The Temperature Dependence of ^{121,123}Sb, ^{35}Cl, ^{79,81}Br and ^{127}I NQR Spectra in Complexes $Cs_3Sb_2X_9$ (X = Cl, Br, I)

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The ^{121,123}Sb, ^{35}Cl, ^{79,81}Br and ^{127}I NQR Spectra of the complexes $Cs_3Sb_2X_9$ (X = Cl, Br, I), prepared from CsX and SbX_3 aqueous solutions, were studied at 77–400 K. Analysis of the temperature coefficients of the quadrupole transition frequency (ν), quadrupole coupling constant (e^2Qq_{zz}) and asymmetry parameter of the electric field gradient (η) was carried out.

Key words: Antimony (III); Haloid Complex Compounds; ^{121,123}Sb; ^{35}Cl; ^{79,81}Br; ^{127}I; NQR Spectra.

Introduction

Due to its high sensitivity to structural changes, the NQR method became irreplaceable in studies of the crystal lattice dynamics of solids with quadrupole nuclei. In continuation of our investigations of Sb(III) and Bi(III) complexes by this method [1] we now report on the temperature dependence of the ^{121,123}Sb, ^{35}Cl, ^{79,81}Br and ^{127}I NQR parameters in the complexes $Cs_3Sb_2X_9$ (X = Cl, Br, I), prepared from aqueous solutions.

The compounds $Cs_3Sb_2X_9$ form a large group among the complexes $A_3B_2X_9$, where A = alkali cation, ammonium or protonated organic base cation; B = Al, Ga, In, Tl, V, Cr, W, As, Sb, Bi and other trivalent elements and X = Cl, Br, I. Their crystal structures are rather well known [4]. B (III) polyhedra consist of BX_6 distorted octahedra which bind to each other differently depending on the halogen atom, the cation size and the hydrogen-bonds. All the compounds $A_3B_2X_9$ studied so far are built from two types of construction units.

In the first type, BX_6 polyhedra are bonded in pairs with a common triangular facet so that isolated dimeric complex anions $[B_2X_9]^{3-}$ are formed. The compounds $Cs_3Sb_2X_9$, $Cs_3Bi_2I_9$ [5], $[(CH_3)_4N]_3Bi_2Br_9$ [6], $[(C_2H_5)(CH_3)_2(C_6H_5)N]_3Bi_2Cl_9$ [7] and $[(C_2H_5)NH_2]_3Bi_2I_9$ [8] have such a structure.

The second type of structure contains octahedral groups BX_6 bonded to two octahedral groups by sharing three apexes forming double polymeric chains (for instance β-$Cs_3Sb_2Cl_9$, $Cs_3Bi_2Cl_9$ [9], $(n\text{-}C_3H_7NH_3)_3Sb_2Cl_9$ [10] and $(C_5H_5NH)_3Sb_2Cl_9$ [11]) or crimped polymeric layers $[B_2X_9]_n^{3n-}$ (α-$Cs_3Sb_2Cl_9$ [12], $Cs_3Bi_2Br_9$ [13], $[(CH_3)_3NH]_3Sb_2Cl_9$ [14], $K_3Bi_2F_9$ [15]).

Some of these compounds, like α-$Cs_3Sb_2Cl_9$ and $(C_5H_6N)_3Tl_2Cl_9$ [16], β-$Cs_3Sb_2Cl_9$ and $Cs_3Bi_2Cl_9$ [9], $A_3Sb_2Br_9$ (A = K, Rb, Cs) [17], and $A_3Sb(Bi)_2I_9$ (A = Rb, NH_4) [18, 19] form isostructural series.

The quadrupole resonance of the halogen nuclei in $A_3B_2X_9$ (X = Cl, Br, I) is widely studied [20]. As a rule, the NQR spectra of these compounds consist of two well-separated groups of lines. The number of lines corresponds to the number of halogen atoms occupying similar positions in B_2X_9 polyhedra. The group of lines with higher frequencies corresponds to the terminal X atoms and the group with lower frequencies to the bridging ones. The NQR spectra at the halogen nuclei in $Cs_3Sb_2X_9$ (X = Cl, Br, I) at 77 K were studied earlier (Table 1) [17, 18, 21, 22]. The ^{127}I NQR spectrum of $Cs_3Sb_2I_9$ crystals grown from the melt has another set of line [23, 24] which shows the presence of three different $^{127}I_{\text{terminal}}$ atoms, indicating a correlation between the method of preparation of the complex and its structure.

