^{121,123}Sb and ^{209}Bi Nuclear Quadrupole Resonance Study of Complex Compounds of Antimony(III) and Bismuth(III) in the Temperature Range 77–400 K*

L. A. Zemnukhova and R. L. Davidovich

Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences 159, Prospect 100-letiya Vladivostoka, Vladivostok, 690022, Russia

Z. Naturforsch. **53a,** 573–584 (1998); received May 4, 1998

A large number of solid fluoride and heteroligand acidocomplex compounds of antimony(III) and bismuth(III) with single and mixed cations has been prepared from aqueous solutions. Their crystal structures and ^{121,123}Sb and ^{209}Bi NQR spectra have been investigated in a wide temperature range.

Preface

The present paper complex compounds of Sb(III) and Bi(III) are studied by the ^{121,123}Sb and ^{209}Bi NQR spectroscopy.

All the crystal line substances delt with in this work were prepared from aqueous solutions. Some complexes of Sb(III) and Bi(III) have analogs among complexes of trivalent aluminium, gallium, indium, and thallium, whose NQR spectra were reported and discussed by Deeg and Weiss [1, 2], Ramakrishnan and co-authors [3], Chihara and Nakamura [4], Guibé and Jugie [5], and Semin with co-authors [6].

The NQR spectra of ^{121,123}Sb and ^{209}Bi were measured with an ISSh-1-13 pulse NQR spectrometer equipped with a temperature accessory. The first work on NQR study of antimony(III) complexes was carried out with the help of Dr. Kravchenko [7], some successive works on temperature dependences of NQR spectra were carried out jointly with Professor G. K. Semin's Laboratory at the Institute of Organoelement Compounds, Russian Academy of Sciences. The calculations of temperature parameters of some NQR spectra were performed by Professor R. Sh. Lotfullin. X-ray analysis and another physical methods were used to study the complexes obtained along with the NQR method.

Results and Discussion

I. Antimony Trifluoride, SbF_3

Each antimony atom in the crystal structure of SbF_3 is bound to three fluorine atoms (Fig. 1), and the SbF_3 groups form a three-dimensional network through fluoride bonds [8]. The coordination polyhedron of antimony is a distorted $SbEF_6$ octahedron, where E indicates a lone electron-pair. The complete ^{121,123}Sb NQR spectrum at 77 K was reported in [7, 9]. The study of the temperature dependence of the NQR parameters for SbF_3 [10] showed the following:

1) both ^{121}Sb and ^{123}Sb NQR spectra are singlet, the signals are observed in the range 77–350 K;
2) a phase transition resulting in the piezoelectric phase occurs in the range 190–215 K;
3) the temperature dependence of ^{121}Sb NQR spectral parameters in SbF_3 is explained on the basis of Bayer's

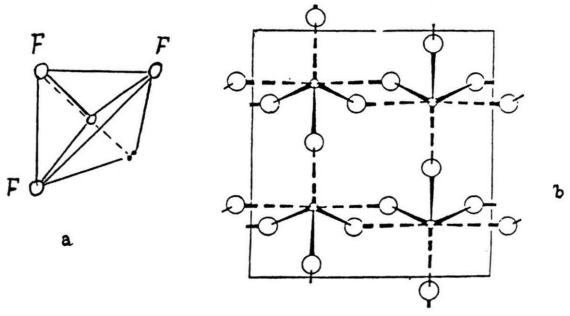


Fig. 1. The scheme of SbF_3 structure: a) antimony(III) polyhedron, b) the projection of the structure SbF_3.

* Presented at the XIVth International Symposium on Nuclear Quadrupole Interactions, Pisa, Italy, July 20–25, 1997.

Reprint requests to Dr. L. A. Zemnukhova;
Fax: 7(4232) 311889; E-mail: chemi@online.ru.

0932-0784 / 98 / 0600-0573 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

theory and described by the formula [11]:

$$\nu_{exp} = \nu_{Bayer} + \sum_{n=0}^{6} B_n T^n . \quad (1)$$

4) unlike $SbCl_3$ [12], the asymmetry parameter varies in the range 4.3÷5.6% and increases nonlinearly as the temperature increases;
5) a zero-magnetic-field splitting of line corresponding to the (1/2↔3/2) transition in the range 92–275 K is observed.

II. Homoligand Fluoride Complexes of Antimony(III)

The NQR spectra of antimony(III) fluoride complexes with monovalent MSb_4F_{13}, MSb_3F_{10}, MSb_2F_7, $M_3Sb_4F_{15}$, $MSbF_4$, and M_2SbF_5 cations are studied.

Complexes MSb_4F_{13}

The MSb_4F_{13} complexes (M = K, Rb, Cs, and NH_4) are isostructural at room temperature. The structure of the complex KSb_4F_{13} [13] contains $[Sb_4F_{13}]^-$ anions built of four SbF_3 molecules shifted to a thirteenth fluorine atom by weaker "secondary" bonds. The investigation of the $^{121,123}Sb$ NQR spectra of MSb_4F_{13} complexes has shown that

1) NQR signals can be observed only at low temperatures;
2) complexes with M=K and Rb [14] exhibit singlet, while those with M=Cs and NH_4 [7] exhibit doublet NQR spectra at 77 K;
3) the temperature coefficients of the NQR frequencies for $RbSb_4F_{13}$ are negative [14] like those for SbF_3, but their values differ from one another in the range 77–270 K (Fig. 2);
4) the complex $RbSb_4F_{13}$ exhibits piezoelectric properties.

Complexes MSb_3F_{10}

Only complex $NaSb_3F_{10}$ was studied. Earlier, it was erroneously described as $NaSb_2F_7$. The structure of $NaSb_3F_{10}$ and its NQR spectrum at 77 K were investigated in [15] and [7], respectively.

