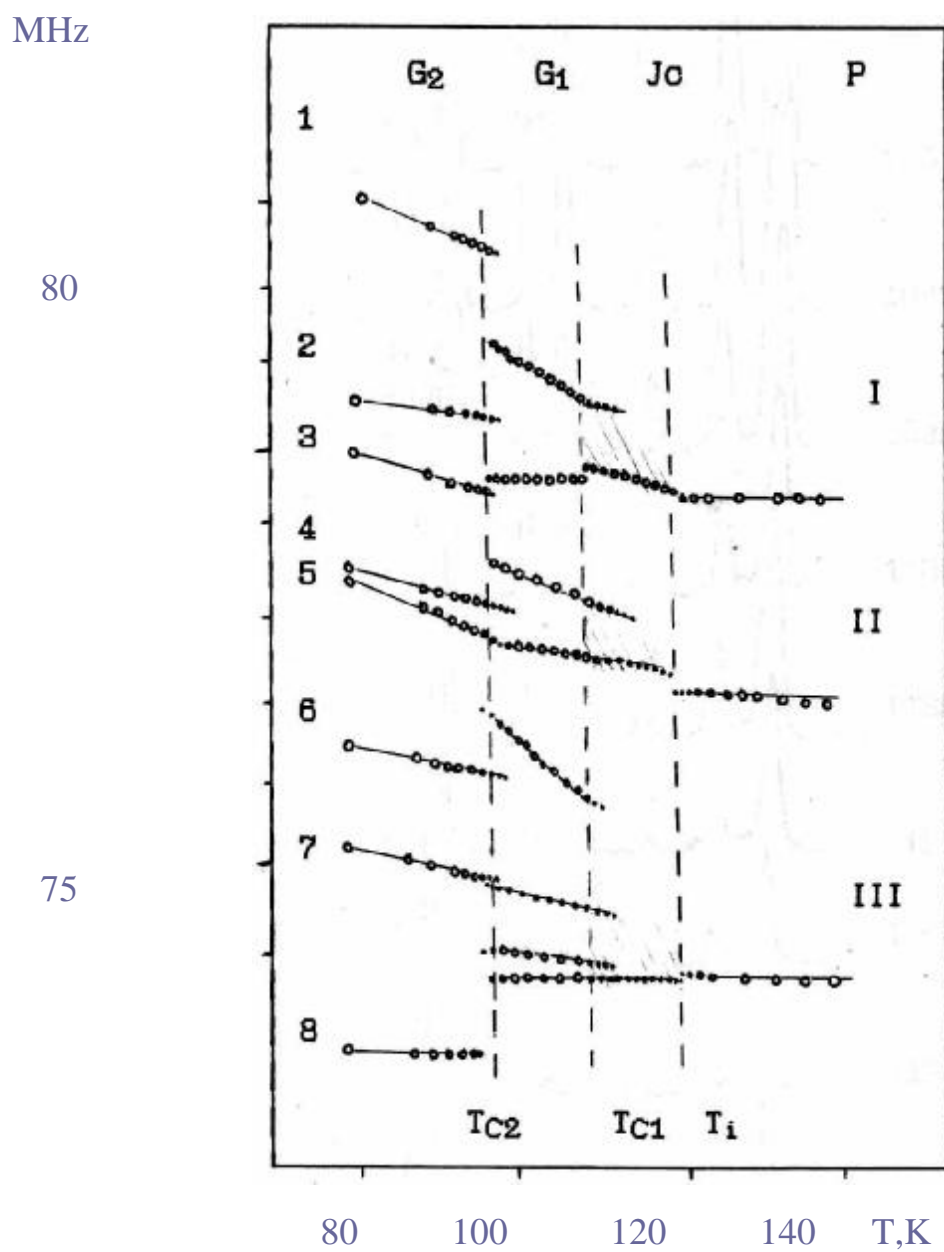
Fig. 3.3. The temperature dependence of the NQR frequencies in the ^{127}J in Cs_2ZnJ_4

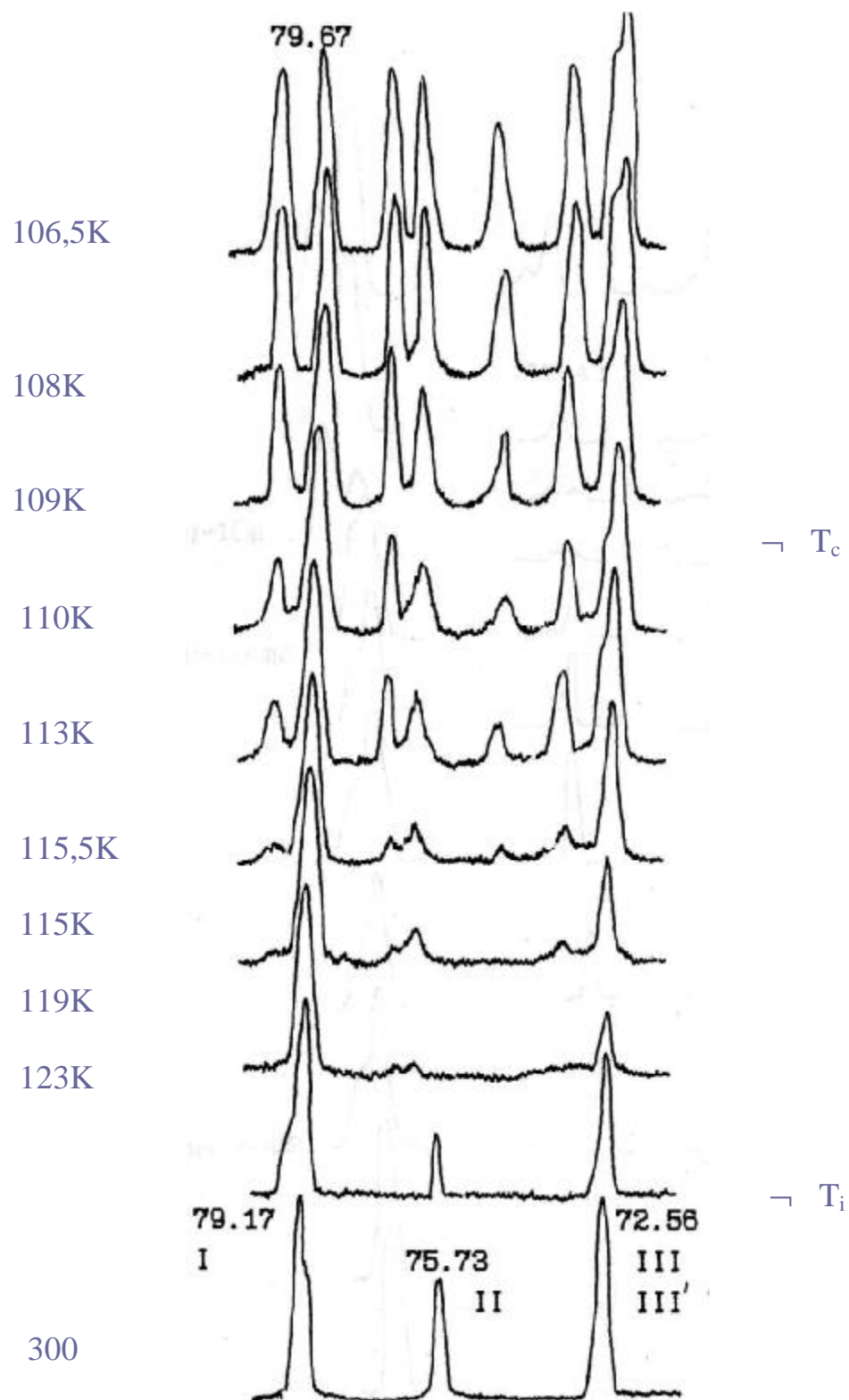Figure 3.4. Type ^{127}J NQR spectrum of Cs_2ZnJ_4 near T_i

