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Investigation of the sequence of phase transitions in compounds with the structure A_2BX_4 β-K_2SO_4 NQR halogens at atmospheric and high pressure.

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Author's abstract.
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Work performed at the Institute of Physics SB RAS. L.V.Kirenskogo Krasnoyarsk branch of the Republican and Technology Center of the Russian government.
Supervisor Candidate of physico-mathematical sciences MOSKALEV AK
Opponents: Dr. tehnicheskin, Professor T.A.Babushkina; Candidate of Sciences matematicheskik D.L.Zagorsky.
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sent to 1995.
Scientific Secretary of the Specialized Council Ph.D., professor V.Ya.Rochev

Study of phase transitions in compounds such A_2BX_4 STRUCTURE β-K_2SO_4 NQR halogens at high and atmospheric pressure.

General characteristics of the work.

Relevance of the topic.

Method of nuclear quadrupole resonance (NQR) is widely used as a method to study the structure of substances including the phase transitions in crystals. Recently, a special place in such studies has been paid partially disordered state, one of the classes which are dielectric crystals with a structure of β-K_2SO_4, were unearthed disproportionate (Inc) phase. Under disproportionate means special structural state of the crystal, which is formed by the interaction of crystalline functions with differing periods. Theoretical models disproportionate state in dielectrics show that the period of the structure of the dipoles can be both multiple and non-multiple grating period of the original high-temperature phase. When converting to the low-symmetric phase, the ordering depending on the nature of atomic interactions may be effected in various ways. On the one hand through a series of long-period phase states by transformations of the first kind, and the other, a continuous way: according to the actual change of the wave vector $\mathbf{q_\delta}$, corresponding to the minimum mode (or the maximum coupling constants) responsible for the stepwise behavior, called simple devil's staircase 'Devil `s Starcase», was recorded and investigated in magnets. After opening the disproportionate state dielectrics diffraction. radiospectroscopic and experimental data indicated the importance of continuous change q_δ.

By the beginning of our studies and, there were only a few compounds A_2BX_4, from the family of β-K_2SO_4, where it was possible to detect incommensurate phases and study them in detail. Due to the fact that the NQR method is very sensitive to the gradient of the intracrystalline electric fields, its use for research disproportionate state in the dipole system is not in doubt. However, when initially applying it to this class of crystals detected very weak signals of radio frequency absorption mainly in the low temperature region of the incommensurate phase. In this regard, the intermediate objective was to increase the sensitivity of the method, from which depended the success of the study compounds with β-K_2SO_4 type and finds in them a thorough study of incommensurate phases.

Objective.

Study of nuclear quadrupole resonance of halogens (Cl, Br, J), and other methods, the family of crystals with β-K_2SO_4 structural disproportion. Elucidation of changes in the spectral features of the resonance parameters in phase transitions; Analysis investigated the local environment of the nuclei, and its transformation into compounds of the series when the high temperature and hydrostatic pressure. Study processes of spin dynamics in combination with other methods of analysis of the crystal symmetry changes at structural phase transitions.

New scientific results.

First NQR using the methods of X-ray diffraction, calorimetry, electro-optics and dielectric measurements studied sequence of transitions in the compounds Cs_2CdJ_4, Cs_2ZnJ_4. and $(NH)_2ZnJ_4$ with an incommensurate phase.

The spatial point symmetry groups and commensurate phases.

In compounds Rb_2ZnBr_4 , Cs_2ZnJ_4 and found two polymorphs α and β. While β-modification, where realized sequence of phase transitions with incommensurate structure is unsustainable and stabilization of metastable conditions, such as moisture, becomes α-modification.

In a first for Cs_2ZnJ_4 $\mathbf{A_2BX_4}$ family connections with cesium cation registered full range $^{127}\mathbf{J}$ NQR frequency scale throughout the incommensurate phase below Ti. Before TC found wide temperature range before ordering transition. Change NQR spectrum in this area can be interpreted in terms of phase transitions with clusters predecessors.

In β-Rb_2ZnBr_4 updated temperature frequency dependence of the NQR spectrum $^{79,81}\mathbf{Br}$ at atmospheric pressure and obtained navye data. Established that the phase transition at Ti decreases fluctuations before the first race. At low temperatures, the incommensurate phase at TC, along with the basic structure according to a tripling of the unit cell of the crystal ($\mathbf{q_\delta}$ ~1/3), in the form of the NQR spectrum indicated a different structure. In studies under a pressure established that the latter refers to the state of the crystal, characterized wavevector $\mathbf{q_\delta}$~1/4 and the other branch fashion ∑. $^{79,81}\mathbf{Br}$ NQR under high pressure is detected and investigated in detail the sequence of highly symmetric and disproportionate-ordered phases in β-Rb_2ZnBr_4. The phase P-T diagram in the region of 170-360^{0}K at pressures up to 1 GPa. Recorded sequence of phase transitions in the Inc P-T field Rb_2ZnBr_4, interpreted in the framework of the "'devil's staircase." Analysis of transformation of the NQR spectrum indicates that the low temperature portion of the incommensurate phase observed behavior of the type simple stairs (complete D'S), and in the medium temperature is possible mixed (incomplete) view "satanic stairs" A comparison-with the theoretical phase diagrams of pseudo-spin model with phonon coupling.