Complexes MSb_2F_7

A group of heptafluoroantimonates MSb_2F_7 (M=K, Rb, Cs, Tl, NH_4, Et_2NH_2, CN_3H_6, CN_4H_7, $C_2N_3H_4$, Nic, and Gly) has been investigated. The crystal structures of KSb_2F_7 [16], $CsSb_2F_7$ [17], and $(C_2N_3H_4)Sb_2F_7$ [14] are known. All the antimonates(III), except $CsSb_2F_7$, have

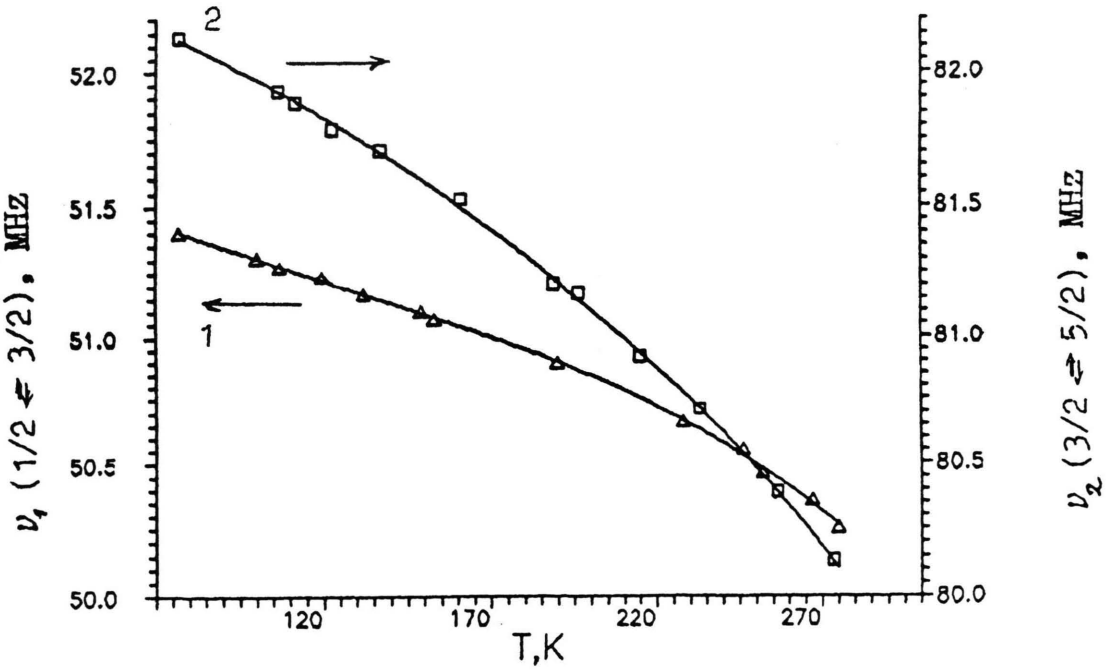


Fig. 2. Temperature dependence of the ^{123}Sb NQR frequencies in $RbSb_4F_{13}$: 1 – ν_1=±(1/2 ↔ 3/2); 2 – ν_2=±(3/2 ↔ 5/2).

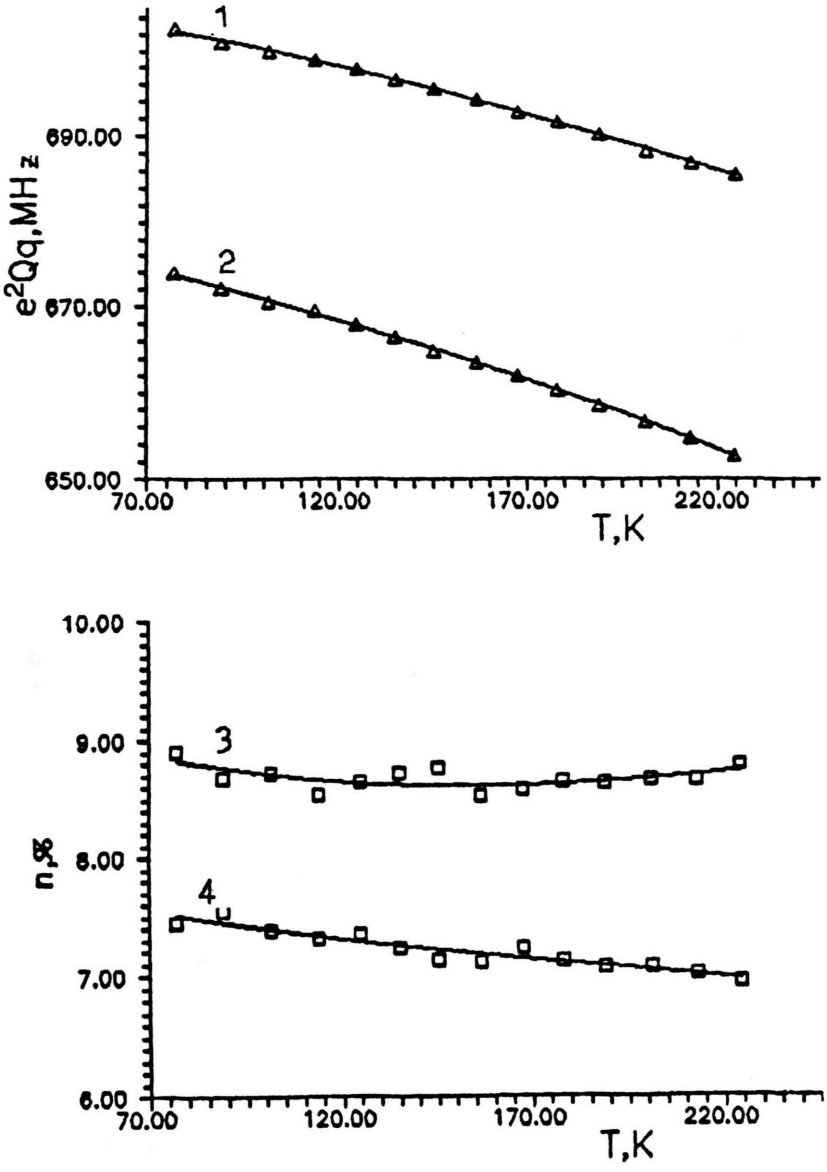


Fig. 3. Temperature dependence of the quadrupole coupling constants e^2Qq (1 and 2 for Sb_1 and Sb_2) and asymmetry parameters η (3 and 4 for Sb_1 and Sb_2) for the antimony atoms ^{123}Sb in KSb_2F_7.

