^{121,123}Sb NQR investigation of chlorofluoroantimonates(III) $M_2SbCl_3F_2$ (M = Rb, Cs, and NH_4)

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Antimony(III) chlorofluoride complexes $M_2SbCl_3F_2$ (M = Rb, Cs, or NH_4) were studied by the ^{121,123}Sb NQR method. A temperature range (77—285 K) with anomalous change in the NQR parameters and a second-order phase transition at 250—280 K for $(NH_4)_2SbCl_3F_2$ were found.

Key words: ^{121,123}Sb NQR spectra, antimony(III), chlorofluoroantimonates(III).

In this work, in continuation of the publications[1—3] on study of complex compounds of Sb^{III} by the NQR method (this method provides valuable information about solids containing quadrupole nuclei due to their high sensitivity to structural changes), the changes in the parameters of the ^{121,123}Sb NQR spectra of chlorofluoroantimonate(III) $(NH_4)_2SbCl_3F_2$ at 77—330 K are discussed and compared with its crystalline structure[4] as well as with the NQR and structural data for the compounds $M_2SbCl_3F_2$ (M = Rb and Cs).[4,5]

Experimental

The compounds $M_2SbCl_3F_2$ (M = Rb, Cs, and NH_4) were synthesized by the known procedure.[6] ^{121,123}Sb NQR spectra (Table 1) were obtained in the range 77—330 K on an ISSh-2-13 spectrometer with a temperature attachment. The accuracy of the temperature measurements was 0.1 K. Since the spins of ^{121}Sb and ^{123}Sb are equal to 5/2 and 7/2, respectively, five signals of the antimony atoms, which occupy equivalent sites in the crystal lattice, are observed in the NQR spectrum. When the temperature dependence of the NQR spectrum was studied, the frequencies of two transitions of ^{121}Sb atoms were measured: $\pm(1/2 \rightleftharpoons 3/2)$ and $\pm(3/2 \rightleftharpoons 5/2)$ (Fig. 1), from which, according to the procedure published previously,[7] the values of the quadrupole coupling constant (QCC, e^2Qqh^{-1}/MHz) and the asymmetry parameter (η (%)) of the electric field gradient (EFG) tensor of antimony atoms were calculated (Fig. 2).

Results and Discussion

Three chlorofluoride compounds of antimony(III) $M_2SbCl_3F_2$ (M = Rb, Cs, and NH_4) were synthesized.[6] Analysis of their crystalline structures has shown[4] that the compounds with Rb^+ and Cs^+ cations are isostructural.

Antimony atoms occupy two nonequivalent sites in the structure of $Rb_2SbCl_3F_2$. The coordination polyhedrons of Sb(1) atoms are deformed octahedrons $[SbCl_3F_3]^{3-}$ sharing common edge Cl(1)—Cl(1′) and common vertex Cl(2) to form polymeric zigzag-like chains. The deviations of bond angles in such polyhedrons range from 1.7 to 7.3° compared to a regular octahedron. The polyhedrons of Sb(2) atoms are discrete, almost regular octahedrons $[SbCl_6]^{3-}$ with the Sb(2)—Cl distances equal to 2.61 and 2.65 Å, and the deviations of bond angles (from 90°) range from 0.2 to 0.4°.

The signals of only one type of antimony atoms, Sb(1), are observed in the NQR spectra of the compounds $Rb_2SbCl_3F_2$ and $Cs_2SbCl_3F_2$ instead of two types of atoms (see Table 1). This confirms the presence of Sb(2) atoms with highly symmetric surroundings in these structures, because no NQR spectra are recorded for the atoms, which have no or very low electric field gradients.[7]

In the crystalline structure of $(NH_4)_2SbCl_3F_2$, the antimony atoms also occupy two crystallographically independent sites, but their coordination polyhedrons have different structures.[4] The polyhedrons of Sb(1), which are the deformed octahedrons $[SbCl_4F_2]^{3-}$, are linked by common vertices *via* bridged Cl(1) and Cl(2) atoms to form zigzag-like polymeric chains. The description of the Sb(2) polyhedron is dual[4]: it can be presented either as distorted isolated semioctahedrons $[SbCl_3F_2]^{2-}$ or as the same chains of octahedrons $[SbCl_4F_2]^{3-}$ as those for Sb(1).