115,5K

118K

120K

$T_N=10ms$ 121K

77.43

$T_N=100ms$ 122K

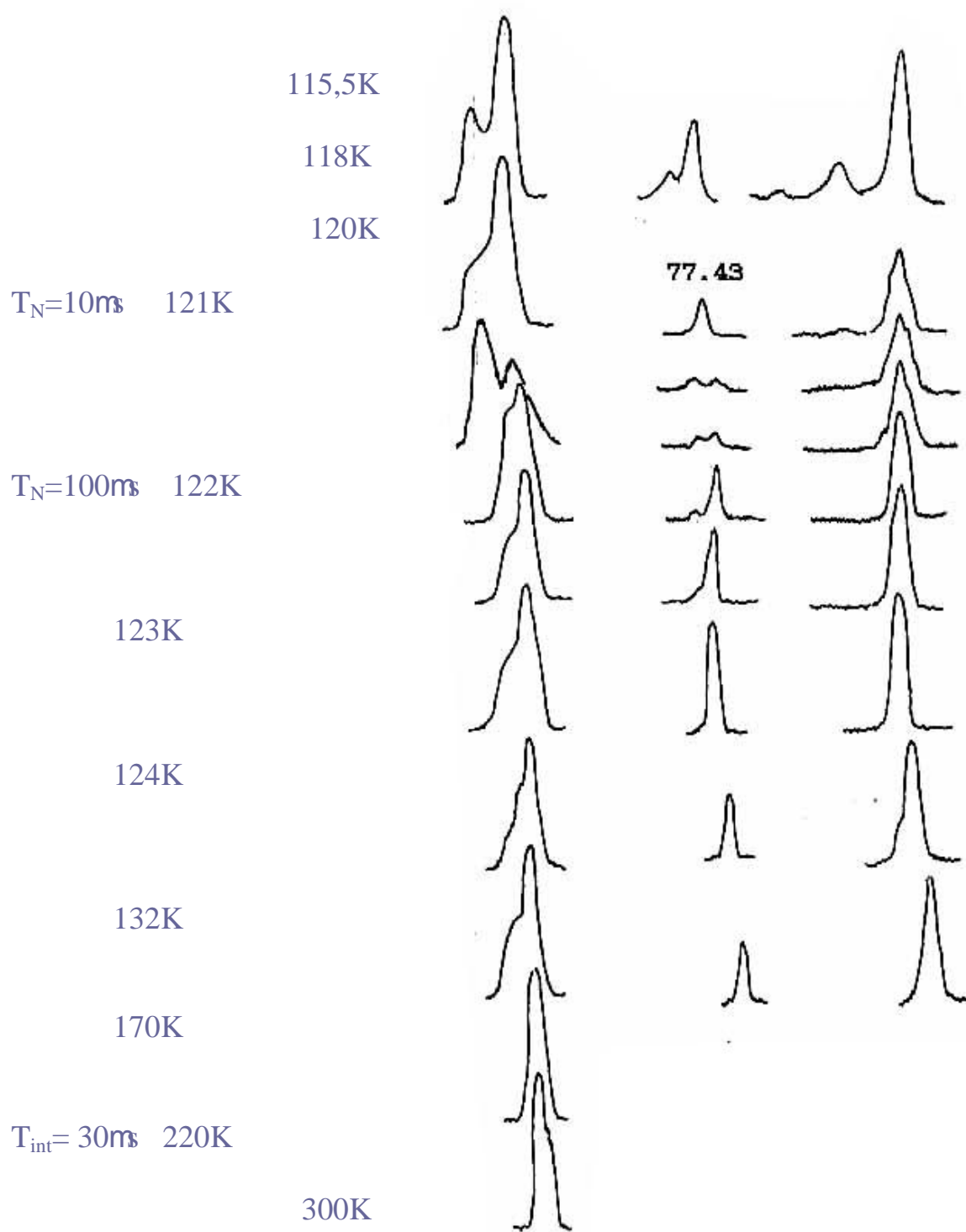123K

124K

132K

170K

$T_{int}= 30ms$ 220K

300K

Figure 3.4. Type ^{127}J NQR spectrum of Cs_2ZnJ_4 near T_i
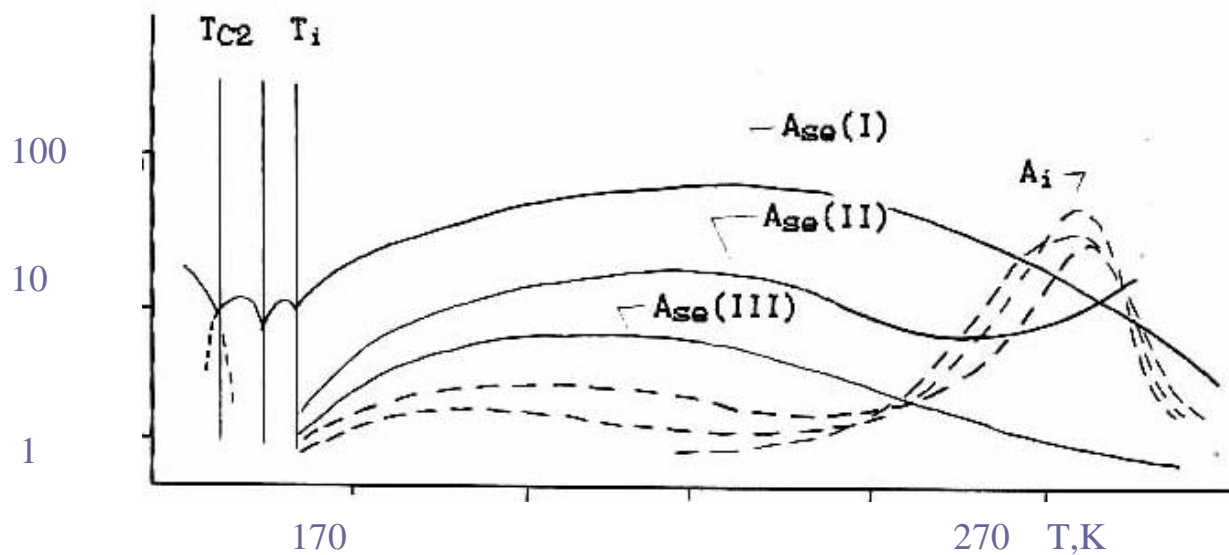
Int. (relative units)

Figure 3.6. Changing the signal amplitude of the spin-echo (A_{se} and induction (A_i on the temperature at some parameters of the pulse setting.
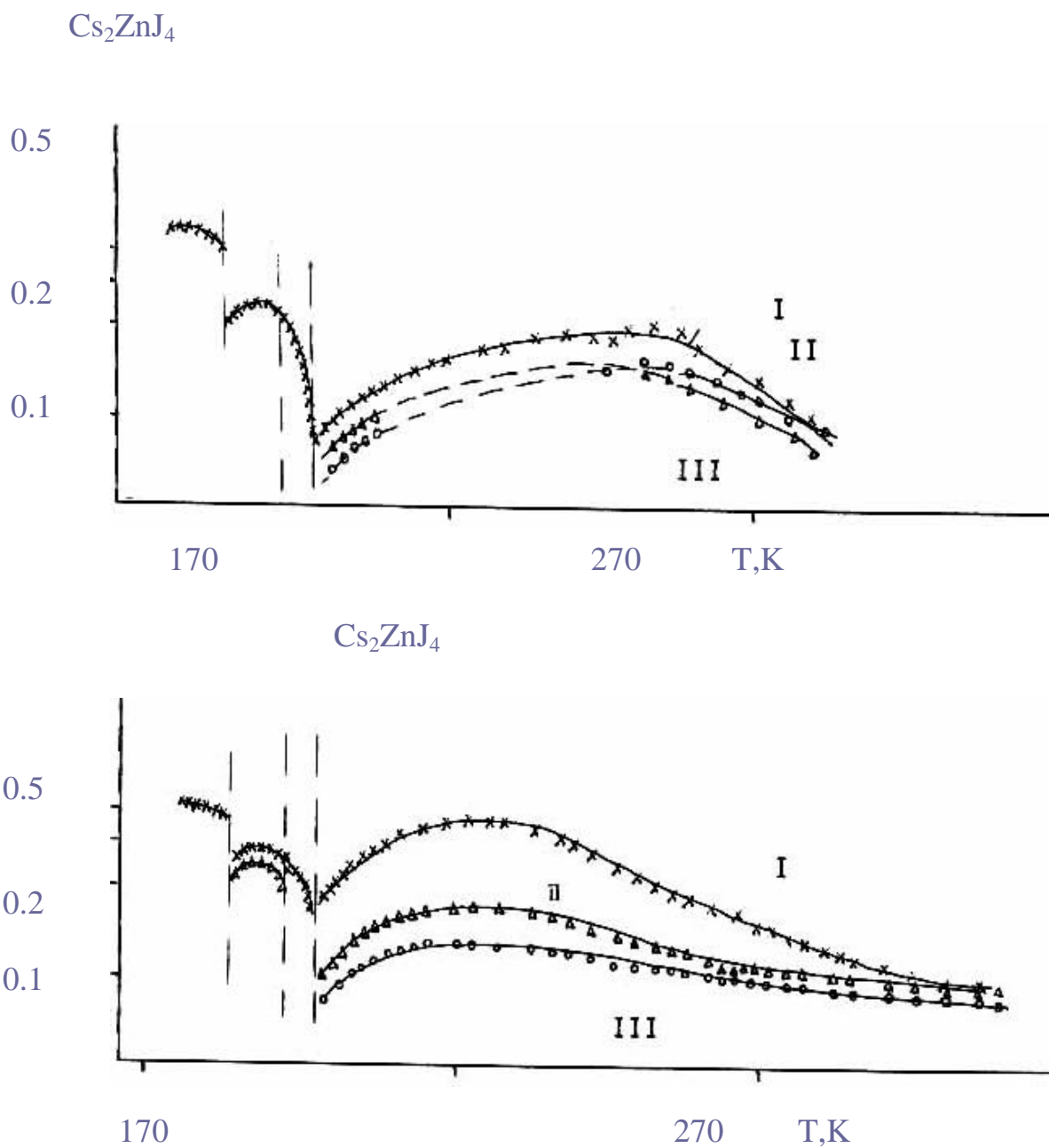
Cs_2ZnJ_4