multiplet $^{121,123}Sb$ NQR spectra at 77 K [7, 18–23], similarly to analogous gallium compounds [1]. $TlSb_2F_7$ [18] has the most complicated NQR spectrum corresponding to six nonequivalent sites of the antimony atoms in the crystal lattice. The temperature variations of the NQR parameters for MSb_2F_7 (M = K, Tl, and CN_3H_6) are studied [14]. Their NQR spectra are characterized by fading the signals in the range 220–290 K (Figs. 3–5). A superionic phase transition occurs in $TlSb_2F_7$ at 240 K [24].

Complexes $M_3Sb_4F_{15}$

The study of the crystal structure of $M_3Sb_4F_{15}$ complexes (M = K and Cs) is now in progress. $K_3Sb_4F_{15}$ exhibits piezoelectric properties. The complexes have multiplet spectra at 77 K [14].

Complexes $MSbF_4$

Tetrafluoroantimonates $MSbF_4$ (M = Na, K, Rb, Cs, Tl, NH_4, Pr_2NH_2, Et_2NH_2, Et_4N, CN_3H_6, CN_4H_7, Nic,

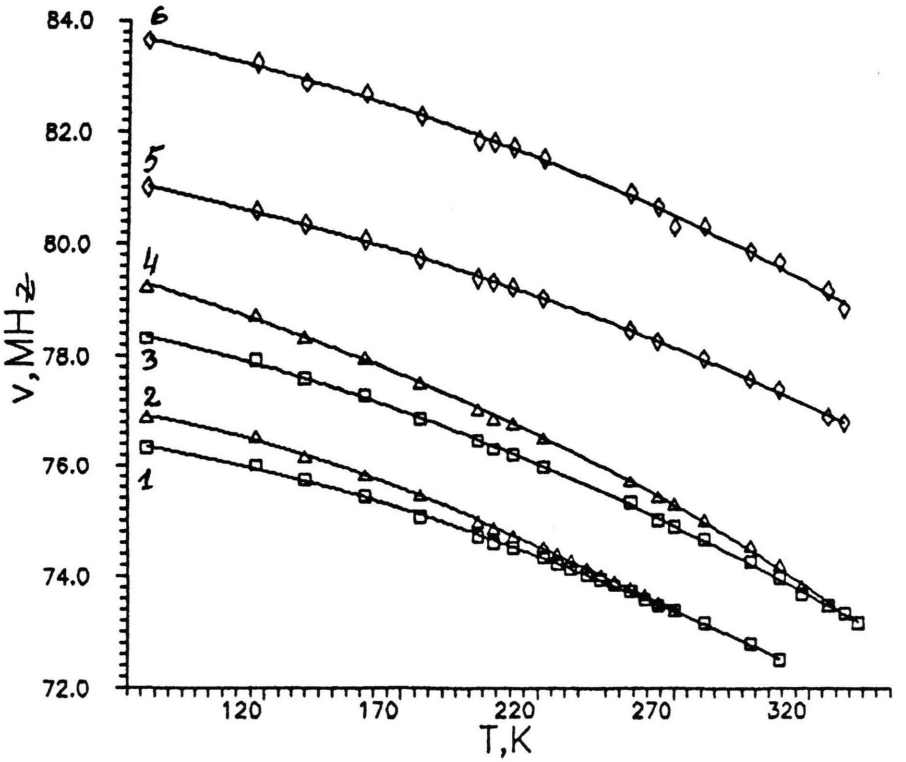


Fig. 4. Temperature dependence of the ^{121}Sb NQR frequencies $\nu = \pm(1/2 \leftrightarrow 3/2)$ in $TlSb_2F_7$ (1–6 for Sb_{1-6}).

and Gly) are not isostructural. The crystal structures were determined for $NaSbF_4$ [25], $KSbF_4$ [26], $TlSbF_4$ [27], $CN_3H_6SbF_4$ [28], $CsSbF_4$ [27a], and NH_4SbF_4 [27]. The NQR spectra of $MSbF_4$ at 77 K have different multiplicity depending on the character of the cation [7, 18–23]. $KSbF_4$, containing the $[Sb_4F_{16}]^{4-}$ anion in its structure, has the most complicated quadruplet spectrum. The temperature dependence of the NQR spectra for $MSbF_4$ (M = Na, K, Tl, NH_4, and CN_3H_6) was studied [29–31]. The temperature range in which the signals are observed depends on the cation. A phase transition in $KSbF_4$ at 190 K was found from its NQR spectrum. The asymmetry parameter η for $MSbF_4$ (M = NH_4 and CN_3H_6) increases with temperature; this may be due to the presence of hydrogen bonds in these complexes. Superionic phase transitions in complexes $MSbF_4$ (M = K and CN_3H_6) were also observed at 483 and 253 K [29, 32].

Complexes M_2SbF_5

Pentafluoroantimonates M_2SbF_5 (M = Na, K, Rb, Cs, Tl, NH_4, Et_2NH_2, Et_4N, Bu_4N, CN_3H_6, and CN_4H_7) are the most investigated group among fluoride complexes of antimony(III). Some of them form the isostructural series. The structures of the following pentafluoroantimonates(III) are known: Na_2SbF_5 [33], K_2SbF_5 [34, 35] and $(NH_4)_2SbF_5$ [36, 37]. The $[SbF_5]^{2-}$ anion in M_2SbF_5 was shown to have a distorted octahedral SbF_5 configuration with the lone pair in one of its vertices.