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Table 1. Parameters of the $^{121,123}Sb$ NQR spectra of antimony compounds at 77 K

Compound	Atom	Transition frequency/MHz					$e^2Qq \cdot h^{-1}$/MHz		η (%)
		^{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			
$Rb_2SbCl_3F_2$[a]	Sb(1)	68.33	136.57	41.47	82.83	124.15	454.9	579.7	2.0
	Sb(2)	No signals are recorded							
$Cs_2SbCl_3F_2$[a]	Sb(1)	68.01	135.97	41.40	82.47	123.81	453.3	577.7	2.0
	Sb(2)	No signals are recorded							
$(NH_4)_2SbCl_3F_2$	Sb(1)	53.39	92.04	39.72	54.40	84.88	314.3	404.2	36.0
	Sb(2)	56.32	98.82	41.02	58.41	90.82	336.5	428.5	33.5
SbF_3[b]		80.67	169.96	49.17	97.64	146.59	536.7	684.2	4.3
$SbCl_3$[c]		59.72		39.12	68.64		383.6	488.8	18.8

[a] See Ref. 5. [b] See Refs. 5 and 8. [c] See Ref. 7.

The data of the $^{121,123}Sb$ NQR spectra for $(NH_4)_2SbCl_3F_2$ at 77 K are presented in Table 1 and indicate unambiguously to two nonequivalent sites of the antimony atoms that are in the low-symmetric surroundings, which corresponds to the results obtained previously.[4] The antimony atoms in $(NH_4)_2SbCl_3F_2$ are characterized by lower values of QCC than those in $M_2SbCl_3F_2$ (M = Rb, Cs) or SbF_3 and $SbCl_3$ (see Table 1).

Analysis of the change in the values of QCC and η of the EFG tensor of the antimony atoms in the compounds $M_2SbCl_3F_2$ (M = Rb, Cs, and NH_4) shows that these values depend on the Cl : F ratio in the antimony polyhedrons. For example, in the $[SbCl_3F_3]^{3-}$ polyhedrons (Cl : F = 1) determined in the structure of $Rb_2SbCl_3F_2$, the asymmetry parameter is low, and the value of QCC exhibits an approximately equal shift from the analogous values for SbF_3 and $SbCl_3$. The ligand Cl : F ratio is equal to two in the $[SbCl_4F_2]^{3-}$ polyhedrons of the compound $(NH_4)_2SbCl_3F_2$. In this case, the η values for two nonequivalent antimony atoms increase to 33—36 %, and the QCC values shift closer to the values for $SbCl_3$ (see Table 1).

The close values of the $^{121,123}Sb$ NQR parameters for $(NH_4)_2SbCl_3F_2$ allow one to draw the conclusion that the ligand surroundings of the antimony atoms are similar for both polyhedrons, which should be described as $[SbCl_4F_2]$.[4]

The $^{121,123}Sb$ NQR frequencies in the spectrum of $(NH_4)_2SbCl_3F_2$ for the polyhedrons of Sb(1) and Sb(2) are assigned on the basis of the following assumption: the NQR frequencies of one of the antimony polyhedrons are spaced at 5.9 % on the average. The antimony atoms characterized by the low-frequency spectrum have the higher EFG asymmetry parameter. The analysis of bond angles in the antimony polyhedrons[4] shows that the Sb(1) polyhedrons are more distorted than those of Sb(2). In addition, the bridging Sb(1)—Cl(1′) bond (3.12 Å) in the Sb(1) polyhedrons is shorter than those in the Sb(2) polyhedrons, in which the length of the analogous Sb(2)—Cl(4′) bond is equal to 3.33 Å. A decrease in the bond length should result in a decrease in the NQR frequency on the central atom,[7] which is observed in the experiment (see Table 1). The low-frequency line of the NQR spectrum is assigned to the signals of Sb(1) atoms on the basis of the aforesaid.

No signals of ^{35}Cl atoms at the frequencies higher than 10 MHz were not observed in the spectrum of $M_2SbCl_3F_2$.