Our previous studies [17, 18, 21, 22] showed that the compounds $A_3Sb_2X_9$ may be separated into two groups according to their ^{121,123}Sb NQR spectra at 77 K: complexes with A = K, Rb, NH_4 and X = Br, I, which contain two types of antimony polyhedra in

Table 1. ^{121,123}Sb and ^{127}I NQR parameters in the complex compounds $Cs_3Sb_2X_9$ (X = Cl, Br, I).

Compound	T, K	NQR frequency, MHz					e^2Qqh^{-1}, MHz		η, %	T*, K
		^{121}Sb		^{123}Sb			^{121}Sb	^{123}Sb		
		1/2 ↔ 3/2	3/2 ↔ 5/2	1/2 ↔ 3/2	3/2 ↔ 5/2	5/2 ↔ 7/2				
$SbCl_3$	77 [20]	59.72	…	39.12	68.64	…	383.6	488.8	18.8	
$SbBr_3$	77 [17]	49.35	95.00	32.03	57.10	86.76	318.6	406.1	17.4	
SbI_3	77 [20]	12.7	25.40	…	15.40	23.10	84.7	107.8	0.3	
$Cs_3Sb_2Cl_9$	77 [21]	14.64	29.27	8.85	17.75	26.65	97.5	124.1	4.1	> 293
	160	15.02	29.77				99.4	126.7**	4.6	
	200	15.14	30.01				100.2	127.7**	4.7	
	293	15.93	30.34				101.3	129.2**	2.8	
$Cs_3Sb_2Br_9$	77 [17]	10.30	20.62	6.22	12.45	18.68	68.7	87.1	0.8	360
	150			6.36	12.71	19.06	69.8**	89.0	1.1	
	200			6.42	12.84	19.26	70.5**	89.9	1.3	
	250			6.48	12.93	19.40	71.1**	90.6	2.1	
	300			6.49	12.96	19.44	71.2**	90.7	2.3	
$Cs_3Sb_2I_9$	77 [18]	8.63	17.26	5.24	10.48	15.72	57.5	73.3	0	> 300

^{127}I NQR parameters

T, K	1/2 ↔ 3/2	3/2 ↔ 5/2	e^2Qqh^{-1}, MHz	η, %	T*, K
77 [18]	130.65	208.67	722.1	45.8	390
	67.80	103.29	360.5	51.4	
150	130.42	207.38	718.3	46.3	
	66.80	103.42	359.9	49.5	
200	131.31	206.26	714.9	46.9	
	66.50	102.73	357.60	49.8	
250	130.17	204.84	710.7	47.6	
	66.26	102.14	355.7	50.0	
300	129.85	202.72	704.4	48.5	
	66.00	101.68	354.1	50.2	

* Temperature of NQR signal fading. ** The calculated values for the QCC ^{121,123}Sb which have been found from the known ratio [3]: QCC ^{121}Sb/QCC ^{123}Sb = 1.27475.

their structures, and complexes with A = Cs and X = Cl, Br, I, in which these polyhedra occupy equivalent positions.

Experimental

The compounds $Cs_3Sb_2X_9$ (X = Cl, Br, I) were prepared from CsX and SbX_3 aqueous solutions in the presence of the corresponding acid HX [2]. The ^{121,123}Sb, ^{35}Cl, ^{79,81}Br and ^{127}I NQR spectra of polycrystalline samples were recorded on an ISSh-2-13 spectrometer equipped with a temperature device for the range 77 – 400 K. The quadrupole coupling constant e^2Qq_{zz} (QCC) and asymmetry parameter of the electric field gradient (EFG) η for ^{121,123}Sb and ^{127}I were calculated from the experimental NQR frequencies [3]. The errors (Δ) of the experimental and calculated data are $\Delta T = \pm 0.1$ K; $\Delta\nu = \pm 0.01$ MHz; Δ(QCC) = ±0.1 MHz; $\Delta\eta = \pm 0.1\%$.