All pentafluoroantimonates(III), except $(CN_4H_7)_2SbF_5$, have singlet ^{121,123}Sb NQR spectra at 77 K [7, 18–20]. Their NQR parameters depend on the cation. The temperature dependence of NQR parameters for all (even isostructural) complexes are different, and their specific features depend on the character on the cation [31, 38–41]. A change in the multiplicity of the NQR spectrum was found in K_2SbF_5, and the transition from the paraelectric phase to the commensurate one was shown to pass via incommensurate and then commensurate-modulated phases. The NQR frequencies in $(NH_4)_2SbF_5$ increase anomalously with temperature. This complex was also studied by Nakamura [38].

A nonlinear change of the asymmetry parameter η is observed for the remaining M_2SbF_5 (M = Na, Rb, Cs, Tl, and CN_3H_6) complexes. The complexes M_2SbF_5

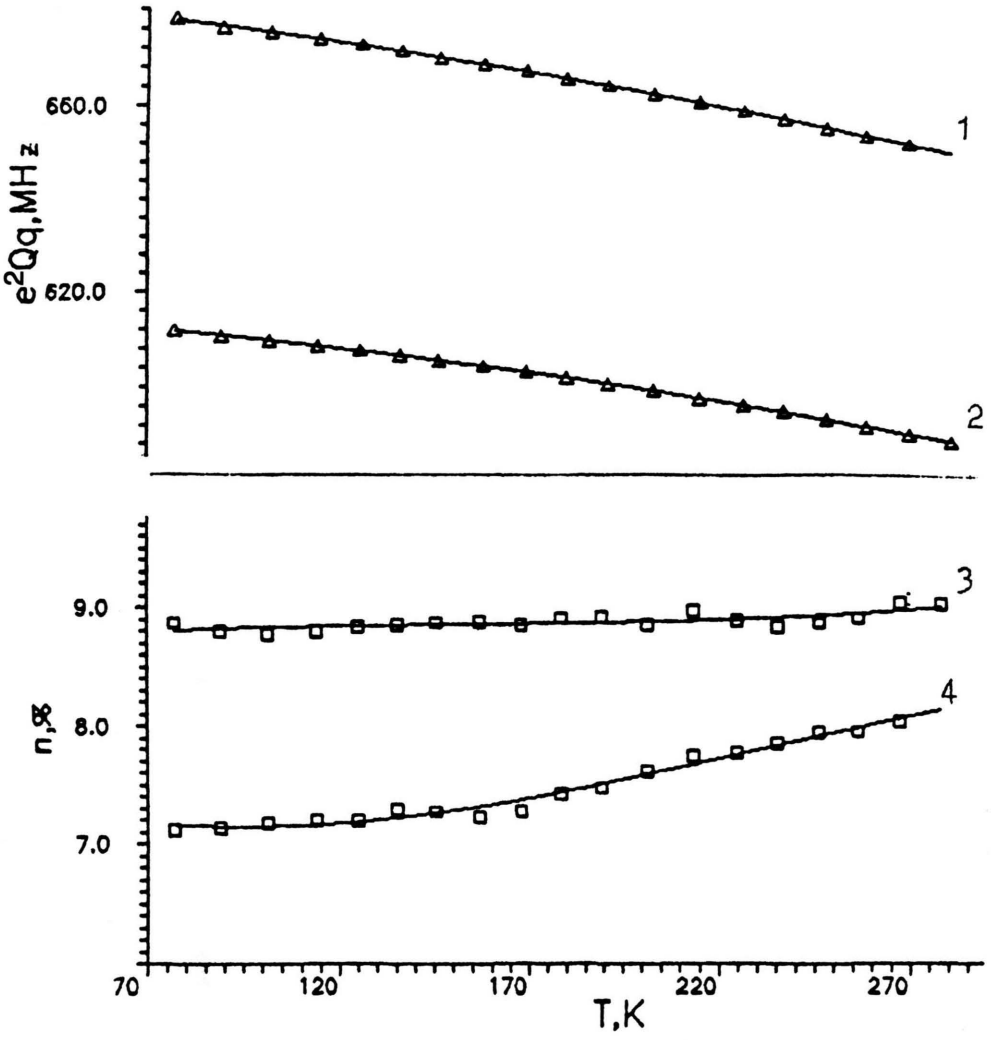


Fig. 5. Temperature dependence of the quadrupole coupling constants e^2Qq (1 and 2 for Sb_2 and Sb_1) and asymmetry parameters η (3 and 4 for Sb_1 and Sb_2) for the antimony atoms ^{123}Sb in $CN_3H_6Sb_2F_7$.

(M=Na, K, Rb, Cs, and NH_4) were also shown to be ionic conductors, while $(NH_4)_2SbF_5$ is a superionic conductor [42]. Moreover, Na_2SbF_5 exhibits piezoelectric properties.

III. Fluorocomplexes of Antimony(III) with Mixed Cations

Two types of antimony(III) fluorocomplexes with mixed cations, $M_{2-x}M'_xSbF_5$ and $M_{1-x}M'_xSbF_4$ (M, M′=Na, K, Rb, Cs, and NH_4), were prepared.

Pentafluoride Complexes $M_{2-x}M'_xSbF_5$.