We studied the temperature dependences of ^{121}Sb NQR frequencies (see Fig. 1), quadrupole coupling constants, and EFG asymmetry parameters (see Fig. 2) for $(NH_4)_2SbCl_3F_2$. The NQR signals of two nonequivalent sites of antimony, whose amplitudes decrease gradually as the temperature increases, are observed up to 330 K. No signals were recorded above 330 K.

According to the Bayer—Kushida theory,[7] all NQR parameters should decrease as the temperature increases due to time averaging of the electric field gradient as the amplitude of thermal vibrations increases. The analysis of the temperature dependences of the NQR parameters for $(NH_4)_2SbCl_3F_2$ shows that they are characterized by different temperature coefficients. The temperature coefficient was found to be positive ($\partial\nu/\partial T = 2.94 \cdot 10^{-2}$ MHz deg^{-1}) for the $^{121}Sb(1)$ NQR frequency corresponding to the ±(3/2 ⇌ 5/2) transition in the temperature range of 77—285 K and negative in the temperature range of 290—330 K ($\partial\nu/\partial T = -4.75 \cdot 10^{-3}$ MHz deg^{-1}), while the changes in the other frequencies have the "Bayer" character (see Fig. 1).

The temperature dependence of QCC of the Sb(1) atoms has a minimum (314.4 MHz) at 77 K and a maximum (330.4 MHz) at 285 K. The anomalous temperature dependence for QCC of the antimony atoms has been observed[1,9] for the compound $(NH_4)_2SbF_5$ in the range of 110—168 K as well as for several other ammonium salts,[10,11] which was explained by the effect of hydrogen bonds on the character of reorientation of NH_4 groups. It has been shown previously[12] that the reorientation motions of the NH_4 groups of the $[SbF_5E]$ octahedrons (E is the lone electron pair) in $(NH_4)_2SbF_5$, whose activation energies are equal to 4.5 and 10.2 kcal mol^{-1}, begin to manifest themselves in the NQR spectra at 145 and 233 K, respectively. Therefore, in order to interpret the positive temperature dependence

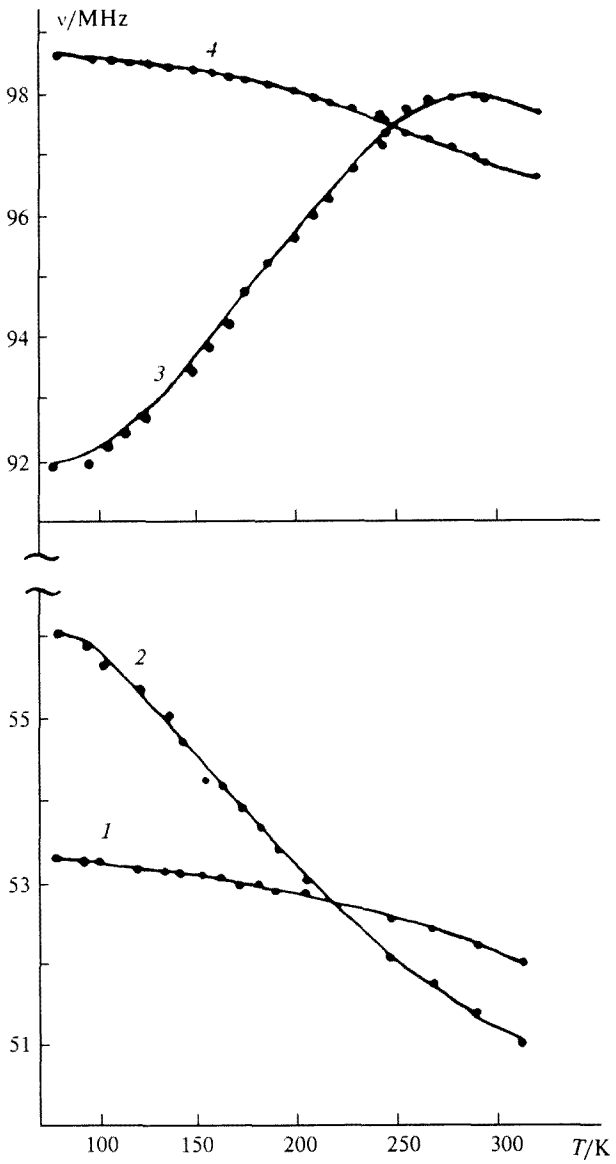

Fig. 1. Temperature dependence of the ^{121}Sb NQR frequencies (ν/MHz) in $(NH_4)_2SbCl_3F_2$ for the $\pm(1/2 \rightleftharpoons 3/2)$ and $\pm(3/2 \rightleftharpoons 5/2)$ transitions: *1* and *3*, for Sb(1); *2* and *4*, for Sb(2), respectively.