Scientific and practical value.

1. Realizovany Methods and devices that increase the sensitivity of pulsed NQR spectrometer for the purpose of detection of weak signals of radio frequency absorption and precision temperature measurements under high hydrostatic pressure.

2. Construct a high pressure, which is used with a standard NQR spectrometer in the study of the structural features of the phase transitions in disordered crystalline systems,

3. New experimental data on the structure transformation in compounds with symmetry Pnma $\mathbf{A_2BX_4}$ temperature changes. Not detected previously observed phase transitions,

4. NQR built P-T phase diagram of β-Rb_2ZnBr_4. Existing data can be used to construct a molecular model of the transformation of the family structure in the compounds β-K_2SO_4,

5. First, in some connection $\mathbf{A_2BX_4}$, revealed the existence of another polymorph - α. We propose to search for new members of the family $\mathbf{A_2BX_4}$ with a metastable structure type β-K_2SO_4

6. The spin-spin and spin-lattice relaxation of nuclei halogen NQR incommensurate phases. Shown that the new level of quality research is necessary to extend the lower range of equipment for temporary permission microsecond limit.

7. NQR analysis of spectral data indicated the need to revise the previously accepted model to describe the shape of the resonance lines in the incommensurate phases.

Personal contribution of the author.

Developed and implemented a device for temperature and hydrostatic pressure vysokog research. Synthesized compounds Cs_2ZnJ_4 and $(NH)_2ZnJ_4$. Conducted all the experimental NQR measurements

and their analysis. Developed and used applications for numerical simulation of the NQR line shape in the modulated phases. The author participated in the preparation and implementation of other experimental studies of teaching and learning, supported by research quadrupole resonance.

Testing work.

The main part of the dissertation presented and discussed at the All-Union scientific conferences:

-on rf, Kazan, 1984.

-on the physics of ferroelectrics: Chernivtsi, 1986., Rostov-on-Don, 1989.;

- International conferences and symposia; -XI conference MAVRID .. High Pressure Science and Technology. Kiev. 1987.:

-X Symposium on NQR, Takayama, Japan, 1989.;

Crystallographic-European conferences:

XI-Poznan (Poland), 1987. , XII-Moskva, 1989.; Symposium - Sat 23rd Congress Ampere, Novosibirsk Shushenskoe 198g.;

-IV Japan-Soviet Symposium on ferroelectrics, 1988;

-7th Symposium on ferroelectricity Sarbryuker, Germany, 1989;

-Soviet-Polish seminar on ferroelectrics, Lvov, 1990;

-XII Symposium on NQR, Zurich, Switzerland, 1993.

Publications: On the topic of the dissertation is published 22 print jobs.

Structure and scope of work:

The work consists of an introduction, four chapters, conclusions, list of references of 135 titles.

Dissertation presented in 172 pages of text, 5 tables and 70 figures.

• **HIGHLIGHTS OF WORK.**

Introduction. The place of research topics in the general range of problems in solid state physics. The features of dielectric crystals, where the first place stands the ordering of chemical bonds via dipole-dipole interaction. Is the objective of research.

Chapter 1.

Disproportionately - modulated phases in dielectrics with a structure of β-K_2SO_4.

A brief overview of the theory of phase transitions in the concept of the soft mode and Ising models, taking into account for the nearest neighbors interaction cluster picture of phase transitions of the displacement type and order-disorder.

The theoretical principles of the NQR method and its application to the study of critical phenomena and phase transitions. Presented a phenomenological model of the line shape of the nuclear quadrupole resonance in the plane-wave approximation and the soliton. The theoretical data on the processes of nuclear relaxation in the incommensurate phase.

Discussed the experimental data on the study at atmospheric pressure A_2BX_4 compounds with tetrahedral coordination of the anions and the high-temperature phase with the space group Pnma: Rb_2ZnJ_4, Cs_2HgBr_4 and others.

Given P-T phase diagram. investigated in dielectric crystals of various experimental methods. At the end of an overview chapter summarizes the state of research in dielectrics structure β-K_2SO_4, and formulated the problem of work.

CHAPTER 2. Equipment and measurement technique.

2.1 equiv ... remote sensor NQR and conditions optimum adaptation to the measuring chamber. The ways to increase the sensitivity of pulse NQR experiments in conditions of prolonged tracking of temperature and pressure dependences. As follows from the dissertation in electrodynamic calculations, signal to noise ratio (SN) radio spectrometer increases with radius r and length l of the receiving sensor, r * as the square root of l. However, there is an optimal ratio between the size of the sensor and the internal dimensions of the measurement chamber, in which a balance is achieved between the reduction in the ratio of SN, because of the inductive-capacitive coupling and receiving radio frequency measurement and hardware circuits, and an increase in SN due to increased take-up spool. Taking account of this and the use of suitable materials design allows ultimately increase the sensitivity of the method. The fruitfulness of this approach was confirmed after manufacturing thermal tops and high-

pressure cells for measuring weak signals in the ^{35}Cl NQR K_2ZnCl_4, where the author of the absorption line not to register earlier.

