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NMR and NQR investigation of the lattice dynamics in $(CH_3)_2CHNH_3CdBr_3$

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The temperature dependences of the Br^{79} quadrupole resonance, Br^{79} and proton spin-lattice relaxation times have been studied in the perovskite layer structure compounds $(CH_3)_2CHNH_3CdBr_3$. It is shown that anomalies in the temperature behaviours of NQR frequencies and quadrupole relaxation of Br^{79} are related to the reorientation of NH_3 groups. The main mechanisms of Br^{79} and proton spin relaxation as well as their correlations with motion nature of the methylammonium groups and their fragments are discussed.

Приведены результаты исследований температурных зависимостей частот ядерного квадрупольного резонанса Br^{79}, квадрупольной спин-решеточной релаксации ядер Br^{79} и протонной ЯМР релаксации в кристалле $(CH_3)_2CHNH_3CdBr_3$ с перовскито-подобной структурой. Показано, что аномальное температурное поведение частот ЯКР и квадрупольной релаксации ядер брома обусловлено реориентацией NH_3 групп и динамикой водородной связи N–H...Br. Обсуждаются механизмы релаксации протонов и ядер брома, а также их связь с характером движения метиламмонийных групп и их фрагментов.

The perovskyte-type layered structures of the general formula $MAMX_3$, where MA is methylammonium cation, M= Mn, Cd, Ni, Zn; X = Cl, Br, J show structural and magnetic phase transitions, including that to ferroelectric or ferroelastic phases [1–3], and in some crystals of this type, transitions to an incommensurate phase [4, 5] are observed. In crystals of this family, the crystal lattice differs by presence of infinite $–M–X_3–M–X_3$-chains separated by methylammonium cations. NH_3 groups included in these cations are attached to chains $M–X_3$ with weak N–H...X bonds.

The structure of isopropyl tribromocadmate, $[(CH_3)_2CHNH_3CdBr_3]$, under consideration brought up for the first time by one of us (Z.Chapla), is not determined to date though it is known that $(CH_3)_2CHNH_3CdBr_3$ isomorphic thereto belongs to monoclinic system with *P2/c* symmetry and shows a transition to a ferroelectric phase at low temperatures [6].

To study the role of methylammonium groups in the crystal lattice dynamics and their influence on nuclear quadruple resonance (NQR) spectrum parameters of Br^{79} nucleus, we have been investigated the temperature dependences of NQR frequencies and spin-lattice relaxation time of Br^{79} and H^1 nuclei. Measurements have been carried out using a pulse radiospectrometer ISSh-2-13. To determine the spin-lattice relaxation time, the pulse sequence $90°–\tau–90°$ was used, the measurements of a proton relaxation were carried out at 31.1 MHz. The cryostatic and thermostatic system used provided the temperature stability not worse than 0.05 K in the low temperature range at NQR measurements and 0.5 K at NHR ones. Results of measurements are shown on Fig. 1–3.

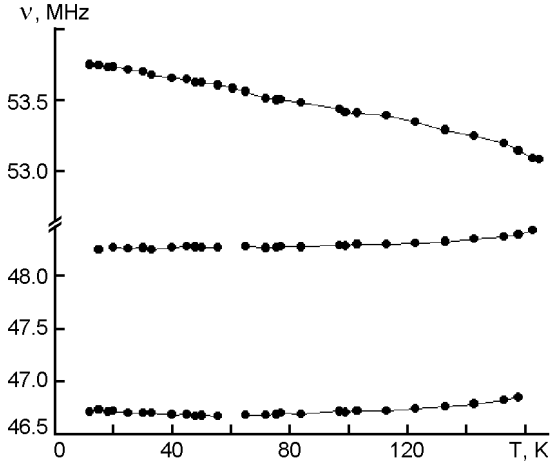

Fig. 1. Temperature dependence of Br^{79} NQR frequency.

Temperature dependence of Br^{79} nuclear quadruple resonance is shown in Fig. 1. Three resonance lines of NQR spectrum correspond to three nonequivalent positions of bromine nuclei in the crystal. At temperatures higher than 165 K, NQR signals disappear and are not observed up to room temperatures. Temperature dependence of the high-frequency spectral line is well described by the dependence obtained in the Bayer-Kushida theory for torsion oscillations in a crystal: $\nu(T) = a + bT$, where $a = 53.8 \cdot 10^6$ s^{-1}, $b = -3.81 \cdot 10^{-3}$ $s^{-1}K^{-1}$. The deviation from the specified dependence is observed near the temperature of disappearance of NQR signal. Linear character of NQR frequency dependence indicates a rather low Debye temperature for this crystal. At the same time, two other spectral lines have small positive temperature coefficient, and anomalous dependence increases as approaching to the temperature of the signal disappearance. In the whole researched temperature interval, the frequency shift between the low-frequency lines remains approximately constant.