Cs_2ZnJ_4

Fig.3.7. Temperature dependence of the time T_{Q1} and T_{Q2} cpinovoy relaxation in Cs_2ZnJ_4

As we approach the T_i peak intensity of the lines decreases (Figure 3.6) **I** have high-frequency component of the spectrum, long before T_i, there is a marked asymmetry of shape. For the other two lines of the spectrum asymmetry is observed at lower temperatures. When passing the phase transition diminishes the intensity of lines in the field of asymmetric wing, a new spectral component. The change in the spectrum can be interpreted and register as the existence of three closely spaced components whose frequencies are continuously follow through T_i. Below 118K spectrum shape is typical for the incommensurate phase (Figure 3.5). It should be noted that the optimal matching method for the first time were able to observe the full range of NQR in incommensurate phase tsezevogo compound (Cs_2BX_4) with iskhodnoi structure Pnma. The advantage of the optimal matching can be demonstrated by comparison with similar measurements [87,88], where T_i near signals are not observed. The hysteresis transition at T_i, the peak intensity changes along lines I, I and III, no.

Although continuum frequency distribution, limited terminal peaks typical of the NQR spectrum of the incommensurate phase in the temperature dependence of the line shape, there are significant deviation from existing models [34]. Directly below T_i less intensity "singularity" of the spectrum is very blurred and far from the form predicted by the model. However, with decreasing temperature, shrinks to a spectrum intensity corresponding to a peak that becomes pronounced in the middle well disproportionate phase. Line III below T_i is split into two strongly overlapped continual distribution, one of which is weaker in intensity. High-frequency part of this distribution appears above the noise level only in the middle temperature range nesoraamernoy phase.

As the temperature decreases, the sharp change in intensities (Figure 3.6), and notes the jump frequencies, at least the line at frequency 80MHz, tilting frequency dependencies, well fixed phase transition Jc« G1 at T_{C1} =108K. This behavior is also not consistent *with the* model [34], where the frequency of boundary singularities continuously converted into singlet line low-temperature phase. In the G1 phase, we observed eight ravnointensivnyh NQR lines. Hysteresis transition at T_{C1} about 3K. In addition to the continuing progress of the frequency spectrum of the line III in the G1 phase at temperatures of 96-105K at a frequency of 73.6 MHz observed Intense induction signal that accompanies the bass line NQR in this phase, fixed by the spin-echo signal. According to our data here, as in Rb_2ZnBr_4 observed cross-relaxation resonant excitation of a certain level of connectivity Cs_2ZnJ_4 within the contour line of the low-frequency phase G1.

At 96K observed a pronounced phase transition G1 « G2. with the number of lines in the spectrum does not change, change their frequency. Observed phase coexistence. Hysteresis transition is absent. Coexistence region depends on the quality of the samples and for the more perfect crystals is »2K.

Temperature dependence of time and T_{Q1} and T_{Q1}, measured by the resonant response of the absorption of iodine nuclei in positions I and III of the crystal structure of tetra cesium iodine zincate indicates existence of a critical slowing down at T ® T_i. In this case directly with T_i, due to approximating the values of the relaxation time to the limit of time resolution of the spectrometer (»30-20ms for T_{Q2} and »100ms for T_{Q1} measurements were performed with low accuracy.

Near T_{C2}, also observed critical slowing down prior to the jump relaxation times at first-order transition.

At temperatures above T_i NQR signals consist of heterogeneous as well as from homogeneous component. At the same amplitude value the contribution of these signals igmenyaetsya with temperature (Fig. 3.6). Below 273K is most clearly expressed spin echo reply nucleus and above this temperature observed area where in the equipment range temporal resolution prevails uniform contribution fixed by the decay of the free precession. There is a slight frequency shift ($\approx$ 50 kHz) between the longitudinal and transverse components of the nuclear absorption. These data indicate a significant spin-relaxation properties of the system. In the available time scale, we performed measurements only time T_{Q1L} and T_{Q2L} (Figure 3.7). As can be seen from the figure, clearly a decrease in T_{Q1L} and T_{Q2L} positions of the nucleus in the structure **I** Cs_2ZnJ_4, whereas nucleus positions II and III (III') the spin-spin relaxation in a wide temperature range varies only slightly.

Note that in the Cs_2ZnJ_4 according NQR no polymorphism and expression of non-equilibrium phenomena. However, at a frequency of 83.3 MHz, by induction, we observed an unidentified NQR signal. Temperature dependence of the frequency of this signal is linear in the temperature range from 300 to TKA, with a small value $\P n / \P T \gg 0{,}85$ kHz/K Signal amplitude during cooling-heating cycle varies as shown in Figure 3.8. In the cooled signal value increases rapidly approaching the T_i. When the sample is heated in a wide temperature range, a more smooth-change.
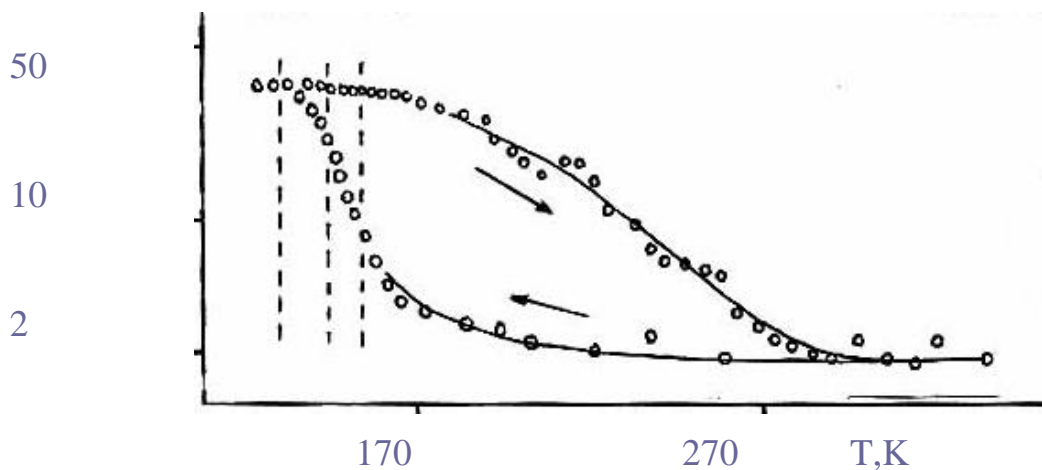