2.2. Temperature consoles to the spectrometer ISSH research phase transitions. Set out details of the construction of thermo-gradient-top boxes for the study of phase transitions NQR. The basic idea underlying the action of liquid thermal camera is a replacement for liquid gas environment, providing better heat transfer properties. The design of this thermal camera was not realized by the author based on the standard thermo-top box to the spectrometer ISSH. As coolants used N-pentane (a liquid-state 138-308^{0}K), hexane, high oil ($T_{кип}$ <600^{0}C). With vigorous stirring, the temperature gradient in the fluid volume measuring chamber out (with an accuracy of ±0.01^{0}K/sm).

Due to the fact that the storage of liquids at room temperature with a melting point <110^{0}K requires special measures that impede the use of liquid thermal cameras below these temperatures was developed another design that has a heat transfer fluid circulation mode and can be used in an embodiment of the gas conditioning. The design of this camera is significantly different from the presentation. In a liquid coolant mixing mode is carried Circulator. To equalize the gradients at the gas conditioning (blowing), a system of grids and channels contributing self-mixing hydrodynamic gas streams. In this case the temperature gradient on the sample was 0.1÷0.2^{0}K/sm.

Distance of the sensor to the NQR solderless socket sensor NQR spectrometer and using the principles of optimal maTChing possible to increase the ratio of SN to 10 times.

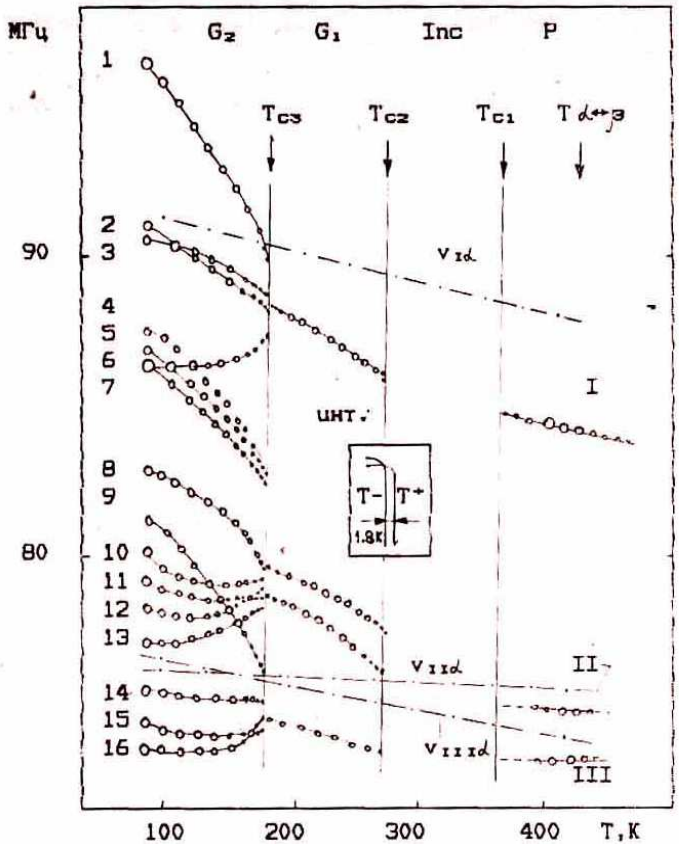
2.3. Synthesis of samples made in **A_2BX_4** labopatory crystallophysics Institute of Physics SB RAS, and I.T.Kokov , V.A.Grankina based on chemical AX and BX_2 as Bridgman method from the melt and from aqueous solutions.

Connection of A_2BX_4 type structure β-K_2SO_4 usually crystallized in the form of single-crystal plate splices sizes up to 40mm and a thickness of 5mm. Some samples, to remove impurities, two; recrystallized three times. Before NQR measurements and samples were ground in a thin-walled container placed in NQR sensor. Been tested influence operations preconditioning on the measurement results, and found that the samples grown and (or) inhomogeneously deformed in the temperature range of the incommensurate phase have different spectral characteristics in comparison with the samples or are born in the high-temperature phase. Detailed information on this, the example Rb_2ZnBr_4 given in paragraph 4.1 of the dissertation,

2.4. Apparatus for NQR studies under high hydrostatic pressure. Described, created with the direct participation of the author and requires the highest level of the experiment, setting the research in atmospheric and high hydrostatic pressure P-T phase diagrams and critical behavior near singular P-T states of crystals. Instrumental complex includes NQR pulse spectrometer ISSH1-13 (Made in the USSR) , electronic assembly changes, control and maintain the temperature and pressure, high-pressure apparatus (multiplier, pumping station, a high-pressure bomb) or thermo-console , precision graphic recorder.

