^{121,123}Sb NQR study of solid phases formed in systems $(MF)_{1-x}$—$(M'F)_x$—SbF_3—H_2O (M, M' = Na, K, Rb, Cs, and NH_4)

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Crystalline substances formed in the $(MF)_{1-x}$—$(M'F)_x$—SbF_3—H_2O systems (M, M' = Na, K, Rb, Cs, and NH_4; x = 0 to 1) were investigated by ^{121,123}Sb NQR spectroscopy at 77 K. The formation of individual Sb^{III} complexes $NaCs_3Sb_4F_{16} \cdot H_2O$ and $NaKSbF_5 \cdot 1.5H_2O$, and statistically disordered mixed crystals M_{1-x}—M'_x—SbF_4 (M, M' = K, Rb, Cs, and NH_4) was established.

Key words: antimony(III), fluoride complexes, statistically disordered mixed crystals; ^{121,123}Sb NQR spectra.

Because of high sensitivity to changes in the electric field gradient (EFG) in atoms with quadrupole nuclei, to which nuclei of the ^{121}Sb and ^{123}Sb antimony isotopes belong, the method of nuclear quadrupole resonance (NQR) can be effectively used for studying the electron density distribution in molecules.[1]

Previously,[2,3] crystalline substances obtained in MF—SbF_3—H_2O systems at an MF : SbF_3 molar ratio of 1 : 1 have been studied by the ^{121,123}Sb NQR spectroscopy. This work is a continuation of investigations of the stereochemistry of antimony(III) coordination compounds by the ^{121,123}Sb NQR spectroscopy and is dedicated to the phase analysis of crystalline products formed in the $(MF)_{1-x}$—$(M'F)_x$—SbF_3—H_2O systems, where M, M' = Na, K, Rb, Cs, and NH_4; and x = 0 to 1.

Experimental

Antimony trifluoride and fluorides of alkali metals and ammonium served as starting compounds for syntheses. The interaction between SbF_3, MF, and M'F was studied in aqueous solutions in the range of the MF : M'F : SbF_3 molar ratios from 1 : 0 : 1 to 0 : 1 : 1. Individuality of the crystalline substances obtained was established by elemental and X-ray diffraction analysis and by IR spectroscopy following the procedure described previously.[2]

The ^{121,123}Sb NQR spectra of polycrystalline specimens were recorded on an ISSh-1-13 NQR spectrometer at 77 K. The values of the quadrupole coupling constant (QCC) e^2Qq_{zz} and the asymmetry parameter of the EFG tensor η were calculated from experimental NQR frequencies, as described in Ref. 1.

Results and Discussion

The interaction of alkali metal and ammonium fluorides with antimony trifluoride in aqueous solutions at an MF : SbF_3 molar ratio of 1 : 1 (M = Na, K, Rb, Cs, and NH_4) results in the formation of non-isostructural individual compounds of composition $MSbF_4$.[2] The crystal structures of $NaSbF_4$,[4] $KSbF_4$,[5] $CsSbF_4$,[6] and NH_4SbF_4 [7] are known.

The composition of solid phases formed in the $(MF)_{1-x}$—$(M'F)_x$—SbF_3—H_2O systems upon slow evaporation of the solvent depends on the nature and concentration of univalent cations of the interacting fluorides. At an MF : SbF_3 molar ratio of 1 : 1, tetrafluoroantimonates(III) are obtained whose ^{121,123}Sb NQR spectra have been studied in a wide temperature range.[3,8,9]

Systems $(NaF)_{1-x}$—$(M'F)_x$—SbF_3—H_2O (M' = K, Cs, and NH_4)

For M' = K, an individual mixed cation compound, $NaKSbF_5 \cdot 1.5H_2O$, crystallizes in the concentration range $0.25 \le x \le 0.75$. The ^{121,123}Sb NQR spectra of this compound were decribed prevously.[10]

For M' = Cs, three diferent compounds are successively formed as x increases from 0 to 1. Fragments of the ^{121,123}Sb NQR spectra (in the region 74—86 MHz) of the solid phases isolated from this system are shown in Fig. 1. By analyzing the NQR spectra we found lines of $NaSbF_4$ (see Fig. 1, spectra *1* and *2*), $CsSbF_4$ (*4*), and a new compound (*3*) whose composition is described by the empirical formula $NaCs_3Sb_4F_{16} \cdot H_2O$ (found (%): Na, 2.0; Cs, 33.1; Sb, 40.3; F, 23.7; H_2O, 1.5; calculated (%): Na, 1.90; Cs, 32.90; Sb, 40.19; F, 23.52; H_2O, 1.48).