Figure 3.8. Temeraturny stroke amplitude of the signal decay of the free precession frequency 83.3 MHz.
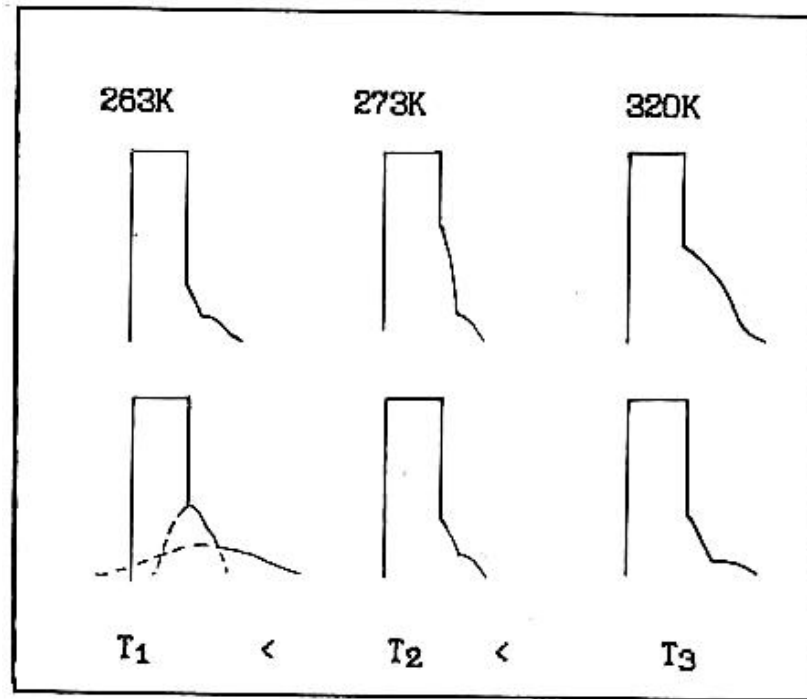
Cs_2ZnJ_4

Fig. 3.9. Two-exponential decay envelope shape of the free precession.

As is well known and customary for all the compounds of structure β-K_2SO_4, the phase transition in the paraelectric willows Jc phase transition is of the second kind, but for Cs_2ZnJ_4 observed phase coexistence region near the transition point T_i, which usually characterizes the transition as original. On the other hand, the original transition should be observed temperature hysteresis width of the order of the phase coexistence region. However, from our data suggest that hysteresis effects are fixed only by the homogeneous unidentified NQR signal (Figure 3.8). According to this we can assume that in the Cs_2ZnJ_4 (see below and also Rb_2ZnBr_4), there is a microscopic substructure affecting the nature of the phase transition, and hysteresis of the main structure is masked by a large temperature region of frequency overlap of homogeneous and inhomogeneous contributions to the signal NQR. Microscopic nature of observed substructure is confirmed by the presence of trivets cross-relaxation absorption of one of its levels with the level of the basic structure of the NQR frequency 73.7 MHz. Thus there is reason to assume that the phase transition to the incommensurate phase is smeared in a 100K above T_i Around the same area observed asymmetry of the line shape NQR redistribution contributions homogeneous and heterogeneous components NQR signal plateau in the temperature dependence of the spin - lattice relaxation, strong anisotropic scattering by point radiographs. At a temperature change in the slope 280K measured temperature variation electro-piezo-optical coefficients dDn1 and dDn2 [78], the softening of the optical mode [89]. Thus, in this temperature range is marked with non-standard behavior of macroscopically and microscopically smooth blurred anomaly at 240-270K. Anomaly is associated with a slight restructuring and is accompanied by changes in the spin dynamics of the system.

To describe the observed behavior of the NQR spectral parameters we performed additional NQR study. It turned out that the form of induction decay signals at frequencies of I, II and III is at least two-exponential (Fig.3.9), wherein it is not connected to the interlevel spin transitions of 5/2. This indicates the existence of two systems in the dynamics of the scale of the spin-lattice relaxation time - short T_{Q1s} and long T_{Q1sL}.

With increasing temperature, the shape of the envelope of the induction signal is clearly observed redistribution of these deposits. The existence of two time scales fixed and spin-echo sequence. Line shape at different setting conditions (Figure 3.5) revealed that the frequency dependence of the complex spectral line I can be represented as shown in Fig.3.10.

Analysis of the spectral data in the NQR Cs_2ZnJ_4 may be conducted under the assumption that between the high and incommensurate phases of the intermediate region. By lowering the temperature of 330K, where there are narrow homogeneous line (which can be explained by the high mobility of iodine ions [97]), the temperature is lowered NQR line shape is broadened by developing fast motions of the atoms are concentrated in clusters and are in the resulting double-well (configuration) potential. After T_{CI} and T_C transition atom selects a specific position so that rotation occurs cooperative ZnJ_4 tetrahedra in opposite directions with the equilibrium configuration of positions filled building.

Less clearly described behavior, as will be shown below, is also observed in $(NH_4)_2ZnJ_4$ and Rb_2ZnBr_4 (signs: an extensive area of dynamic disorder, the presence of an incommensurate phase, a two-time scale dynamics, the existence of substructure).

Very similar behavior was observed in another type A_2BX_6 crystals [20].
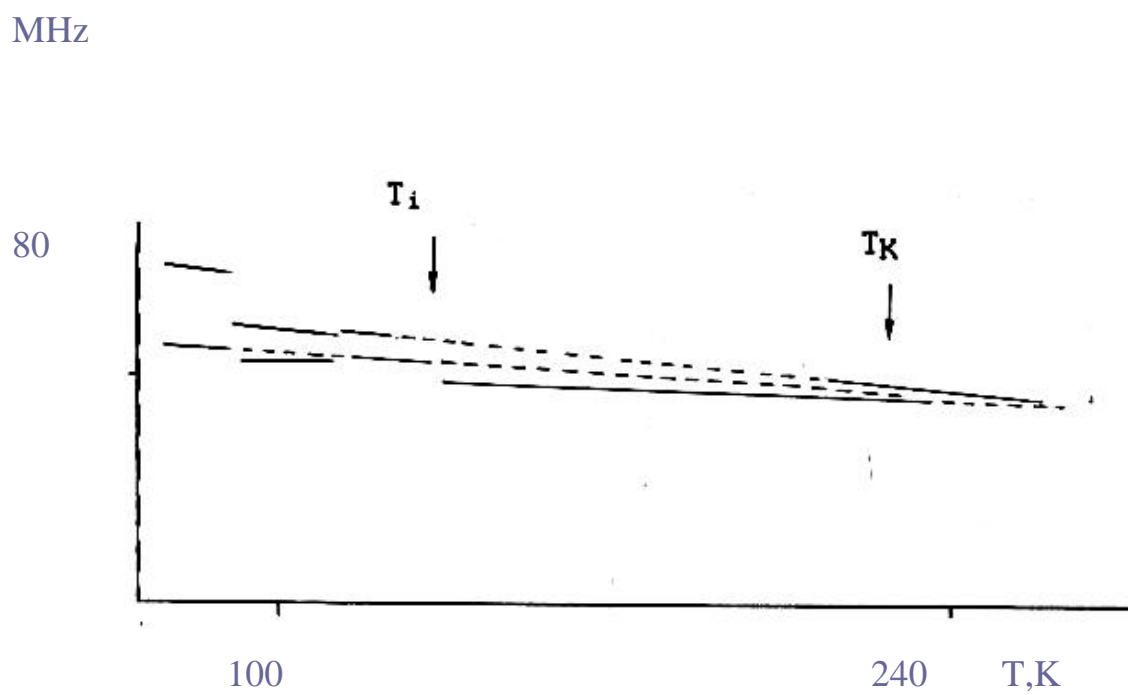
MHz

T_i

T_K

80

100

240   T,K

Fig.3.10. Scheme of the temperature dependence of the frequency components of the nonsinglet line (I) Cs_2ZnJ_4

In addition to the NQR data, we have made and the x-ray diffraction studies dielectric Cs_2ZnJ_4 at temperatures ranging from 300 to 93K [85]. Dielectric changes along the c axis showed a peak in T_i and fractures T_{C1} and T_{C1}. These data correspond well to similar measurements Gezi [90], made around the same time. X-ray diffraction, it was found that at room temperature the crystal has a rhombic pseudohexagonal cell D_2^{16h} with parameters: a = 10.835; b = 8.318; c = 14.440A; c/b = 1/3, Z=4, which allows this compound is sure to carry the structural type -$K_2$2SO_4. When the sample is cooled from 237 to 107K view radiographs does not change. At 107K radiograph well displayed in the orthorhombic cell with a = 10,744; b = 8.231; c = 14.341 . At 108K a splitting of some X-ray line.