Particular attention is paid to the design of the dissertation high-pressure chambers (HPC) for studies at low temperatures. One of them - HPC1 having a lumen diameter of 16mm, allowed to observe NQR signals at pressures up to 1.5 GPa, Seal performed indentation chopper with a set of rings on the chamfer channel bomb. This design allows you to work with the sample to 3sm3 has radiospectroscopic sensitivity and a half orders of magnitude lower than the standard dimensions and is designed for intensive observation NQR signals. Another cell (HPC2) specially developed by the author for registration absorption signals from quadrupolar nuclei in incommensurate phases at pressures up to 400MPa. Diameter of the channel, where the coil NQR increased to 40mm. Construction of the obturator and seal have fundamental differences from the standard and are to reduce its axial size; increasing the diameter of the channel under electric high voltage input; in the hydraulic seal cavity bombs flattening bronze ring of triangular section. To reduce RFI (radio frequency interference) and delinking conductors and high frequency P-T sensors, the latter is supplied through an additional seal. This design has achieved the conditions of observation NQR signals approximate to standard conditions.

Chapter 3. Sequence of phase transitions in compounds A_2BX_4 (X = J). Experimental data on the study of phase transitions in compounds not previously studied A_2BX_4 NQR: Cs_2CdJ_4 (CCJ), Cs_2ZnJ_4 (CZJ) and $(NH_4)_2ZnJ_4$ (AZJ).



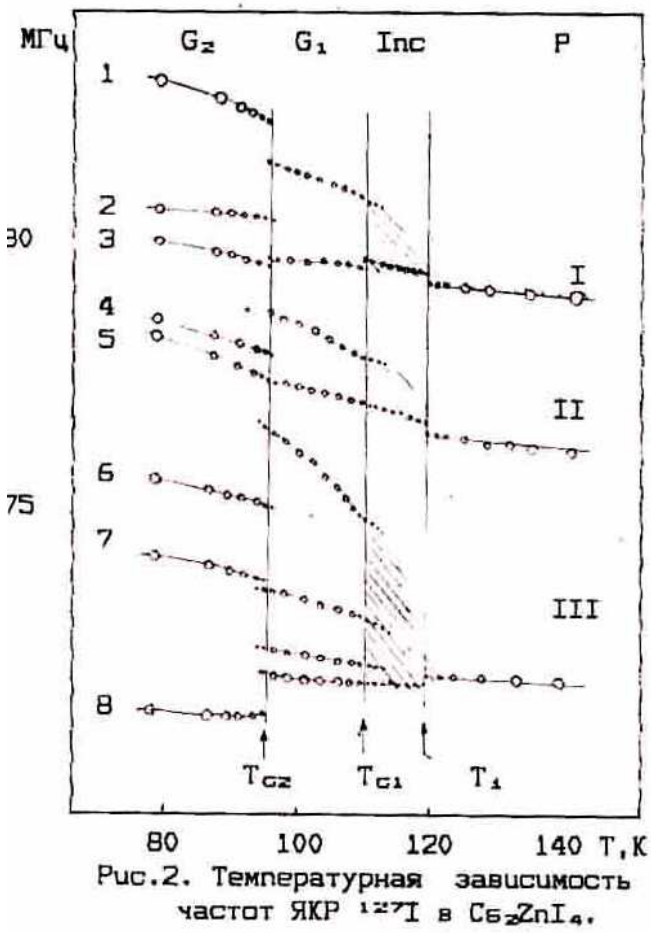


Рис.2. Температурная зависимость частот ЯКР ^{127}I в Cs_2ZnI_4.

3.1. Phase transitions in Cs_2CdJ_4. In 1986, by NQR method in Cs_2CdJ_4 author found two modifications - **α** and **β**. Modification of **α** is stable in conditions of high humidity and changes in **β** modification by drying the crystal, for example, after heating the sample in vacuum above 100^OC When thermally induced α → **β** transition, there is no reduction of the sample weight and absent (with an accuracy of ~ 2%) NMR signals from protons associated crystal. On this basis, it is concluded that the α-phase is the phase of the polymorphic compounds**β** a metastable phase, since in the presence of atmospheric moisture rapidly into α modification.

In Cs_2CdJ_4 NQR in the range $420 \div 77^0K$ found three phase transitions at T_{C1}=335; T_{C2}=260 and $T_{C3} = 184^0K$ with changes multiplicity range from three to four lines of equal intensity 16 (Fig. l). In the temperature range 335 ÷ 260^0K absorption recorded in the narrow neighborhood before T_{C2}, where the view of the spectrum typical for Inc phase. As was explained, the absence of signals due to the fact that the spin-spin T_{Q2} and spin- lattice T_{Q1} relaxation are below the resolution limit of the temporary pulse spectrometer ($T_Q < 10^{-8}$s). Below T_{C2} is fixed below 4 absorption signal abruptly transforming at T_{C3} in 16 singlet NQR lines. In this case the temperature dependence of the frequency, critical slowing T_{Q1} and phase coexistence ~ 2^0K clearly indicates close to the tricritical point phase transition at T_{C3}. Multidisciplinary studies involving methods calorimetry, electro-optics and X-ray diffraction allowed to establish a framework for the transformation of **β**-modified tetra-iodo- cadmiat cesium

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

Figure 1. Temperature dependence of NQR frequencies in ^{127}J Cs_2CdJ_4.