The ^{121,123}Sb NQR spectrum of $NaCs_3Sb_4F_{16} \cdot H_2O$ (Table 1) consists of twenty signals and corresponds to four crystallographically (structurally) nonequivalent Sb atoms in the unit cell. The EFG symmetry at the nuclei

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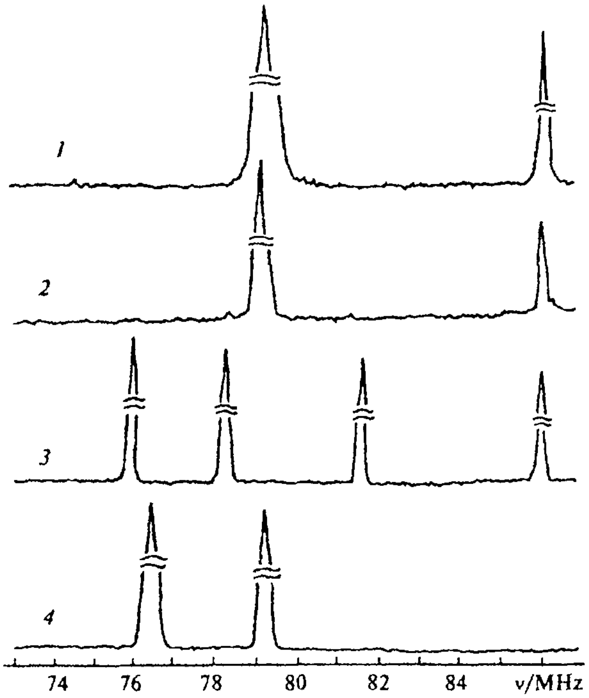

Fig. 1. Fragments of the ^{121,123}Sb NQR spectra of $NaSbF_4$ (*1*, $x = 0$; *2*, $x = 0.5$), $NaCs_3Sb_4F_{16} \cdot H_2O$ (*3*, $x = 0.5$), and $CsSbF_4$ (*4*, $x = 1$) formed in the $(NaF)_{1-x}$—$(CsF)_x$—SbF_3—H_2O system ($T = 77$ K).

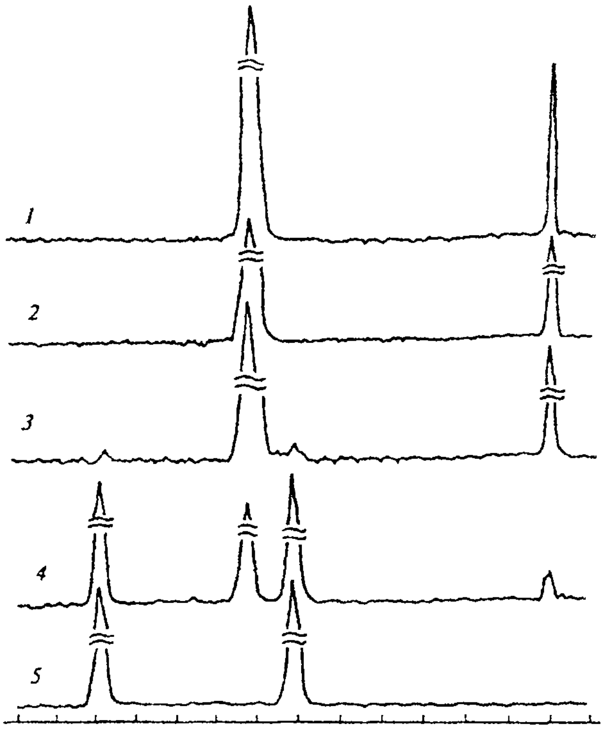

Fig. 2. Fragments of the ^{121,123}Sb NQR spectra of $NaSbF_4$ (*1*, $x = 0$; *2*, $x = 0.25$), NH_4SbF_4 (*5*, $x = 1$), and their mixture (*3*, $x = 0.5$; *4*, $x = 0.75$) formed in the $(NaF)_{1-x}$—$(NH_4)_x$—SbF_3—H_2O system ($T = 77$ K).

of antimony atoms is close to axial symmetry (the η values lie in the range from 2.6 to 4.3%), which indicates a slight distortion of the coordination polyhedra of Sb atoms in the structure of this compound. The values of the QCC shifts for $^{121(123)}$Sb in $NaCs_3Sb_4F_{16} \cdot H_2O$ relative to the antimony QCC in SbF_3 (see Ref. 3) lie within the range from −5.1 to 63.9 MHz (and from −4.5 to 77.8 MHz, respectively), which indicates a marked distinction in the electronic structure of Sb atoms in the coordination polyhedra. The study of the crystal structure of this compound is currently in progress.