Character splitting indicated monoclinic distortion of the cell. By analysis of the extinction reflexes involving elektropticheokih and NQR data has been proposed that has a G_i phase structure with a spatial group or $P2_1(Z=4)$ with a polar or nonpolar axis **b** $P2_1/n(Z=8)$. Below 95K on X-ray data, has a triclinic cell distortion. General analysis of structural data (including NQR) gives G_2 phase space group P1(Z=4).

However, radiographs in Jc phase initially failed to fix superstructure reflections. Only in high-precision X-ray studies performed at the University of Orsay (France) F.Denovue was recorded appearance satellite reflections below T_i, with the value of the wave vector [91]

$$q_d = (1 + d)\ a^*/2,\ d \approx 0{,}15 \quad at\ T = 112.$$

Thus in conjunction CS_2ZnJ_4 discovered and investigated the phase sequence:

$$\textbf{Pnma(Z=4)} \ll \ \textbf{Jc, } q_d = (1+d)a^*/2 \ll \ \textbf{P2}_1\textbf{/n(Z=8)} \ll \ \overline{P1}(Z=4)$$

The transition to the incommensurate phase is accompanied by an extensive pre-transition region and the specific evolution of the line shape transition NQR signals.

§ 3.3 NQR Studies of phase transitions in $(NH_4)_2ZnJ_4$

Synthesis and crystal growth tetrayodtsinkata ammonium author performed using chemically pure **NH₄** and ZnJ_2, which were taken in stoichiometric ratio, a method of evaporating an aqueous solution and melt ive.

In the first case, crystallization is carried out at a temperature of 293 K under conditions **of** low atmospheric moisture for 10-15 days.

Depending on the variation of the starting components of various crystallizations were prepared with different crystal habit. When r excess NH_4J grew predominantly hexagonal prismatic crystals with a diameter of 5 mm. With excess ZnJ_2 obtainedlamellar intergrowths willows crystallites up to 25 mm in length. To remove any residual crystals were washed with a solution of a chemically neutral fluid. A homogeneous melt of colored iodine compound, which after grinding and annealing was a light gray powder. An x-ray test crystals with hexagonal form the habit of no interest.

Methods of NQR investigations was the same as described above. Temperature measurements were carried out in 380-77K.

Studies have shown [92] that observed at room temperature from6 to 8 NQR lines at 77 and 16 lines of varying intensity. Analie number and intensities of the spectral lines
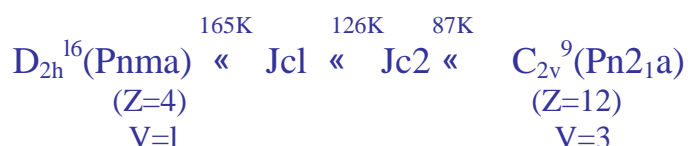
samhles different methods of growth and crystallization allowed to correlate them on two structurally different states. So to a certain structure *and* spectral lines correspond to type νaI - νa5; and-other structure in lines νI, νII, νIII (in-line). Fig.3.11.

Later studies were conducted on samples two N1 and N2. From sample Nl at T-290K fixed intensity of the NQR lines at frequencies νa1 - νa5 and structure, and from the sample N2 simultaneously observed NQR signals of a and β-structures in proportion intensely about 1:1. At 77 K from both samples were also observed and in-line type NQR, and from sample N1 signals approaching the noise level of the spectrometer. Upon annealing the samples (T = 380K) within 4 hours, an increase in the intensities of the NQR signal type b. Spectral line type *and* traced throughout the temperature range and do not have any anomalies in the temperature dependence of ν(T) (dashed lines in Fig.3.11) and intensities I(T). Stroke frequency NQR lines in the linear type to T) 170K with $_I$/T = 34,5; $_{II}$/T = 14,8; $_{III}$/T = -2,0 kHz/K. At a temperature Ti - 165K anomaly in the behavior of the spectra. Peak intensities of the lines ν and νIII diminish lines and νI νIII when passing through the Ti vary in frequency (Fig.3.11). The second anomaly is observed at Tci = l26K, where there is a change in the multiplicity of the spectrum. The low-frequency component is split into three lines with an intensity ratio of »1:2:1, and the high frequency components pass into the two NQR lines each. When the transition 1/2 - 3/2 fixed 12 NQR lines ^{127}J.

Temperature changes in the group of high-frequency lines indicate the temperature of the third spectral anomaly : T_{C2} = 87+2K.

At temperatures 210-370K NQR signals from b state of the crystal are observed as a spin-eco signal $A_{se,}$ and in the free precession signal decay $A_{i.}$ With increasing temperature, the amplitude of signal A_{se} for all of the component ν. Fig.3.12 spectrum decreases, and the amplitude ratio of $A_{se}(I) : A_{se}(II) : A_{se}(III)$, characterized by the ratio of 1:1:3. Amplitude A increase of the noise level and reaching a maximum at T»310K, fall at higher temperatures. After annealing the sample at T^3 310K and subsequent cooling, the quantities A_{se} and A_i decrease in size, but restored after low-temperature cycles. Such changes in NQR spectra reflect the resonant nature of the observed relaxation of nonequilibrium phenomena. However, due to technical limitations, these affects on this compound investigated is not sufficiently clear.

Based on a comparison with the data obtained by this NQR for compounds Rb_2ZnBr_4 (Fig. 3.13, etc.), $Rb_2ZnCl_4,$ Cs_2ZnJ_4 and other assumption was made that the investigated compounds belong to the structural type $β-K_2SO_4$ symmetry transformation of the scheme:

$$D_{2h}^{16}(Pnma) \underset{(Z=4)}{\underset{V=1}{«}} \overset{165K}{Jcl} « \overset{126K}{Jc2} \overset{87K}{«} \underset{(Z=12)}{\underset{V=3}{C_{2v}^{9}(Pn2_1a)}}$$

The phase between 126 and 87K interpreted as disproportionate, rather arbitrary, and is likely to increase in the period phase q_S = 2/5 or 3/8) and the symmetry Pn21a.