In the incommensurate phase detected X-ray satellites in the position $\mathbf{q}_\delta$ ≈0.24÷0.25a*. Symmetry of α-modification identified by us as $P2_1/m$ (Z=2). A relaxation of the NQR data indicate the nature of its slow spin dynamics ($T_{Q1} \geq$ l ms; $T_{Q2} \approx 200\mu$ks) with respect to the **β**-phase.

Fig. 2. Temperature dependence of the NQR frequencies ^{127}J Cs_2ZnJ_4.

3.2. Investigation of the sequence of phase transitions in Cs_2ZnJ_4.

In CZJ change the multiplicity of the spectrum of the complex spectrum through three to eight, and again to eight lines, and the temperature dependence of the frequency quadrupole transition **1/2 ↔ 3/2** isotope ^{127}J observed three phase transitions at Ti = 118; T_{C1} =108, and T_{C2} =95^{0}K (Fig. 2). In the temperature range 118÷108^{0}K throughout the frequency scale for the first time with cesium cation of compounds A_2XB_4 registered NQR spectrum of the detected author of the incommensurate phase. With the use of complementary techniques were established symmetry phases: Pnma(Z=4) ↔ Jc, $q_\delta = (1+\delta)a^*/2$ ↔ $P2_1/n$(Z=8) ↔ P1 (Z=4), and X-ray studies recorded below T_i satellite reflections with the value $q_\delta \approx 0.15a^*$ at T = 112^{0}K.

According to the quadrupole transition 1/2↔3/2 times the temperature dependence tracked T_{Q1} and T_{Q2} in 380÷77^{0}K from all cores ^{127}J nonequivalent positions structure Pnma.

Feature relaxation characteristics CZI is a distinct two-scale character associated with structural features. In a wide temperature range ~100^{0}K before T_i signals recorded as the decay of free precession and asymmetric inhomogeneous broadening of the spin-echo signals nuclear response. Changes in the relative intensity of the longitudinal and transverse contributions absorption and asymmetry last indicates abnormal change in the nature of atomic motions at 320^{0}K, below which develop cluster-type fluctuations structure of the incommensurate phase.

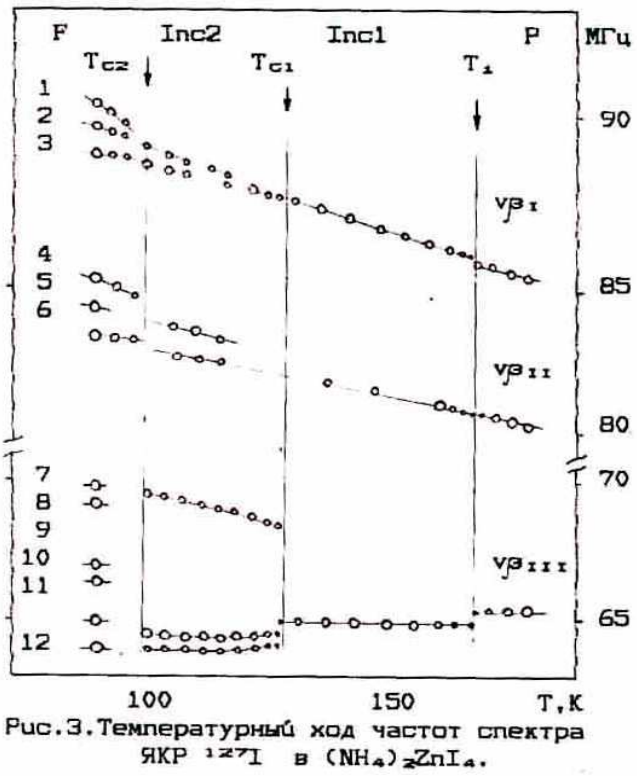


Рис.3.Температурный ход частот спектра ЯКР ^{127}I в $(NH_4)_2ZnI_4$.

Fig. 3. Temperature dependence of the frequency of the NQR spectrum $(NH_4)_2ZnJ_4$.

3.3. NQR study of phase transitions in $(NH_4)_2ZnJ_4$.

Author first synthesized and studied by NQR ^{127}J compound $(NH_4)_2ZnJ_4$. In the temperature range 77÷400^{0}K found three phase transitions at T_i=165^{0}K, T_{C1} = 126^{0}K and T_{C2}= 87^{0}K (Fig. 3).