Results and Discussion

The asymmetry parameter of the EFG calculated from the ^{121,123}Sb NQR singlet spectra of $Cs_3Sb_2X_9$ (Table 1) shows a high axial symmetry of the electron density distribution at the antimony atoms at 77 K, which rises in the series X = Cl → Br → I. The antimony atoms in $Cs_3Sb_2I_9$ crystals are in fact in an axially symmetric electric field ($\eta = 0$). The quadrupole coupling constant of the antimony atoms in $Cs_3Sb_2X_9$ relative to those in SbX_3 is lower by approximately 75 and 80% for X = Cl and Br, and by only 32% for X = I.

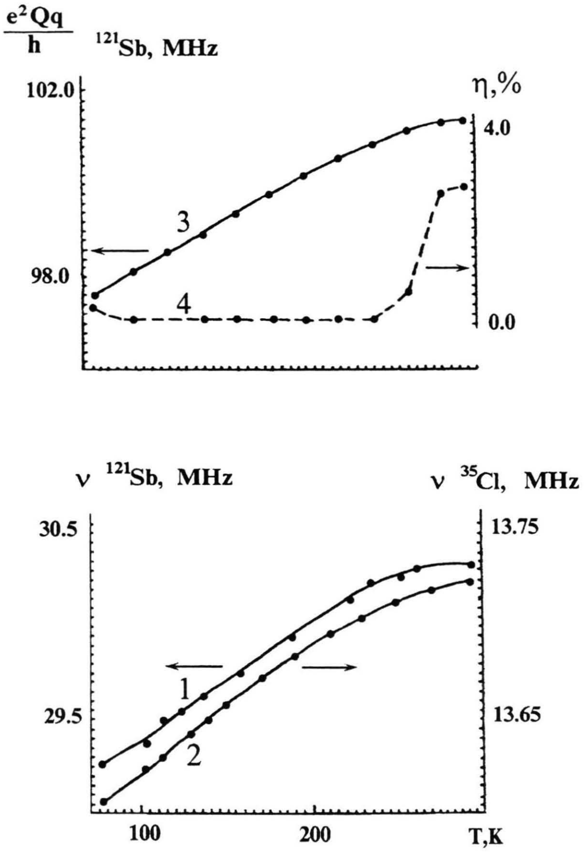

Fig. 1. Temperature dependence of the ^{121}Sb and ^{35}Cl NQR parameters of $Cs_3Sb_2Cl_9$: 1) $\nu_1 = \pm(3/2 \leftrightarrow 5/2)$ ^{121}Sb, 2) $\nu_2 = \pm(1/2 \leftrightarrow 3/2)$ ^{35}Cl, 3) e^2Qqh^{-1} ^{121}Sb, 4) η ^{121}Sb.

The peculiarities of the changes with temperature of the NQR of $Cs_3Sb_2X_9$ (X=Cl, Br, I) in the range 77–400 K are described in the following for each compound investigated.

α-$Cs_3Sb_2Cl_9$

We have prepared the compound $Cs_3Sb_2Cl_9$ in the α-form [12]. Figure 1 shows the temperature dependence of the ^{121}Sb and ^{35}Cl NQR parameters for $Cs_3Sb_2Cl_9$ in the range 77–293 K and their changes with temperature differ from the usual "Bayer's" curves. NQR signals were not detected for this compound above 293 K.

The ^{35}Cl NQR spectrum of $Cs_3Sb_2Cl_9$ at 77 K consists of only one line (13.47 MHz) which corresponds to the terminal chlorine atoms, confirmings the equivalence of all Sb–Cl terminal bonds in the polymeric anionic layers $[Sb_3Cl_9]_n^{3n-}$. It must be pointed out that the ^{35}Cl resonance signals of the bridging chlorine atoms occur at a lower frequency which is not detectable by our spectrometer.