For M′ = NH_4, we found that no new compounds are formed in the $(NaF)_{1-x}$—$(NH_4F)_x$—SbF_3—H_2O system in the whole range of concentrations of its initial components. Fragments of the ^{121,123}Sb NQR spectra of the solid phases formed in this system are shown in Fig. 2. Only signals of $NaSbF_4$ (see Fig. 2, spectra *1* and *2*), NH_4SbF_4 (*5*), or those of their mechanical mixture (*3* and *4*) are observed (*cf.* Ref. 3).

Systems $(MF)_{1-x}$—$(M'F)_x$—SbF_3—H_2O (M, M′ = K, Rb, Cs, and NH_4)

At $x = 0$ and 0.25, the signals of $MSbF_4$ compounds (M = K, Rb, Cs, and NH_4) studied previously[3] are observed in the ^{121,123}Sb NQR spectra of the crystalline phases obtained in the above systems. In the region $0.25 \le x \le 0.75$, the spectral lines become drastically

Table 1. ^{121,123}Sb NQR spectral parameters of $NaCs_3Sb_4F_{16} \cdot H_2O$ at 77 K

Antimony atom	Transition frequency, ν/MHz					e^2Qq_{zz}/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)			
Sb(1)	71.40	142.58	43.50	86.58	129.94	472.8	606.4	3.4
Sb(2)	75.92	151.48	46.34	91.97	138.07	505.1	644.4	4.3
Sb(3)	78.04	155.94	47.49	94.71	142.11	519.9	663.2	2.6
Sb(4)	81.38	162.51	49.41	98.33	147.50	541.8	688.7	3.4