Above Ti observed three intense absorption line (1/2 ↔ 3/2) with the character of the dependence Bayer ν (T). When Ti marked decrease in the intensity of lines and race frequencies. Shape of the spectrum, fixed below T_{C1} indicates disparity observed structure. Below T_{C1} multiplicity spectrum changes to seven broadened lines are not of equal intensity, and at the boiling point of nitrogen absorption signals recorded 12 NQR. Stroke frequency ν(T), intensities, and shapes NQR signals are comparable with those observed in Rb_2ZnCl_4 and Rb_2ZnBr_4, confirms the assumption that the author of symmetry transformation in tetra-iodo ammonium zincate under the scheme:

$D_{2h}^{16}(Pnma)$ ↔ Inc1 ↔ Inc2 ↔ $C_{2v}^{9}(Pn2_1a)$,

while the phase between 125 and 87^{0}K may be interpreted as incommensurate rather arbitrary and is rather long-periodic ($q_\delta \approx 2/7$) with symmetry $Pn2_1a$. Noted the existence of another structure of the compound with the same observation conditions for modifying α - Cs_2CdJ_4.

At the end of the third chapter of the comparison data for NQR A_2BHa1_4 compounds, which exhibit phase Inc. The greatest amount of frequency decoupling $\Delta\nu_{I\text{-}III}$, noted for ammonium compounds (31%) and the smallest for cesium (up 7%). It is poorly explained from the viewpoint of crystal chemical relationships, because radii of the cations NH_4 and Cs are close in value, and indicates significant chemical (electronic) contribution to the nature of this splitting. Temperature dependence of v(T) below T_i unusual and poorly explained by known types of molecular motions. Significant line widths in the initial phases Inc and at extremely short time values T_{Q1} and T_{Q2} indicate structural dynamic disordering of the molecular fragments. Largest $\Delta\nu_{I\text{-}III}$ and especially in the form of components ν_I celebrated a special position compound Cs_2ZnJ_4.

Significant impact on the correctness of the nuclear dynamics registering frequency spectral characteristics NQR involves revising the phenomenological model describing the shape of the resonance line Inc phases.

Comparison of the data with the results of NQR spectroscopy in other crystal systems (with charge density waves, one-dimensional organic conductors, octahedral crystals with Jahn-Teller complexes) allows to plan a way to explain the data NQR through electron-nuclear movements in the two-scale timeline.

3.4. Polymorphism in the family A_2BX_4. After the discovery of the author in 1986. α-polymorphic modifications Cs_2CdJ_4 and later Rb_2ZnBr_4, K_2ZnBr_4 etc. , with symmetry group $P2_1/m$ and the establishment of the fact that in these compounds is metastable β-form, the question arises about the generality of this phenomenon in the family A_2BX_4. The classification of compounds A_2BX_4 on experimentally known for their space groups: Pnma and $P2_1/m$ and the method of implementation of the structure type β-K_2SO_4 in other compounds of the family.

On the basis of experimental data the mechanism of the α↔β transition: through surface orientation ordering β structure to α, the dipoles of water molecules. The reverse process is carried out by removing traces of water and thermal induction of metastable modification with the accelerated nature of the spin dynamics.

At the end of this section discusses the cause of the observed phenomena in terms of mathematical theory for systems with long-range interatomic interactions.

Chapter 4. Sequence of phase transitions in Rb_2ZnBr_4 at atmospheric and high hydrostatic pressure. The results of studies of phase transitions in tetrabromzincates rubidium NQR. High pressure is a factor that allows to obtain fundamentally new information on the transformation of the structure in the compounds A_2BX_4.

4.1. ^{79,81}Br absorption spectra in the incommensurate phase at atmospheric pressure.

At the initial stage of the study in Rb_2ZnBr_4 using NQR found: 1) the dependence of signal intensity on the number of cycles in the cooling phase, Inc; 2) that the majority of freshly grown or present during wet (≈ 50%) atmosphere crystals are fully or partially, or are moving to another structure with symmetry $P2_1/m$. Conditions for its stabilization and transition to the metastable β-modification with an incommensurate phase completely analogous α ↔β transformation in Cs_2CdJ_4 and differs only significantly longer duration of α ↔ β process; 3) induction of non-hydrostatic stress, residual growth and thermal stresses nonequilibrium state structure β-Rb_2ZnBr_4, disappearing after annealing.

Precision study of the temperature dependence of the NQR frequencies Rb_2ZnBr_4 in T_i transition at 1 atm revealed races frequency spectral lines from Br nuclei in positions II and III structure Pnma, as well as unusual splitting frequency spectrum component T_i in the incommensurate phase. On these grounds it has been found that a phase transition at a T_i close to first-order. In the transition to the ferroelectric phase F was registered racing frequencies and additional absorption lines not previously observed. The complex shape of the spectrum was numerically explained: 1) manifestation in the crystal structure of another type (different from the symmetry of the soft mode Σ submission) or another branch (except Σ_2) symmetry; 2) the coexistence of multiple modulation sequences of "devil's staircase." To clarify these issues, the study was used at high pressure.