The individual complexes $NaM'SbF_5 \cdot 1.5\ H_2O$ (M′= K and Rb) are isostructural only at room temperature, and the solid solutions of composition $M_{2-x}M'_xSbF_5$ (M=K, Rb, and Cs; M′=Rb and NH_4), isostructural to M_2SbF_5, contain a complex $[SbF_5]^{2-}$ anion [43]. The $^{121,123}Sb$ NQR spectra of these substances have the following peculiarities:

1) unlike M_2SbF_5, the singlet spectra of all pentafluoroantimonates with mixed cations are observed only at low temperatures;

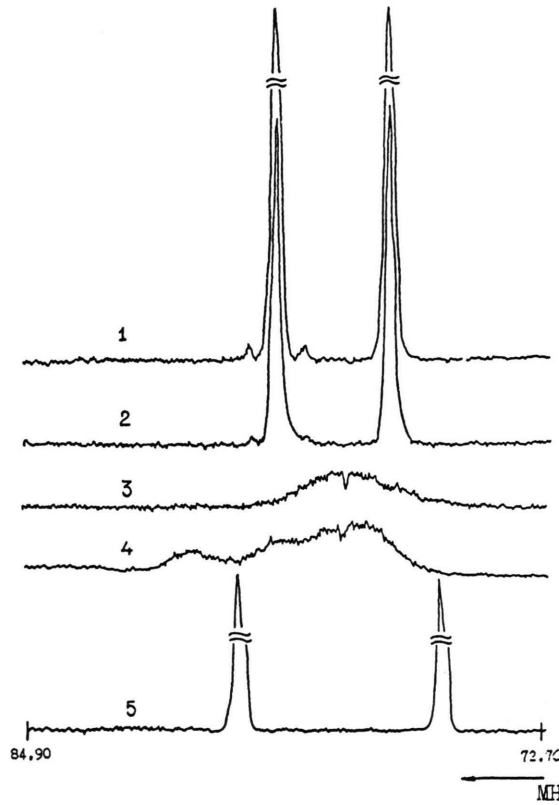


Fig. 6. The NQR ^{123}Sb spectrum of the system CsF : NH_4F : SbF_3 in the region 72.70–84.90 MHz at 77 K for the molar ratios: 1 : 0 : 1 (1); 0.75 : 0.25 : 1 (2); 0.5 : 0.5 : 1 (3); 0.25 : 0.75 : 1 (4); 0 : 1 : 1 (5).

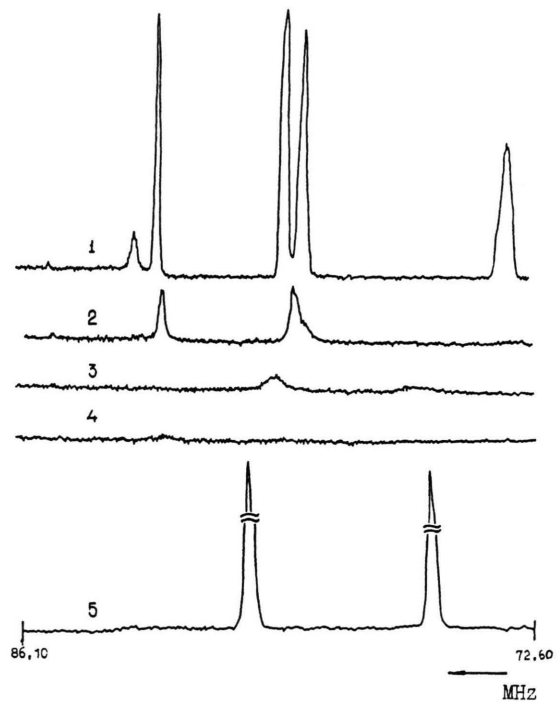


Fig. 7. The NQR ^{123}Sb spectrum of the system KF : NH_4F : SbF_3 in the region 72.60–86.10 MHz at 77 K for the molar ratios: 1 : 0 : 1 (1); 0.75 : 0.25 : 1 (2); 0.5 : 0.5 : 1 (3); 0.25 : 0.75 : 1 (4); 0 : 1 : 1 (5).

2) a second-order phase transition occurs for the complexes $NaM'SbF_5 \cdot 1.5\ H_2O$ in the range 160–180 K;
3) the complete NQR spectrum for the solid solutions of composition $M_{2-x}M'_xSbF_5$ is observed in a narrow temperature range (77–120 K);
4) a sharp decrease in the integrated intensities of the signals and the line broadening from 180 to 1400 kHz are observed at $x > 0.25$; no NQR signals for the substances with $M' = NH_4$ are observed even at 77 K;
5) the $[SbF_5]^{2-}$ polyhedra show an increase in the symmetry of the electric field gradient on the antimony atom.

Tetrafluoride Complexes $M_{1-x}M'_xSbF_4$

The solid solutions of composition $MM'SbF_4$ (M = K and Cs; M' = Cs and NH_4) and a new complex $NaCs_3Sb_4F_{16} \cdot H_2O$ were prepared by the reaction of tetrafluoroantimonates $MSbF_4$ and $M'SbF_4$ [14]. A preliminary investigation shows that $NaCs_3Sb_4F_{16} \cdot H_2O$ probably has the $[Sb_4F_{16}]^{4-}$ anion, as $KSbF_4$. This new complex has a multiplet NQR spectrum corresponding to four nonequivalent positions of the antimony atoms in the unit cell, and the complex $[Sb_4F_{16}]^{4-}$ anion exists in the temperature range 77–295 K. The NQR spectra of the solid solutions of composition $M_{1-x}M'_xSbF_4$ either have very broad lines at 77 K (Fig. 6) or are not detected at all (Figure 7).

IV. Fluorocomplexes of Antimony with Mixed Ligands

A large number of heteroligand complexes of antimony(III) was synthesized. Their compositions belong to six types: $M_4Sb_3F_{13-x}Y_x$, $M_3Sb_2F_{9-x}Y_x$, $MSb_2F_{7-x}Y_x$, $MSbF_{4-x}Y_x$, $M_2SbF_{5-x}Y_x$, and $M_3SbF_{6-x}Y_x$.