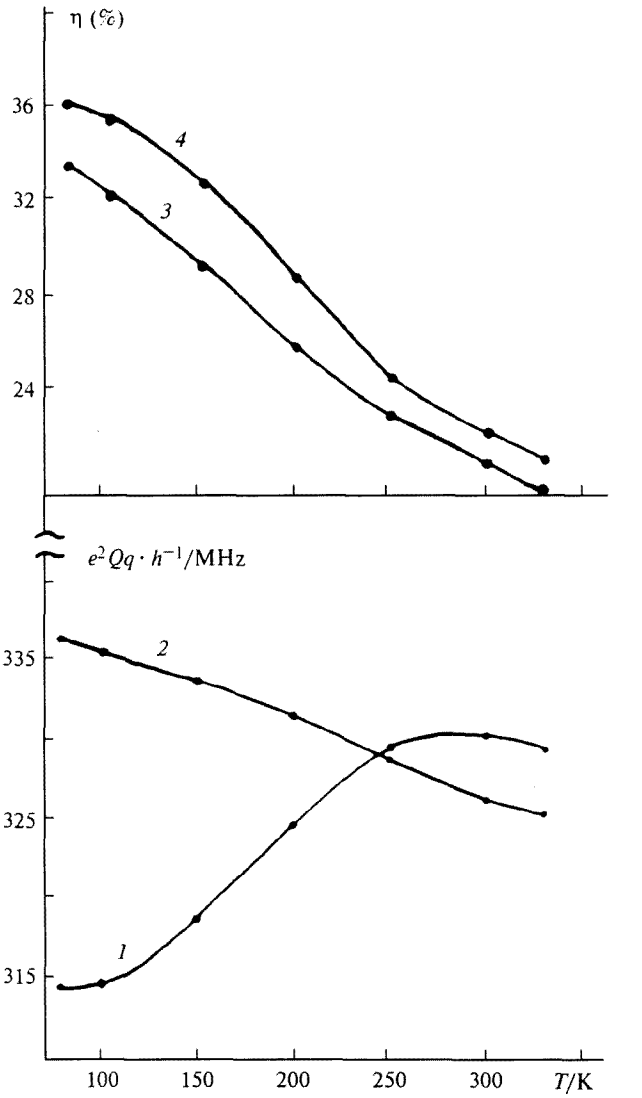

Fig. 2. Temperature dependences of the quadrupole coupling constants (QCC or $e^2Qq \cdot h^{-1}$/MHz) and asymmetry parameters of the electric field gradient (η (%)) for antimony atoms in $(NH_4)_2SbCl_3F_2$: *1* and *2* are QCC for Sb(1) and Sb(2); *3* and *4* are η for Sb(2) and Sb(1), respectively.

of QCC of the Sb(1) atoms in $(NH_4)_2SbCl_3F_2$, one should first of all elucidate the effect of the ammonium groups, which occupy four nonequivalent sites in the crystal lattice, on the electric field gradient of antimony atoms.[4]

Analysis of the temperature dependence of the EFG asymmetry parameters of the antimony atoms in $(NH_4)_2SbCl_3F_2$ points to the existence of an anomaly in the range around 250 K that is weak for Sb(2) and is more pronounced for Sb(1) (see Fig. 2, lines *3* and *4*). Comparison of these data with the temperatures at which $\partial(e^2Qq \cdot h^{-1})\partial T$ changes makes it possible to draw a conclusion about the existence of the blurred phase transition in $(NH_4)_2SbCl_3F_2$ in the range 250—285 K. Since the temperature dependences of the NQR parameters of this compound contain no jump changes and no sharp broadening of the NQR lines, this transition can be assigned to a second-order phase transition.[7]

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