4.2. P-T phase diagram Rb_2ZnBr_4.

In the first part of this section examines the structure of the phase P-T diagram RZB obtained using HPC1. In this first tracked P-T region existence paraelectric (P), F , Inc phases and detected

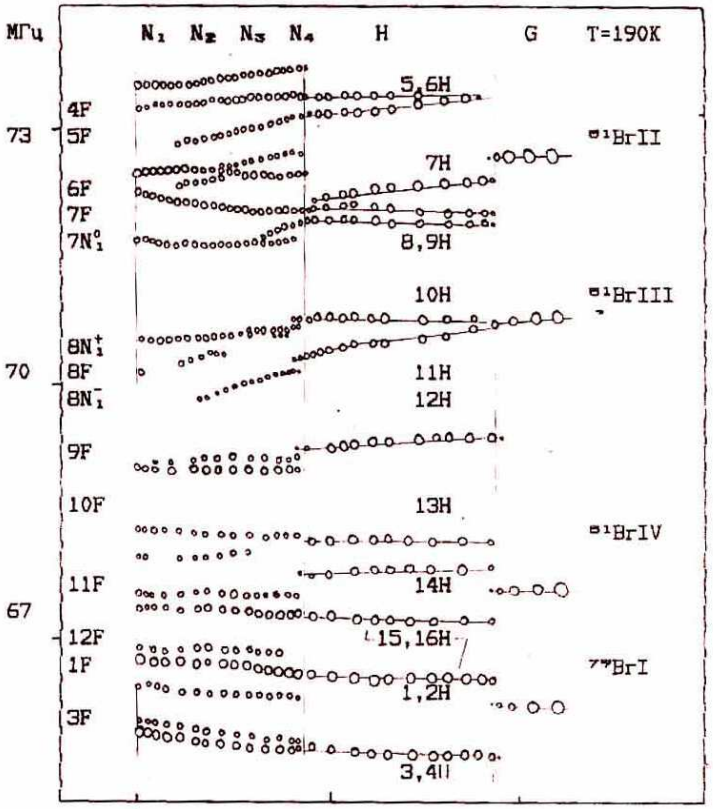


Рис.4. Барический ход частот ЯКР ^{79,81}Br в Rb_2ZnBr_4.

sequence of disordered phases Inc↔M_1↔M_2↔ M_3 to G phase. On the anomalies in the dependencies ν(P), I(P), Δν(P) P-T installed P-T lines of phase transitions. All of these transitions have the first order with the values of the pressure hysteresis ΔP from 20 to 160MPa, and ΔP increases with increase decreasing T and decrease P, and essentially depends on the direction of change of P-T parameters. Changing pressure phase transition temperature of the paraelectric phase to the incommensurate obtained involving DTA method.

Fig. 5. Rb_2ZnBr_4 phase diagram according to the NQR.

symmetrical high-pressure phase G and H (Fig. 5). The multiplicity of the NQR spectrum of twelve F-phase lines, through a complex range of intermediate N-phase and four to fourteen powerful singlet phase lines H and G, respectively (Fig. 4). A detailed study of the transformations of the NQR lines isotopes ^{81}Br and ^{79}Br in the incommensurate phase performed using bombs HPC2.

Figure 4. Baric move ^{81}Br NQR frequencies in Rb_2ZnBr_4.

20 iso-thermal and isobaric P-T sections, in which high-resolution spectra were recorded from all NQR nonequivalent positions ^{81}Br , scanned the temperature and pressure dependences of the frequency ν(P, T), the intensities I (P, T) and linewidths Δν(P).. Tracked items transformation spectra of phase F through N to H phase, and in the middle region of the incommensurate phase through a

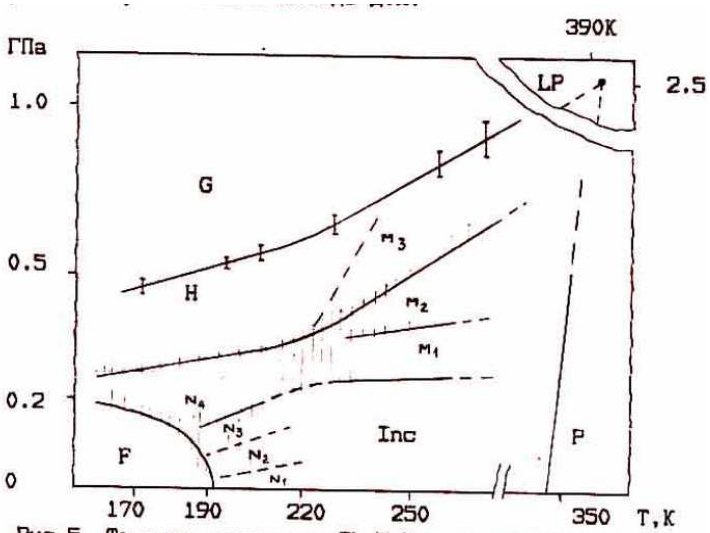
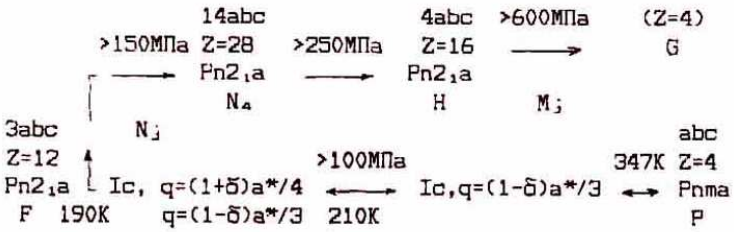


Рис.5. Фазовая диаграмма Rb_2ZnBr_4 по данным ЯКР.