Complexes $M_4Sb_3F_{13-x}Y_x$

Our attempts to obtain fluoride analogs of such composition from aqueous solutions failed. Only the complex $M_4Sb_3F_{13-x}Y_x$ (M = K; Y = Cl, x=6), erroneously

described as $K_3Sb_2Cl_4F_5$, was studied [44]. The study of the structure of $K_4Sb_3F_7Cl_6$ is now in progress. This compound exhibits piezoelectric properties. Its NQR spectrum, measured at 77 K, has a multiplet pattern that shows that the antimony atoms occupy three nonequivalent sites [14].

Nonaligand Complexes $M_3Sb_2F_{9-x}Y_x$

Five complexes of this composition, belonging to the groups nitrate-fluorides and sulphate-fluorides, were studied. Among complexes $M_3Sb_2F_9$, the crystal structure of $[Co(NH_3)_6]Sb_2F_9$ has been determined. It contains $[Sb_2F_9]^{3-}$ anions which consist of distorted octahedral $SbEF_5$ polyhedra [45]. The structure of $K_3Sb_2F_7(NO_3)_2$ was found to contain the dimeric $[Sb_2F_7]^-$ anions consisting of distorted trigonal $SbEF_4$ bipyramids [46]. The structure of $Cs_3Sb_2F_6(NO_3)_3$ is built of zigzag-like $[Sb_2F_6(NO_3)_3]_n^{3n-}$ ribbons consisting of SbF_2O_3 octahedra [47]. The NQR spectra of these complexes are singlet [48] and have lower frequencies in the octahedral polyhedra.

Complexes $M_6Sb_4F_{12}(SO_4)_3$ (M = Rb, Cs, and NH_4) are isostructural [49]. Compounds with Rb and NH_4 cations are piezoelectric, while the ammonium compound has anomalous dielectric properties in the temperature range from 240 to 260 K. The structure of $(NH_4)_6Sb_4F_{12}(SO_4)_3$ has six nonequivalent sites of the antimony atoms that belong to the octahedra of two different types: $SbEF_4O_2$ and $SbEF_3O_3$ [50]. The NQR spectra studied by us [51] and Chihara [52] at 77 K have a complicated multiplet structure corresponding to four nonequivalent sites of the antimony atoms and weak broad lines.

Heptaligand Complexes $MSb_2F_{7-x}Y_x$

The NQR spectra of two complexes with mixed ligands, $NaSb_2F_6(OH) \cdot H_2O$ [53] and $RbSb_2F_5C_2O_4$ [54], were investigated. The structure of $NaSb_2F_6(OH) \cdot H_2O$ contains dimeric $[Sb_2F_6(OH)]^-$ anions consisting of two SbF_3 groups linked via a bridge hydroxyl group. The structure of $[Sb_2F_6OH]^-$ anions is similar to that of $CsSb_2F_7$. However, unlike the singlet spectrum of $CsSb_2F_7$, the heptaligand complex has a doublet NQR spectrum.

The anionic $[Sb_2F_5C_2O_4]_n^{n-}$, layers consisting of two different antimony polyhedra, the pentagonal $Sb(1)EF_5O_2$ bipyramids and the trigonal $Sb(2)EF_2O_2$ bipyramids, form the basis for the structure of complex $RbSb_2F_5C_2O_4$, which has doublet NQR spectra at 77 K and 298 K. The asymmetry parameters differ considerably from one another.

Tetraligand Complexes $MSbF_{4-x}Y_x$

Tetrafluoroantimonates(III) with mixed ligands are the largest group of complexes studied by the NQR method. They can be divided into the following series:

1) complexes $MSbF_3Y$ (Y = Cl [7, 55], Br [56, 57], NO_3 [31, 48], H_2PO_4 [58], and NCS [19]);
2) complexes $MSbF_2Y_2$ (Y = SO_4 [19], SeO_4 [59], C_2O_4 [14], and $C_6H_6O_7$ [19]);
3) complexes $MSbFY_3$ (Y = PO_4 [58]).

As a rule, these complexes have singlet NQR spectra. Their parameters, as well as their temperature dependence, depend on the type of the complex and the nature of the cation. The asymmetry parameters η of the antimony atoms in complexes $MSbF_{4-x}Y_x$ have higher values than those in SbF_3. The NQR spectrum of $CsSbF_3Cl$ has been analysed in more detail in at 77–330 K [60]. The layers of isolated $[Sb_4F_{12}Cl_4]^{4-}$ anions form the basis for the structure of the complex [61]. The coordination polyhedron of antimony is a distorted $SbEF_3Cl_2$ octahedron. The temperature dependence of the experimental values of QCC is described by the formula:

$$\left(e^2 Qq_{zz}\right)_{\exp} = \left(e^2 Qq_{zz}\right)_{Bayer} + \sum_{n=0}^{3} B_n T^n , \qquad (2)$$

where $B_0 = 27.913 \cdot 10^{-2}$; $B_1 = 43.413 \cdot 10^{-4}$; $B_2 = -13.349 \cdot 10^{-5}$; and $B_3 = -23.253 \cdot 10^{-9}$.

The temperature dependence of the asymmetry parameter η is not described by the Bayer's theory. We assume that the redistribution of the electron density between the electric field gradient (EFG) components e^2Qq_{xx} and e^2Qq_{yy} at the ^{123}Sb nucleus, resulting in a change in the asymmetry parameter, is due to the volume effect in $CsSbF_3Cl$ crystal.

Pentaligand Complexes $M_2SbF_{5-x}Y_x$

The $^{121,123}Sb$ NQR spectra of the following compounds were studied:

1) complex $K_4Sb_2F_7(NO_3)_3$ [48];
2) complexes $Rb_2SbF_3(NO_3)_2$ [48] and $M_2SbF_3Y_2$ (Y = SO_4 [9, 41, 51], SeO_4 [59] and C_2O_4 [9]);
3) complexes $M_2SbF_2Cl_3$ [62].

They have different multiplicities depending on the type of the complex and the cation nature.