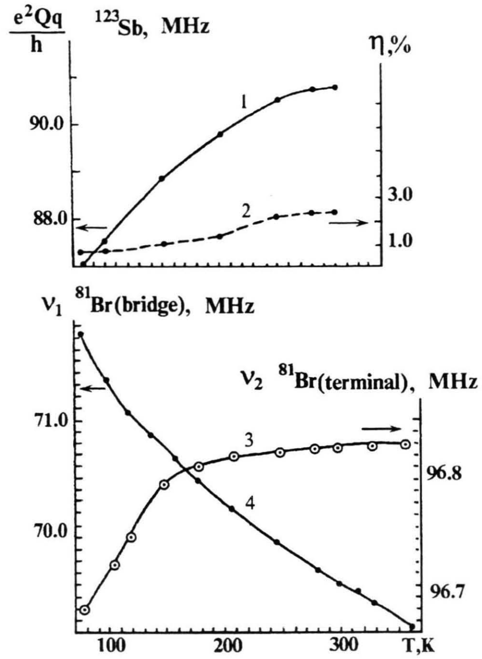

Fig. 2. Temperature dependence of the ^{123}Sb and ^{81}Br NQR parameters of $Cs_3Sb_2Br_9$: 1) e^2Qqh^{-1} ^{123}Sb, 2) η ^{123}Sb, 3) $\nu_2 = \pm(1/2 \leftrightarrow 3/2)$ ^{81}Br(terminal), 4) $\nu_1 = \pm(1/2 \leftrightarrow 3/2)$ ^{81}Br(bridge).

The temperature coefficient of the ^{35}Cl NQR frequency in the range 77–293 K is positive ($\partial\nu/\partial T = 0.68$ kHz · K^{-1}). The ^{121}Sb parameters for α-$Cs_3Sb_2Cl_9$ also have positive temperature coefficients (Fig. 1, curves 1, 3, 4). These data show that both the antimony and chlorine atoms have strong bonds in the polymeric anionic layers $[Sb_2Cl_9]_n^{3n-}$ in the temperature range 77–293 K. The electron density in α-$Cs_3Sb_2Cl_9$ crystals is redistributed with the temperature in such a way that ^{121}Sb atoms keep their axial symmetry in the range from ~ 100 up to 240 K (here the η tendency is practically constant) which lowers in the range 240–280 K.

$Cs_3Sb_2Br_9$

The ^{79,81}Br NQR spectrum of $Cs_3Sb_2Br_9$ at 77 K suggests two types of bromine atoms in its structure. The high-frequency ^{79}Br line (115.72 MHz) corresponds to the terminal bromine atoms and the low-frequency one (85.88 MHz) – to the bridging atoms. Figure 2 shows the temperature variations of the ^{123}Sb and ^{81}Br NQR parameters in $Cs_3Sb_2Br_9$ at 77–360 K. No NQR signals were detected above 360 K.

The temperature dependence of the ^{81}Br NQR parameters for the terminal bromine atoms in $Cs_3Sb_2Br_9$ (Fig. 2, line 3) has a positive coefficient ($\partial\nu_2/\partial T = 0.67$ kHz · K^{-1}), similar to the analogous coefficient for the terminal chlorine atoms in the ^{35}Cl NQR spectrum of α-$Cs_3Sb_2Cl_9$ (Fig. 1, line 2). As for the bridging bromine atoms, their NQR frequency (Fig. 2, line 4) decreases in accordance with Bayer's theory [25] ($\partial\nu_2/\partial T = -8.58$ kHz · K^{-1}).

The temperature dependences of e^2Qq_{zz} and η for ^{123}Sb atoms in both $Cs_3Sb_2Br_9$ and α-$Cs_3Sb_2Cl_9$ have positive coefficients (Fig. 2, lines 1, 2). The η values show that the symmetry of the electron density distribution at the antimony atoms slowly decreases with the temperature. While the bromine signals disappear at $T > 360$ K, ^{123}Sb signals are not detected above 300 K.