The study results of the spin-lattice relaxation rate temperature dependence for Br^{79} nuclei are shown in Fig. 2. For quadruple relaxation caused by fluctuations of the electric field gradient (EFG) at low temperatures, it is just the Raman biphonon process that is the most effective instead of direct interaction of the field gradient and lattice oscillations. According to biphonon model, the temperature dependence of relaxation rate looks as: $T_1^{-1} = a + bT^2$. However, the analysis of experimental data within the framework of this theory has

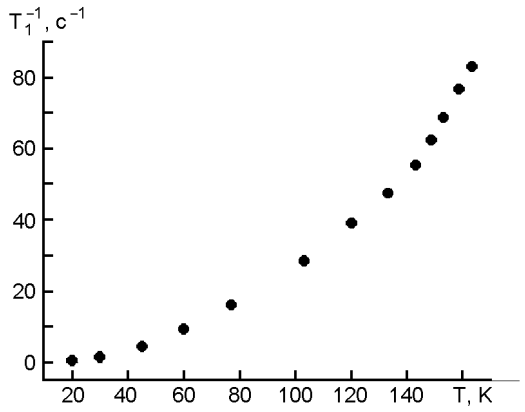

Fig. 2. Tempereture dependence of the quadrupole Br^{79} spin-lattice relaxation rate.

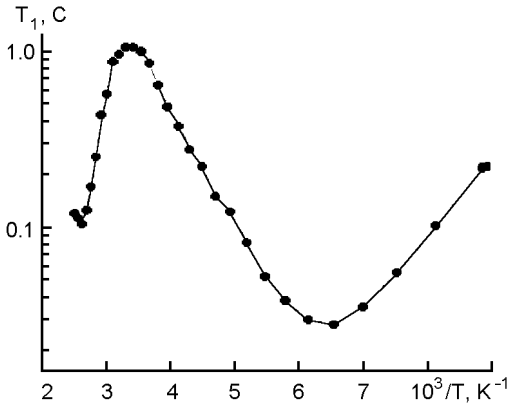

Fig. 3. Proton NMR spin-lattice relaxation time vs. reciprocal temperature.

shown a deviation from square-law dependence at higher temperatures (a continuous curve in Fig. 2) that evidences the appearance of an additional relaxation mechanism.

It is possible to assume that the electric field gradient (EFG) tensor in the Br^{79} site, that determines NQR parameters, represents the sum of the gradient caused by *p*-electron orbits of pyramidal chain $CdBr_3$ and a gradient caused by motion either of the methyl-ammonium cation as a whole or of its fragments. This additional contribution to EFG also results in deviations of temperature dependences of NQR frequency and relaxation time of Br^{79} from classical dependences at 143 K and to disappearance of NQR signal at 165 K. To reveal this contribution, the temperature dependence of proton spin-lattice relaxation time has been measured, which is shown in Fig. 3.

The presence of two relaxation minima at $T = 155$ K and 382 K shows clearly the existence of two relaxation mechanisms in the studied temperature range. The low

temperature minimum can be connected with reorientation motion of NH_3 groups while the high-temperature one, with slow motion of isopropyl groups as a whole. Rotation of CH_3 group is displayed as a rule at lower temperatures. It is also seen from the Figure that both processes have thermoactivated character. Calculations have shown that for NH_3 reorientation and motion of cation as a whole, the corresponding activation energy are $E_{a1} = 3.4$ kcal/mol and $E_{a2} = 8.7$ kcal/mol. The first specified relaxation mechanism dominates within the temperature interval 100–275 K, while the second is displayed only at temperatures above 300 K.

Using conditions of the minimum in the temperature dependence of relaxation time $\omega_0\tau_c = 0.616$, where ω_0 is the Larmor frequency ($\omega_0/2\pi = 31.1$ MHz), τ_c, correlation time of corresponding type of intracrystalline motion, and taking into account that temperature behavior of τ_c is of thermoactivated character: $\tau_c = \tau_0\exp(E/kT)$, we have calculated the correlation times of NH_3 groups reorientation (τ_{c1}) and motion of the whole cation (τ_{c2}). Temperature dependence of time τ_{c1} is shown in Fig. 4. It is seen that at $T = 140$ K, $\tau_{c1} = 6.8\cdot10^{-8}$ s, this time corresponds to the reorientation frequency $\nu = 15\cdot10^6$ s^{-1}, that is comparable to NQR frequency of Br^{79}.