Hexaligand Complexes $M_3SbF_{6-x}Y_x$

The NQR spectra of hexafluoride complexes of such composition are unknown. Among mixed hexafluoroligand complexes, the compounds $M_3SbF_3(NO_3)_3$ (M = Rb and NH_4) with singlet spectra at 77 K [48] and $Cs_3SbF_2(C_2O_4)_2 \cdot 3\ H_2O$ were studied. No NQR signals were detected in the last complex [14].

V. Adducts SbF_3L_n

The acceptor properties of the SbX_3 halides (X = Cl, Br, and I), which are typical Lewis acids, are well known [1–3]. The Lewis acid properties of Sb(III) halides increase in the sequence $SbCl_3 > SbBr_3 > SbI_3$, but the available data are too scarce to place SbF_3 in this series [63].

We have synthesized and investigated by the NQR ^{121,123}Sb method three groups of new adducts of SbF_3 with the oxygen-containing donor ligands (dimethylsulphoxide (DMSO) [64], dimethylformamide (DMF) [19], and glycine (Gly) [22]) and with the nitrogen-containing donor ligands (nicotinic amide (Nic) [21]). Specific features of their spectra follow:

The 2:1 Adducts, $2SbF_3L$ (L = DMSO and Gly)

Such type of complexes of SbF_3 with an organic ligand were prepared for the first time. They have doublet NQR spectra. The transition frequencies and asymmetry parameters for the Sb(1) and Sb(2) atoms are higher than those in SbF_3. The adduct with DMSO exhibits piezoelectric properties.

The 1:1 Adducts, SbF_3L (L = DMSO, DMF, and Gly).

The structure of $SbF_3 \cdot$ Gly consists of molecular complexes $[SbF_3(^+NH_3CH_2COO^-)]$ linked via hydrogen bonds in a three-dimensional framework. The ^{121,123}Sb NQR spectra of the SbF_3L adducts are singlet. The frequencies in the adducts with DMSO and DMF are close to those for SbF_3, but the asymmetry parameters are higher.

The 1:2 Adducts, SbF_3L_2 (L = DMSO and Nic)

The NQR spectrum of $SbF_3 \cdot 2$ DMSO has not been detected. The complex $SbF_3 \cdot 2$ Nic has a singlet NQR spectrum with lower transition frequencies and smaller asymmetry parameter than those in SbF_3.

VI. Oxofluoride Compounds of Sb(III)

Previously, two modifications of antimony oxofluoride SbOF were obtained by hydrolysis of SbF_3 [65]. Their NQR spectra are unknown up to date. We have also synthesized the SbOF · Gly adduct but failed to detect the NQR signals in this compound even at 77 K [22]. We have prepared another oxofluoride, $Sb_3O_2F_5$ [66], and some complexes of the $Sb_2OF_4 \cdot 2$ Urea [67] and $Sb_2OF_4 \cdot MX$ types (M = K, Rb, and Cs; X = Cl, Br, and I [68]).

Oxofluoride $Sb_3O_2F_5$

The structure of $Sb_3O_2F_5$ crystals consists of the polymeric layers $(Sb_3O_2F_5)_n$ of four different polyhedra with mixed ligands $SbEX_4$. The NQR spectrum of this antimony(III) oxofluoride at 77 K has a complicated multiplet structure of 20 lines (Table 1). Moreover, a zero-magnetic-field splitting of line corresponding to the $(1/2 \leftrightarrow 3/2)$ transition similar to that for SbF_3 [14] is observed (Figure 8).

Adduct $Sb_2OF_4 \cdot 2(NH_2)_2CO$

We investigated the structure of $Sb_2OF_4 \cdot 2$ Urea [67] simultaneously and independently of Bourgault and coworkers [69] and showed that it consists of the dimeric molecular complexes $[\{SbF_2CO(NH_2)_2\}_2O]$ with two nonequivalent antimony atoms. This compound has a doublet NQR spectrum in the range 77–365 K. The temperature coefficients of the asymmetry parameters are positive [31].

Table 1. The NQR ^{121}Sb parameters in some compounds of antimony(III).

Compound	T, K	η, %	e^2Qq MHz	Reference
SbF_3	77	4.3	536.7	[7, 9]
	298	5.2	527.1	[10]
$Sb_3O_2F_5$	77	7.7	499.5	[14]
		23.8	499.6	
		36.0	659.2	
		36.7	754.2	
$SbF(SeO_4) \cdot H_2O$	77	2.8	485.4	[70]
		7.6	433.6	
	298	signals were not observed		
$SbF(OH)(HSO_4)$	77	11.8	482.7	[70]
$RbSbF_2SO_4$	77	19.3	542.2	[59]
	298	20.3	524.5	
$CsSbF_2SO_4$	77	1.6	419.2	[59]
K_2SbF_5	77	8.8	462.8	[7, 40]
SbHedta	77	12.7	384.7	[76]

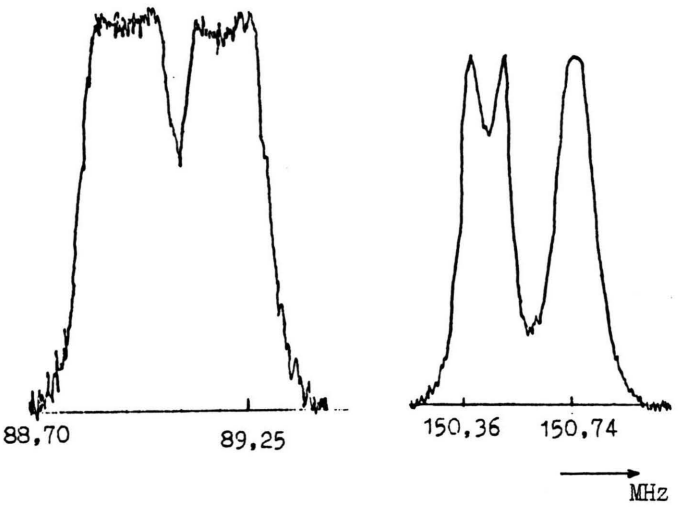
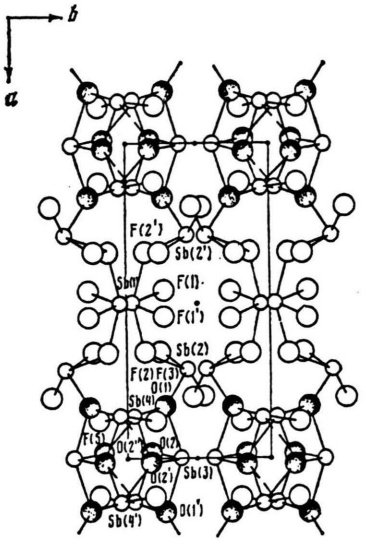