The data obtained suggest that the antimony polyhedra in $Cs_3Sb_2Br_9$ and α-$Cs_3Sb_2Cl_9$ crystals are bound in $[Sb_2Br_6]_n^{3n-}$ polymeric chains where the electron density redistribution with increasing temperature is not a result of the usual "Bayer's" thermal averaging of the EFG at X (Cl, Br) and Sb nuclei. The electron density in these crystals at 77 K may be higher at the bridging halogen atoms causing an EFG decrease at the antimony nuclei and terminal halogen atoms. When the compounds are heated, their thermal motion leads to Sb-X-Sb bond weakening (as indicated by the decrease in the NQR frequency of the bridging bromine atoms) and to a shift of the charge density to the antimony and terminal halogen atoms which gives an increase in their NQR frequencies.

$Cs_3Sb_2I_9$

The compound $Cs_3Sb_2I_9$ is of particular interest because of the possibility of calculating the NQR parameters (QCC and η) both for the antimony and the halogen atoms from their NQR spectra. The ^{127}I NQR spectrum shows four lines at 77 K (Table 1) suggesting two nonequivalent positions for the iodine atoms in the isolated dimeric complex anion $[Sb_2I_9]^{3-}$ of the $Cs_3Sb_2I_9$ crystal structure [5]. The terminal iodine atoms have higher frequencies (130.65 and 208.67 MHz), while the bridging ones have lower frequencies (67.80 and 103.29 MHz). Their EFG asymmetry parameters (Table 1) indicate a low-symmetry of the electron density distribution when compared with the antimony atoms, especially in the case of bridging iodine atoms. The QCC variation for the ^{121}I terminal iodine atoms in $Cs_3Sb_2I_9$ as compared with the same value in SbI_3 at 77 K amounts to 19%, and for the bridging ones to 40%.

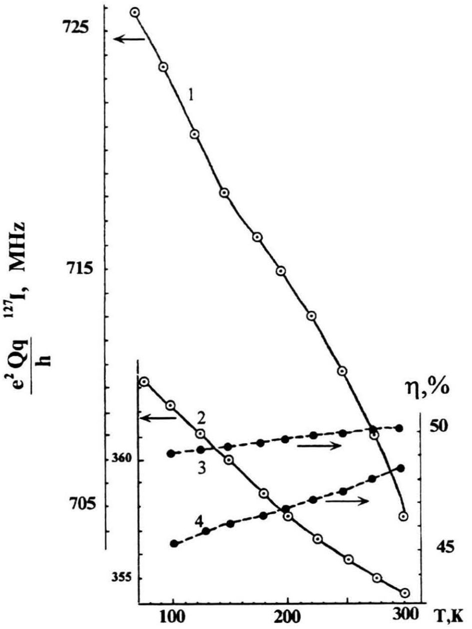

Fig. 3. Temperature dependence of the ^{127}I NQR parameters of $Cs_3Sb_2I_9$: 1) e^2Qqh^{-1} ^{127}I (terminal), 2) e^2Qqh^{-1} ^{127}I (bridge), 3) η ^{127}I (bridge), 4) η ^{127}I (terminal).

In the range 77–300 K all the temperature coefficients of the NQR frequencies and e^2Qq_{zz} for ^{127}I in $Cs_3Sb_2I_9$ have usual but considerably different values: $\partial e^2Qq/\partial T = -96.28$ for the terminal iodine atoms and -41.52 kHz · K^{-1} for the bridging ones (Fig. 3, lines 1 and 2 respectively).

Comparison of the NQR parameters for the halogen atoms in $Cs_3Sb_2X_9$ (X = Cl, Br, I) shows similarity of $\partial\nu/\partial T$ values for $^{127}I_{bridge}$ and $^{81}Br_{bridge}$ (−7.17 and −8.58 kHz · K^{-1}) in the transitions $\nu = \pm(1/2 \leftrightarrow 3/2)$. At the same time the temperature variations of the NQR parameters for $^{127}I_{terminal}$ in $Cs_3Sb_2I_9$ crystals differ from the analogous data for $^{35}Cl_{terminal}$ and $^{79,81}Br_{terminal}$ in $Cs_3Sb_2X_9$ crystals (X = Cl, Br) (Table 1).