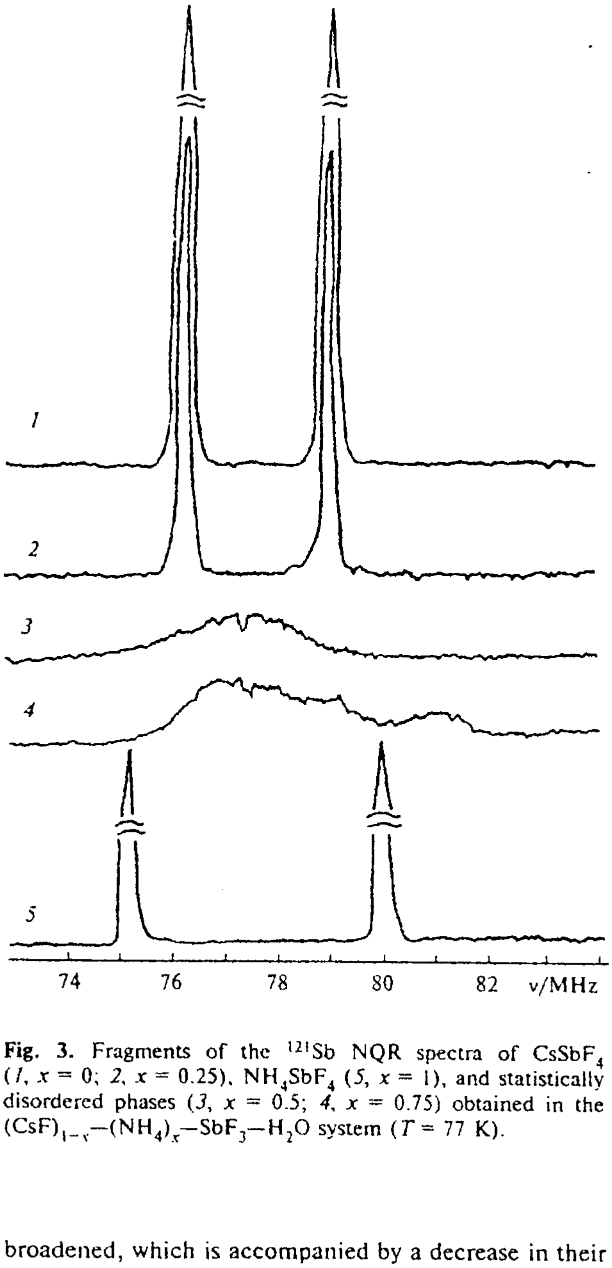

Fig. 3. Fragments of the ^{121}Sb NQR spectra of $CsSbF_4$ (*1*, $x = 0$; *2*, $x = 0.25$), NH_4SbF_4 (*5*, $x = 1$), and statistically disordered phases (*3*, $x = 0.5$; *4*, $x = 0.75$) obtained in the $(CsF)_{1-x}-(NH_4)_x-SbF_3-H_2O$ system ($T = 77$ K).

broadened, which is accompanied by a decrease in their intensities down to the point of disappearance of the signals (Figs. 3 and 4, spectra *2—4*). Broadening of NQR lines is due to the scatter of the EFG values over the entire totality of resonance atoms in the molecule. Such changes observed in the NQR spectra when varying the type and concentration of impurity are characteristic of statistically disordered systems (*cf.* Refs. 10—12). We observed similar changes in the ^{121,123}Sb NQR spectra in our studies of continuous series of substitution solid solutions formed in the interaction of isostructural potassium and rubidium pentafluoroantimonates(III).[10] The existence of disordered structures in mixed cation tetrafluoroaluminates $Rb_x(NH_4)_{1-x}AlF_4$ has also been established by ESR spectroscopy.[13]

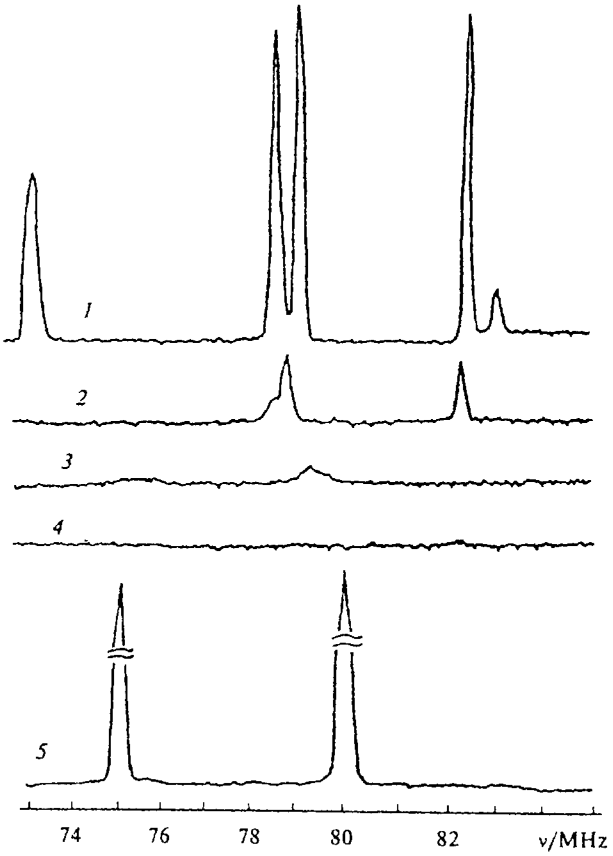

Fig. 4. Fragments of the ^{121,123}Sb NQR spectra of $KSbF_4$ (*1*, $x = 0$), NH_4SbF_4 (*5*, $x = 1$), and statistically disordered phases (*2*, $x = 0.25$; *3*, $x = 0.5$; *4*, $x = 0.75$) obtained in the $(KF)_{1-x}-(NH_4F)_x-SbF_3-H_2O$ system ($T = 77$ K).

Thus, the results of our study of the crystalline products formed in the $(MF)_{1-x}-(M'F)_x-SbF_3-H_2O$ systems (M, M′ = Na, K, Rb, Cs, and NH_4) by the ^{121,123}Sb NQR spectroscopy show that depending on the nature and concentration of univalent cations, individual antimony compounds of compositions $MSbF_4$, $NaKSbF_5 \cdot 1.5H_2O$, and $NaCs_3Sb_4F_{16} \cdot H_2O$, or disordered mixed $M_{1-x}M'_xSbF_4$ crystals can be obtained.

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