4.3. Features transformations spectrum near T_C. Comparison with the diffraction data.

Considered parts of a complex transformation of the NQR spectrum and analyzed its performance in the low P-T region N incommensurate phase near T_C, where we assume a step change in the structure. Analysis of non-monotonic changes in the intensities and spectral distributions of asymmetry possible to detect characteristic mild anomalies between different structurally related states N_1, N_2, N_3, N_4 modulated phase. In an embodiment of the NQR data interpretation in the framework of "devil's staircase" structure N_j correspond to states with different values of a step change in the wave vector q_δ, and observed P-T overlapping area. This interpretation was confirmed by NQR active on the same samples by neutron diffraction in the international scientific center of Orsay (France). Satellites have been detected,



the values of **a*** in units which can be placed on an upward steps of (5/17 → 3/10→ 7/23→ …1/3) and down (3/10→ 8/27→ 5/17→ 7/24→ 2/7→ 1/4) of stairs. At this pressure the following sequence of transforming the structure β-Rb_2ZnBr_4. Fig. 6.

4.4. Discussion The phase diagram in the framework of the "devil's staircase."

A comparison of the experimental phase P-T diagram RZB with the theoretical phase diagrams «Ds" S» and found that phase Inc M_1, M_2, M_3, meet stepwise reduction of the vector q_δ when approaching a Lifshitz point.

At the end of paragraph NQR data discussed based on the theory of the existence of Baka random phase is an intrinsic property of systems with frustrating interactions. In this case, incommensurate phases with wave vectors, for example, $q_\delta \approx l/4+\delta$ и $q_\delta \approx l/3$ can have different states with topologically overlapped structure, different phase shift. On the basis of this comparison indicated that in the M phase diagram observed smoothed (incomplete) mode "Ds" S ", in Inc - classical (smooth), and N region close to the step (complete) behavior.

Based on this discussion, involving the analysis of solutions **φ**-model, which is applicable to describe compounds A_2BX_4 with β-form elements proposed model explaining changes in the structure Rb_2ZnBr_4 no diffraction data and microwave spectroscopy.

In concluding the discussion, based on research conducted by the author, analyzed the experimental data on the temperature change of the wave vector of all known at the time of writing the work, A_2BX_4 compounds with the structure of β-K_2SO_4, and proposed a generalized P-T diagram predicts the possible phase diagrams of these crystals. While cesium compound was isolated subclass, characterized by a particular sequence of symmetry transformations associated with the softening of the phonon spectrum near Γ point of the Brillouin zone, and the rest - in the subclass - Σ along the line.

MAIN RESULTS the operation.

1. NQR for precision studies of phase transitions created gradientless thermo-consoles and high-pressure chamber having an optimal agreement with the receiving part of the standard quadrupole resonance spectrometer.

2. Studied the sequence of phase transitions in Cs_2CdJ_4. First detected NQR incommensurate phase in β-modification of the crystal.

Complementary experimental methods given scheme symmetry changes. X-ray diffraction analysis confirmed the presence of the incommensurate phase.

3. The sequence of phase transitions in the crystal Cs_2ZnJ_4. NQR ^{127}J registered incommensurate phase, found a wide temperature range subtransient ordering. The assumption is made and confirmed the change of symmetry in phase transitions in this compound.

4. Measurements T_{Q1} and T_{Q2} wide range of temperatures show a significant effect of halogen nuclear spin relaxation on the shape of the NQR lines in the incommensurate phase.

5. Author synthesized and studied by NQR compound $(NH_4)_2ZnJ_4$. Nuclear quadrupole absorption between levels 1/2↔3/2 isotope ^{127}J found three phase transitions crystal structure. Form lines and features of the temperature behavior of the frequency suggests that the intermediate phase in β-crystal state are disproportionate.

6. Polymorphic crystals Cs_2CdJ_4 modifications and Rb_2ZnBr_4 - α and β. The conditions of the α ↔ β transition.

7. Method of nuclear quadrupole resonance investigated P-T phase diagram Rb_2ZnBr_4. Revealed two high-symmetry phase high pressure. Change in the spectra in the intermediate P-T field indicates a step change of the wave vector, which is consistent with the diffraction measurements, and does not contradict the theoretical pseudo-spin model of incommensurate phases.

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