Focus on a comparison of the spectral data obtained by us NQR with similar data for other compounds A_2BHal_4 (Hal = Cl, Br, J) and consider-their compliance with femenologicheskoy model [34], proposed to describe the shape of the resonance lines in the incommensurate systems.
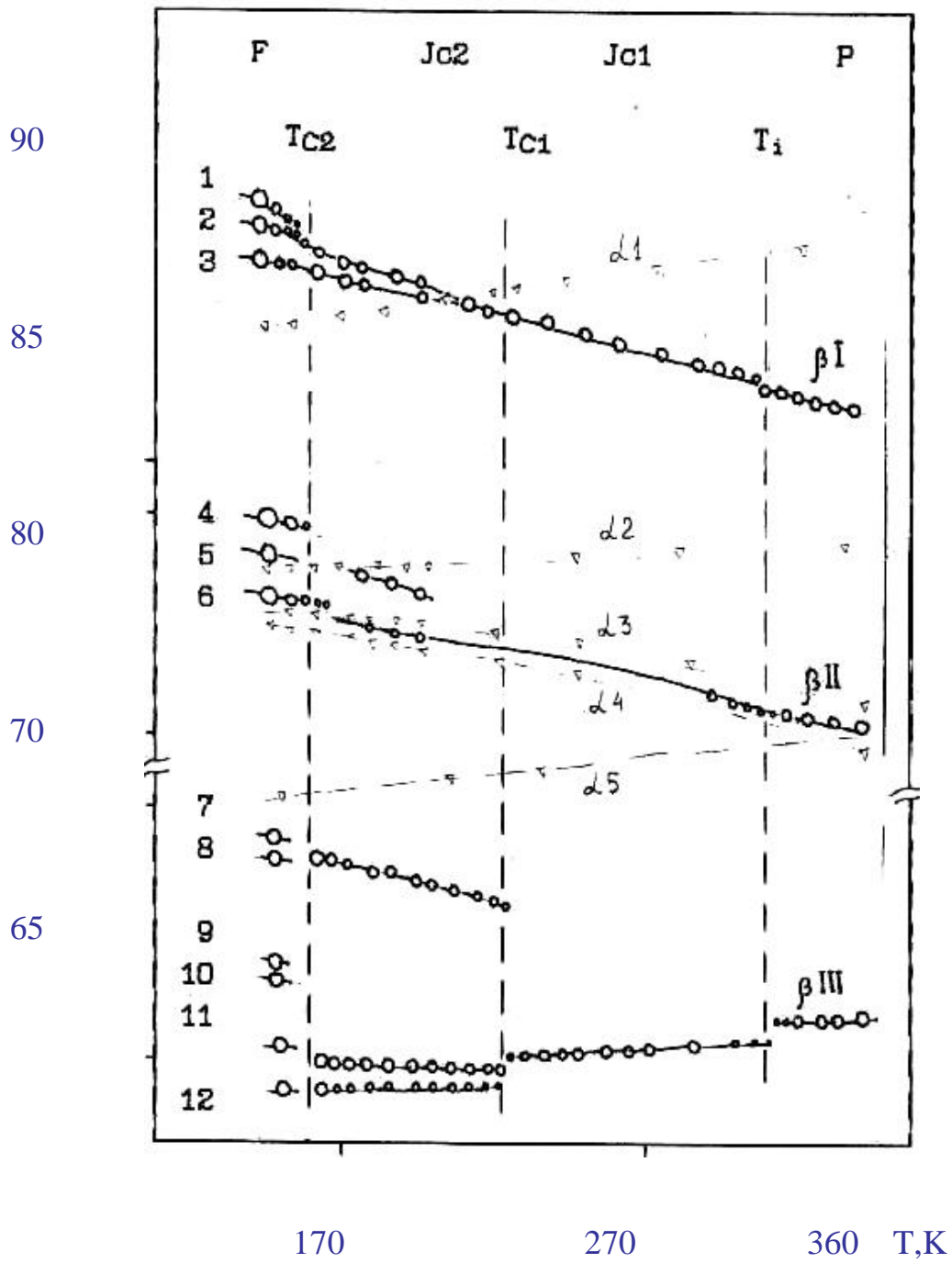
Fig.3.11 Temperature dependence of the frequency spectrum of the NQR [127]J in $(NH_4)_2ZnJ_4$.

Lg A
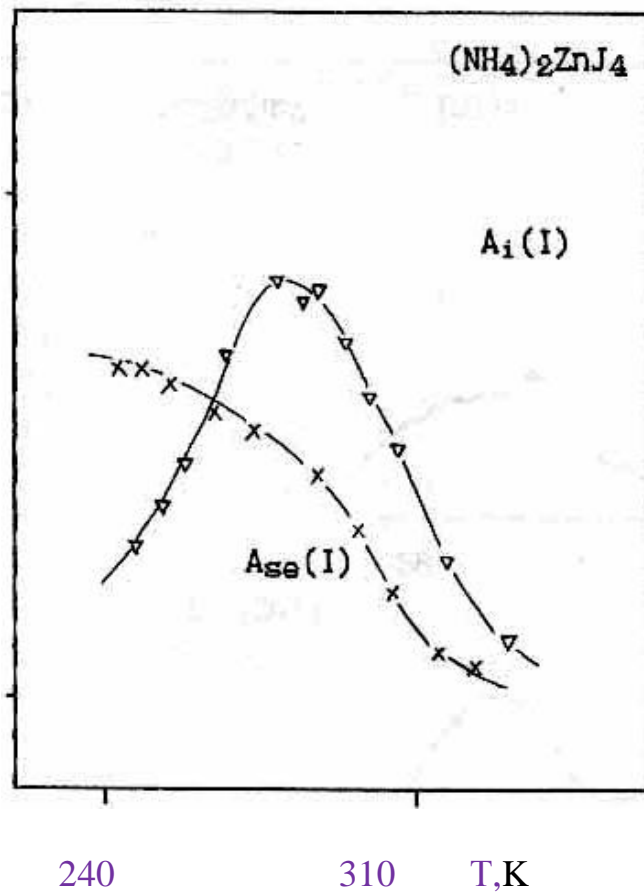
Fig.3.12. Changing the values of the amplitudes A_{se} and A_i in $(NH_4)_2ZnJ_4$

Figure 3.13. The comparison of the NQR spectra of Rb_2ZnBr_4 and $(NH_4)_2ZnJ_4$

Table 3.1 shows the known NQR data for compounds A_2BHal_4 with an incommensurate phase. These data include: 1) the relative splitting of the extreme components of the spectrum near T_i: $_{I\text{-}III} = [_{I\text{-}III}]/_{III}$; the values of the temperaturecoefficients of $/n*\P n/\P T$

Table 3.1
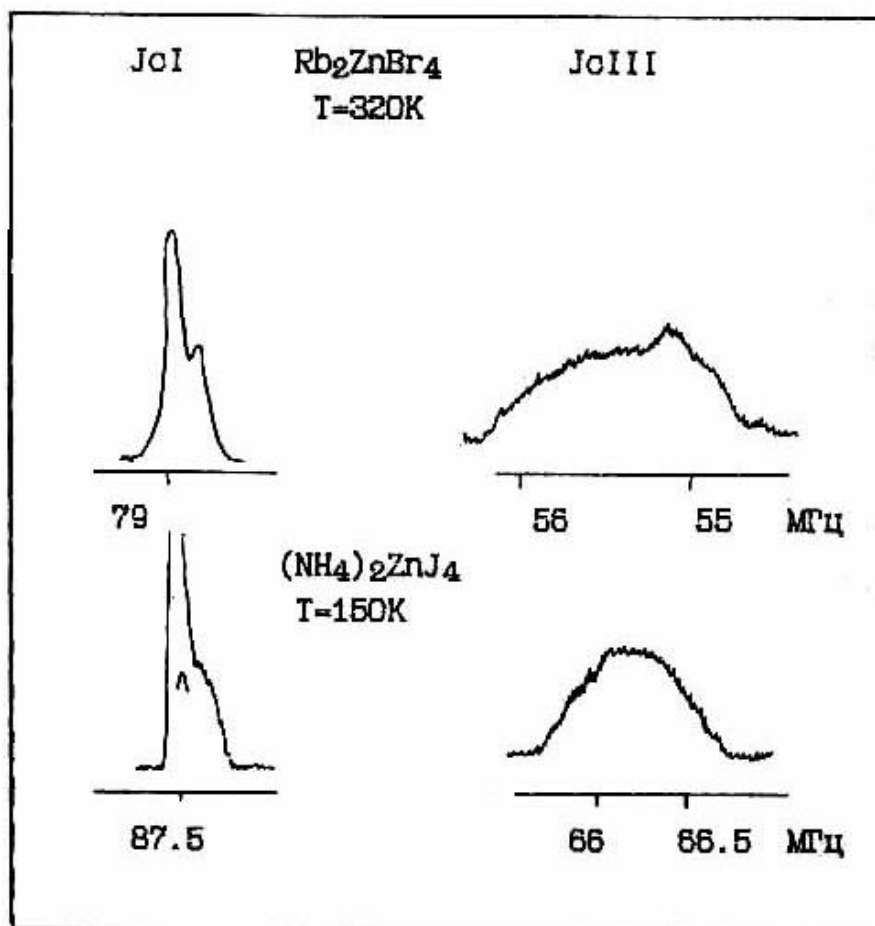
A_2BHal_4	n_I MHz	n_{III} MHz	$Dn_{I\text{-}III}$ %	$\dfrac{1}{n}\times\dfrac{dn_I}{dT}$	$\dfrac{1}{n}\times\dfrac{dn_{III}}{dT}$	$\dfrac{n}{n_0}$ %	T_{Q1} (m
ZnJ₄ (AZJ)	87.0	66.0	31	$3.9*10^{-4}$	$-3*10^{-5}$	280	150
ZnBr₄(AZB	66.0	61.5	<26	$3.0*10^{-4}$	$-1.9*10^{-4}$	400	160
ZnCl₄	9.8	8.0	<27	$2.6*10^{-4}$	$+1.3*10^{-4}$		1000
Cl₄ (CHC)	14.15	11.68	*22	positive	negative		-
Cl₄ (KZC)	9.94	8.08	*20	positive	negative		600
J₄ (RZJ)			>19	positive			
Br₄ (CUB)	93.5	78.6	19	$2.3*10^{-4}$	$+1.6*10^{-4}$		
BT₄ CCCB)	65.9	57.36	15	positive	positive		-
J₄ (CCJ)	83.2	71.5	16	$7.4*10^{-5}$	$+ 4*10^{-5}$		100
Br₄ (RZB)	64.0	55.0	16	$2.5*10^{-4}$	0	320	
Cl₄ (RZC)	9.7	8.3	16	$4.4*10^{-4}$	$+2.4\ 10^{-9}$		
J₄ (CZJ)	79.5	73.9	7	$7.4*10^{-4}$	$+1.5\text{-}10^{-4}$	200	400
Cl₄ (CZC)			8	modulation Cs по ЯМР [127]			
Br₄ (GZB)	62.73	67.62	9	no Jc ?			
dCl₄ (RCC)				structure Immm			