The EFG asymmetry parameters η for both the bridging and terminal iodine atoms in $Cs_3Sb_2I_9$ increase with the temperature (Fig. 3, lines 3 and 4). The $\partial\eta/\partial T$ value for the terminal iodine atom ($13.90 \cdot 10^{-3}$ K^{-1}) is higher than the corresponding value for the bridging one ($4.03 \cdot 10^{-3}$ K^{-1}), indicating a larger distortion in the electron density distribution of the terminal iodine atom as compared with the bridging one in the dimers $[Sb_2I_9]^{3-}$ as the temperature increases. This may be due to the weaker Sb–I–Sb bond in $Cs_3Sb_2I_9$ with respect

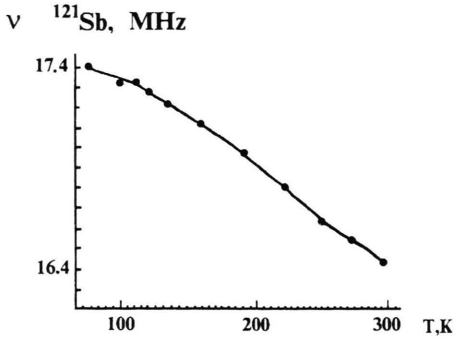

Fig. 4. Temperature dependence of the ^{121}Sb NQR frequency for the transition $\nu = \pm(1/2 \leftrightarrow 3/2)$ of $Cs_3Sb_2I_9$.

Sb–X–Sb bonds in $Cs_3Sb_2X_9$ with X = Cl, Br. These data correlate with "Bayer's" character of the temperature dependence of the ^{121}Sb frequency in $Cs_3Sb_2I_9$ (Fig. 4), where $\partial\nu/\partial T = -4.58$ kHz · K^{-1}, which is different from the anomalous trend found for ^{121,123}Sb in $Cs_3Sb_2X_9$ (X = Cl, Br) (Fig. 1, lines 1 and 3; Fig. 2, line 1).

In the range 150 – 180 K the QCC curve for the terminal ^{127}I atoms in $Cs_3Sb_2I_9$ (Fig. 3, line 1) shows a $\partial e^2Qq/\partial T$ change from – 104.24 (T = 77 – 150 K) to – 92.40 kHz · K^{-1} (T = 150 – 300 K). A weak slope change of the ^{121}Sb NQR frequency curve takes place at 160 K (Figure 4). These data indicate a phase transition of the second type at ~ 160 K. A phase transition of the second type was also observed in $Cs_3Sb_2I_9$, grown from the melt [24], but it took place in a narrow temperature range and at a lower temperature ($T = 86 \pm 1$ K) and resulted in the splitting of the high-frequency line in the ^{127}I NQR spectrum into the triplet.

Conclusion

Our NQR study shows an electron density redistribution at all the antimony and halogen atoms in all the compounds $Cs_3Sb_2X_9$ (X = Cl, Br, I) as the temperature increases from 77 to 300 K. This effect decreases in the order $Cs_3Sb_2Cl_9 > Cs_3Sb_2Br_9 > Cs_3Sb_2I_9$, as indicated by the temperature dependence of the NQR parameters. This trend correlates with a weakening of the $Sb - X_{bridge} - Sb$ interaction in the series Cl > Br > I. The temperature at which the NQR signal disappears decreases in the order I (390 K) > Br (360 K) > Cl (293 K), suggesting that the $Sb - X_{term}$ bond strength increases accordingly. Analysis of the temperature variations of the NQR parameters in $Cs_3Sb_2X_9$ (X = Cl, Br, I) allows to distinguish the isolated dimeric anions $[Sb_2I_9]^{3-}$ from the polymeric chains $[Sb_2X_9]_n^{3n-}$.

Moreover, a phase transition of the second type at ~ 160 K has been observed for the compounds $Cs_3Sb_2I_9$ prepared from aqueous solution.

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