As the quadruple relaxation is defined by fluctuations of electric field gradient tensor in the Br^{79} site: $T_1^{-1} \sim J(\omega)$ where $J(\omega)$ is the spectral density of fluctuations, so it is obvious that since $T = 140$ K, reorientation of NH_3 groups starts to render essential influence on the EFG tensor change, that results in a deviation from usual temperature dependences of NQR frequency and spin-lattice relaxation of Br^{79} nucleus. At 165 K, $\tau_{c1} = 1.8\cdot10^{-8}$, that corresponds to hindered rotation frequency of NH_3 groups $\nu = 50$ MHz. This value already practically coincides with the frequency of the high-frequency NQR line. When the different lengths of hydrogen bonds N–H...Br are formed, the strongly nonuniform broadening of NGR lines arises. A part of hydrogen bonds has a steady length, that results in the usual temperature coefficient of one of the NQR lines. Two lines with anomalous temperature behavior evidence that even under low temperature, changes in the hydrogen bond length take place. At the same time, the lengths of these H-bonds differ essentially,

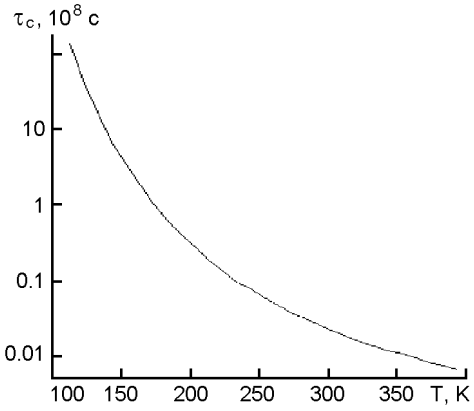

Fig. 4. The temperature dependence of the calculated correlation time of NH_3 reorientation.

that results in a strongly nonuniform broadening of temperature-anomalous NQR lines and to disappearance of these lines at lower temperatures as compared to the high-frequency NQR line.

Since it is shown that the additional contribution to quadruple relaxation is brought by thermoactivated motion of NH_3 groups, it is to expect that the quadruple relaxation rate of Br^{79} will be described by expression:

$$T_1^{-1} = aT^2 + b \cdot \exp(E_a/kT).$$

Fitting of this expression to experimental data has given the good agreement with the experiment in all researched temperature range at the following values of fitting parameters adjustment: $a = 2.66\cdot10^{-3}$ $s^{-1}K^{-2}$, $b = 2.53\cdot10^6$ s^{-1}, $E_a = 3.9$ kcal/mol.

When comparing the obtained value of activation barrier E_a with the barrier of NH_3 group reorientation ($E_{a1} = 3.4$ kcal/mol), we can see their good agreement. At the same time, the calculated values of correlation time of the whole methylammonium cation motion are $\tau_{c2} = 1.4$ s at 165 K and $4.4\cdot10^{-6}$ s at 310 K, i.e. this cation at low temperatures is practically motionless and the motion becomes appreciable only at much higher temperatures. Taking into account this "freezing" of methylammonium group motion, it is possible to speak about its ordering at the temperature lowering. In the NQR study of $(CH_3)_4NCdBr_3$ crystal [7] carried out by us before, it was established that phase transition to ferroelectric phase in this crystal is connected with ordering of tetramethylammonium cation though NMR-researches, as well as in this work, have not revealed any

peculiarities in temperature behavior of the proton relaxation [8]. This allows to assume, that in the crystal considered here, a phase transition of order-disorder type should take place too, however, this transition occurs at temperatures where NQR signal disappears because of averaging of EFG tensor by the hindered rotation of NH_3 groups.

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ЯМР і ЯКР дослідження динаміки гратки в $(CH_3)_2CHNH_3CdBr_3$

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Наведено результати досліджень температурних залежностей частот квадрупольного резонансу Br^{79}, квадрупольної спин-граткової релаксації ядер Br^{79} і протонної ЯМР релаксації у кристалі $(CH_3)_2CHNH_3CdBr_3$ з перовскито-подібною структурою. Показано, що аномальна температурна поведінка частот ЯКР та квадрупольної релаксації ядер брому обумовлена реорієнтацією NH_3 груп і динамікою водневого зв'язку N–H...Br. Обговорюються механізми релаксації протонів та ядер брому, а також їх зв'язок з рухом метиламонійних груп та їх фрагментів.