3) the average half-width of the resonance signals latched by spin-echo above T_i ; 4) The maximum values of the relaxation times T_{Q1} and T_{Q2} the position I Pnma structure of the compounds studied, where the nucleus of halogens.

Comparison of the relative spacing between the high frequency v_I and v_{III} low frequency NQR lines in the high-temperature phase near T_i, shows that the largest amount of splitting $Dv_{I\text{-}III}$ celebrated for ammonium compounds (up 31%) and the smallest for cesium (up *7%).* This fact is explained by difficult from the standpoint of crystal, because radius of the cations NH_4, Gs and close in magnitude and indicates that the cleavage is determined sufficiently dynamic environment nucleus halogen. Some correlation of splitting $Dv_{I\text{-}III}$ observed size of the halogen atom: for compounds A_2BHal_4 same A and B, the splitting decreases with decreasing radius Hal. Due to the fact that the "smaller" Hal atoms polarizability than this may indicate a significant chemical (electronic) contribution to the nature of this splitting. At temperatures close to T_C and 77K major outer frequency splitting observed in average in the compounds with the larger ions. This is in agreement about the importance of data on the dipole-dipole interaction in these compounds. Nor is there any patterns between types of atoms B (Zn, Cd) and the general character of the temperature dependence of frequency: when changing varieties atom B, is transferring to another compound crystallochemically or structural class. This implies that the stability of the tetrahedron defined by the electronic environment.

Significant linewidths temperature phase indicate the presence of structural or chemical disorder in these crystals. Suggest the following details in shape. Hal_I spectral distributions (the position of the nucleus in the structure of halogen I Pnma). If in Cs_2ZnJ_4 line shape in the position of Jc faze Hal_I presented low-intensity and high-intensive low frequency component, the compounds of RZB, CHB, CCB, CCJ observed reverse arrangement in the intensities of these components.

In this case, cesium bromide intensely ratio of these components is about 20, and in the second part CCJ only observed when T_C low intensity as a small wing . As will be described in Chapter 4 of RZB in increased pressure in the Jc phase component intensity ratio discussed approaches unity and becomes comparable with the add-on for AZB and AZC. Since the shape of the line is determined, in particular, the transverse spin relaxation (T_{Q2}), to a marked difference indicates a different character dynamic environment nucleus deviated from position I (II and III) structure Pnma. Most clearly seen when compared Cs_2ZnJ_4 with other cesium analogs.

Temperature dependence of the frequency below T_i unusual and can not be explained by known types (rotary, Vibratory, torsionalny) atomic motions. In the nature of the temperature slope of the NQR frequencies in compounds A_2BX_4 celebrated their graduation large values of sharply positive for high frequency components, to smoothly negative for the lower frequency component of the NQR spectrum. This, along with other data about indicates significantly different character movements and dynamics of structurally nonequivalent nucleus Hal.

When comparing our data with the results of stationary NQR methods [37, 44, 45], there are significant differences. It follows from our relaxation measurements of the T_{Q1} and T_{Q2} due to the fact that when using the latter can be detected only homogeneous (long-lived), contributions to the absorption signal, whereas the use of spin-echo technique allows us to observe inhomogeneously broadened signals. But even in the latter case there are time limitations instrumental that does not allow enough correct record form broad frequency

distributions, as in the case of Cs_2CdJ_4, even with an increase in sensitivity of the method, the signals in the Jo-phase is not fully observable.

Briefly summarizing the results of NQR spectral data presented in this chapter, we can note the following: First, the experimental data obtained under static spectral characteristics indicate a fundamental difference in the nature of their temperature evolution compared to phenomenology model [34]. Secondly, there is a significant impact on the nuclear dynamics observed frequency spectral characteristics of NQR.

Time measurement T_{Q2} spin-spin relaxation in and [103,109] indicate the need to consider the temperature change of the width of the singlet spectral line in Jc phase, whereas in the existing model, the width of individual components of the continuum distribution was chosen to be the width of the line paraelectric paraphase . However, NQR data for Cs_2ZnJ_4 (and especially our studies RZB [109]) shows that this assumption is not always competent, since the relaxation times and T_{Q1} T_{Q2} in Jo phaseincrease rapidly with decreasing temperature, and the intensity of the two end peaks for all of the observed frequency distributions near T_i differs by more than an order of magnitude. The observed shape of the spectra are not always the result of hardware distortion, since the relaxation time $T_{Q2,}$ at least at low temperatures Jo phase, the relation $T_{Q2} > t_1$; t_{INR}; t_2.

Comparing our data with the X-ray data on the measurement of the mean square displacements of atoms in tetrahedral ZnCl paraelectric Rb_2ZnCl_4, where it was established that there are two equal-probable provisions tetrahedra into each other by the libration movement (Fig.3.14) and summarizes literature data on the values of the mean square displacements of atoms in the other A_2BX_4, to some extent consistent with those of the NQR and Raman [42] that the phase transition P-Jc in the compounds studied close to the type of order-disorder. It should be noted that not form symmetric spectral distributions comparable to those observed by us, detected RF methods and systems of other crystalline, such as in compounds with CDW charge density waves (see e.g. 2H-$TaSe_2$ [95,96]), used ion conductors with superlattice ordering (Ag_2HgJ_4 [97]), organic-dimensional conductors CH_x-trans [98] etc. [100]) and even in solid helium-3 not [99]. In all these cases, the observed asymmetry of the resonance line was associated with the anisotropic diffusion of spin or charge against the backdrop of two large-scale spatial or temporal scale. Similar forms registered by EPR in the study of the vibronic interaction A and orbital states in complexes with octahedral symmetry [102]. Overall data analysis allows to chart a path radiospectroscopy explanation NQR experiments in this class of compounds in the direction of electron-nuclear movements in two ambitious timeline.
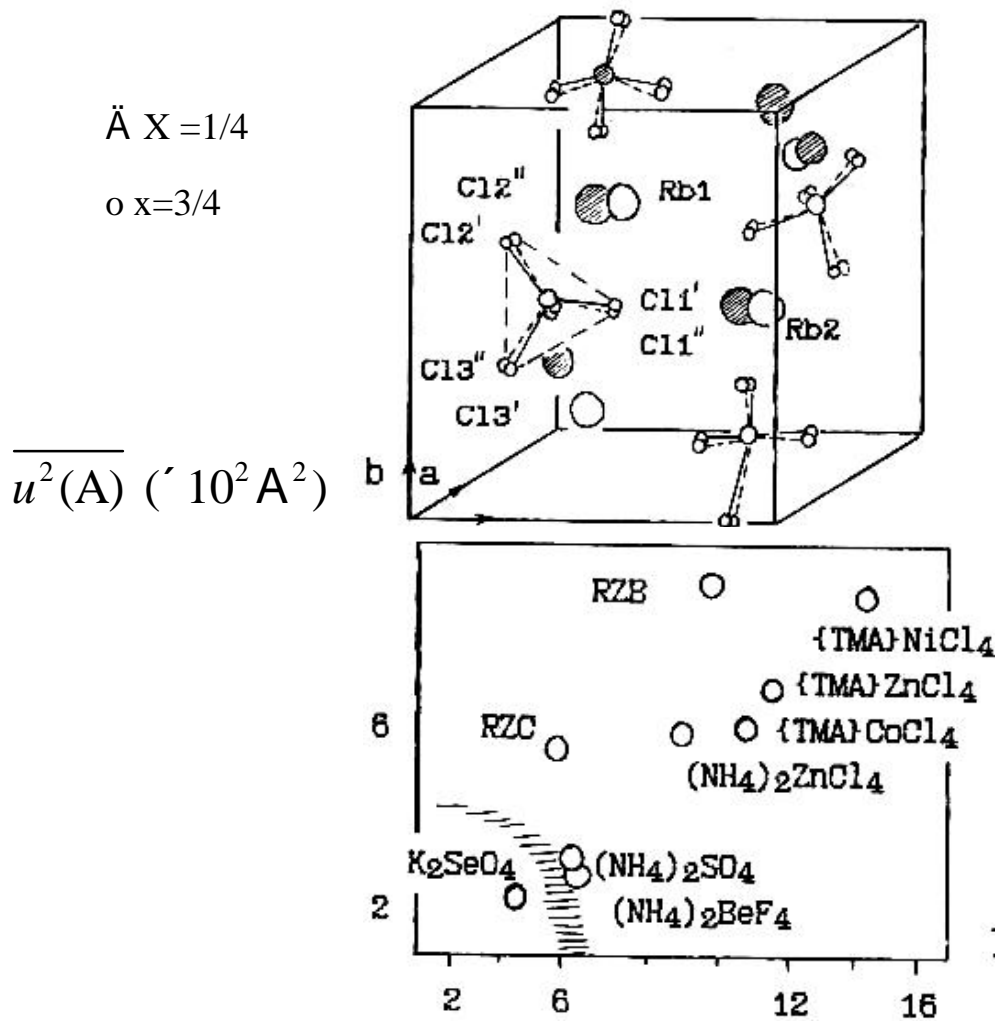
Ä X =1/4

o x=3/4

$$\overline{u^2(A)} \; (´ \, 10^2 A^2)$$

Fig.3.14. *a.)* Libration movement $ZnCl_44$ tetrahedra in the high-temperature phase Rb_2ZnCl_4 according to [41].

b) standard deviations of the atoms grade **A** and **X** for certain compounds A_2BX_4 at room temperature.

§ 3.4 Polymorphs in the family A_2BX_4 with -K_2SO_4.

It follows from our data, the compounds Rb_2ZnBr_4 (see § 4.1), Cs_2ZnJ_4, K_2ZnBr_4 [125] and, presumably, $(NH_{4)2}ZnJ_4$ and Rb_4ZnJ_4 and others may crystallize or relax to more stable crystal structure, described by the space group $_1$ (type structure Sr_2GeS_4). Consequently, the structure type β-K_2SO_4 in these compounds are metastable. As you

know, many of the compounds A_2BX_4 also crystallize into structures in space group Pnma or $P2_1/m$, and few of them reliably or supposedly presented simultaneously these two structural modifications [86]. In Table 3.2, the compositions are A_2BX_4 in which: 1) the only observed structure Pnma; 2) was observed structure Pnma and $P2_1/m$; 3) was observed only structure $P2_1/m$.

My can assume that marked us polymorphic transition α-A_2BX_4 « β-A_2BX_4) is characteristic for the various compounds and can be implemented for other compounds shown in Table A_2BX_4. However, significantly different relaxation times of the structure to the structure and observed us for Rb_2ZnBr_4 (weeks), and for K_2ZnBr_4, Cs_2ZnJ_4 (several minutes), indicate that polymorphic transition may be unrealized in normal conditions. However, we know of no data on detailed studies of the conditions of the transition between these modifications, although these effects were observed and studied in other crystalline objects, and in particular in disordered polymers and molecular crystals with cis-trans isomeric structure chains [43].

According to our research and NMR data on the measurement of the heat capacity [77] in all the compounds A_2BX_4 grown from aqueous solutions or have been in contact with the atmosphere is always a small amount (less than 2%) loosely bound water. On this basis, we can assume that the transition β-α is carried by surface orientational ordering of β-α structure in the dipoles of water molecules. Comparison of the spin relaxation times for the α and β structures indicates that dynamically disordered metastable β structureconverted into a more structurally ordered dynamically stable structure. The possible existence of crystal structures with varying degrees of dynamic stability is predicted by mathematical methods of stability theory for systems with interaction ANNN [104, 130]. As follows from these studies in some symmetrical classes of such systems are possible bifurcation from stable solutions with conditional period of the structure N-1 to dynamically meta-stable states with N = 1,2,3,4 followed by higher order bifurcations to large periods and increasing the degree of instability. How shown in [104] cases N=3 and N=4 and N=2 at some parameters of interatomic interactions are special, because realized only through the bifurcation some dynamically unstable solutions with N=1 (which we can compare the structure Rnma). In the vicinity of a line bifurcation with different solutions in different periods are mixed and separated by raising away from this line.

This approach can, to some extent justify the presence of a dynamically more stable modifications under consideration for compounds which space group $P2_1/m$ has no common subgroup communication with the space group Pnma.

Table 3.2.

1 Pnma	2 Pnma, $P2_1/m$	3 $P2_1/m$
Rb_2ZnCl_4	K_2ZnBr_4 [125]	Cs_2CoJ_4
Cs_2ZnJ_4	Rb_2ZnBr_4 [125]	Cs_2MgJ_4
K_2ZnCl_4	Cs_2CdJ_4 [125]	$KsCoJ_4$
$(NH_4)_2ZnCl_4$	Cs_2CdBr_4[125,129]	$(NH_4)_2CoJ_4$

(NH$_4$)$_2$ZnBr$_4$ Cs$_2$MgBr$_4$	Rb$_2$ZnJ$_4$ [125,132] Cs$_2$CdCl$_4$ К$_2$CoBr$_4$ [134] Te$_2$CoBr$_4$	Rb$_2$CoJ$_4$ T1$_2$CoJ$_4$ [l32] К$_2$MnJ$_4$
	Rb$_2$MnJ$_4$	
	CS$_2$HgJ$_4$ [133] Tl$_2$ZnJ$_4$	

Type β-K$_2$ZO$_4$

Pnma   P2$_1$/m

тип β-K$_2$SO$_4$ тип Sr$_2$GeS$_4$

β-A$_2$BX$_4$ α-A$_2$BX$_4$

Chapter 4. Sequence of phase transitions in Rb$_2$ZnBr$_4$ at atmospheric and high hydrostatic pressure.

In this chapter we present the results of studies of phase transitions in Rb$_2$ZnBr$_4$ NQR [79]Br, [81]Br at atmospheric and under high hydrostatic pressure. External exposure is the factor that allows you to get a fundamentally new information about the sequence of phase transitions, in addition to clarify the issues in the form of the NQR lines incommensurate phases.

The absorption spectra of NQR [79,81]Br in the incommensurate phase at atmospheric pressure.

When NQR study of compounds with incommensurate phases in which there are significant non-equilibrium processes, it is necessary, in particular, have procedures quantitative measurement of the resonance absorption signal for given values of other parameters (T, t, ν, etc.). Such a technique can be designed based on coherent spectrometers. Spectrometer type ISSH the absolute accuracy of the amplitude of the transient resonance signal is small. Therefore, in the research process was used to monitor the intensity of the reference method, which consists in comparing the magnitude of NQR signal recorded at different sample metaequilibrium state, with the value of the equilibrium signal, structural stability of the sample. When working with Rb$_2$ZnBr$_4$ was matched standard, which amounts to less than 10% volume filling of the receiving coil, and the slopes of the temperature and frequency dependences of the pressure of the two NQR lines absorption were sufficient for calibration.