Fig. 8. Fragments of the ^{123}Sb NQR spectrum for $Sb_3O_3F_5$ (77 K).



The projection of the structure of $Sb_2O_3F_5$ along the axis *c*.

Complexes $Sb_2OF_4 \cdot MX$

Oxofluoride complexes $Sb_2OF_4 \cdot MX$ (M = K, Rb, Cs, and NH_4; X = Cl, Br, and I) have not been adequately studied. No NQR signals were observed in these compounds. Since they are often formed as mixtures with heptafluoroantimonates MSb_2F_7 whose signals are well detected, the MSb_2F_6Cl composition was erroneously ascribed to these complexes [7].

VII. The Products of Fluorine Substitution in SbF_3

Two compounds were synthesized: $SbF(SeO_4) \cdot H_2O$ and $SbF(OH)(HSO_4)$ [70]. A distorted $SbEF_5$ octahedron is the coordination polyhedron of antimony in the structure of antimony(III) selenate-fluoride. The $^{121,123}Sb$ NQR spectrum of $SbF(SeO_4) \cdot H_2O$ is a multiplet at 77 K but it has not been observed at room temperature, which likely indicates a phase transition in this compound (Table 1). According to the NQR spectrum of $SbF(OH)(HSO_4)$ measured at 77 K, the antimony atoms in this compound are equivalent, and their asymmetry parameter η is larger than that in selenatofluoroantimonate(III).

VIII. Halogen-Containing Complexes of Bismuth(III)

The NQR ^{209}Bi spectra of complex halogen-containing compounds of bismuth(III) are less investigated than the antimony(III) complexes. This is likely due to the fact that many halogen-containing bismuth(III) complexes have a regular octahedral surrounding in their structures. We have studied the ^{209}Bi NQR spectra of the following compounds: nonaligand dibismuthate, tetraligand and pentaligand bismuthates.

Table 2. The NQR ^{209}Bi parameters in some compounds of bismuth(III).

Compound	*T*, K	η, %	e^2Qq MHz	Reference
$Bi_2(SO_4)_3 \cdot 3H_2O$	77	28.0	446.8	[71]
	298	25.0	437.5	
$MBi(SO_4)_2$	77			[14]
(M-K, Rb, NH_4)	298	signals were not observed		
$Rb_3Bi_2Cl_5(SO_4)_2 \cdot 3\,H_2O$	77	62.3	377.7	[71]
		69.8	405.2	
$KBiCl_2SO_4$	77	77.1	464.8	[71]
	298	81.0	438.1	
$NH_4BiCl_2SO_4$	77	84.0	469.9	[71]
	298	84.5	442.6	
$MBiCl_2SO_4$	77			[14]
(M-Rb, CN_3H_6)	298	signals were not observed		
K_2BiF_5	77	40.7	144.9	[14]
BiHedta	77	39.0	261.1	[76]

Nonaligand Complexes $M_3Bi_2Cl_{9-x}Y_x$

Several chloronitrate and chlorosulphate nonaligand bismuth(III) complexes were studied. Some of them are

piezoelectrics. NQR spectra for most compounds are not detected. A doublet NQR spectrum [71] was observed for $Rb_3Bi_2Cl_5(SO_4)_2 \cdot 3\ H_2O$, whose structure contains two nonequivalent sites of bismuth atoms [72] with high asymmetry parameters (Table 2).

Tetraligand Complexes $MBiCl_{4-x}Y_x$

We synthesized chloronitrate and chlorosulphate bismuth(III) complexes of composition $MBiCl_3NO_3$ (M = K and CN_3H_6) and $MBiCl_2SO_4$ (M = K, Rb, NH_4, and CN_3H_6), respectively [14, 71, 73]. The latter form an isostructural series. Some of these complexes are piezoelectric.

The bismuth polyhedron in $MBiCl_2SO_4$ [74] can be described as a distorted $[BiECl_2O_3]^-$ octahedron similar to the $[SbEF_2O_3]^-$ anions in $MSbF_2SO_4$ compounds [75]. No NQR signals were detected in the compounds (CN_3H_6) $BiCl_3NO_3$ and $MBiCl_2SO_4$ (M = Rb and CN_3H_6); the remaining complexes have singlet spectra observed only at low temperatures and high values of the asymmetry parameters compared to complex tetrafluoroantimonates(III) (Table 2).

Pentafluorobismuthate K_2BiF_5

This complex was prepared from a solution in our laboratory [14]. The ^{209}Bi NQR spectrum of potassium pentafluorobismuthate(III) is a singlet at 77 K and near room temperature, as for K_2SbF_5 (Figure 9). Unlike the antimony complex K_2SbF_5, it has no phase transitions with change of multiplicity in the range 77–270 K. The asymmetry parameter of bismuth atoms in K_2BiF_5 is larger by almost an order of magnitude than that for the antimony atoms in K_2SbF_5 [40]. It should be noted that the asymmetry parameters of bismuth atoms are, as a rule, much larger than those in similar antimony(III) compounds, which was also confirmed in our studies of the ^{121,123}Sb and ^{209}Bi NQR spectra of ethylenediaminetetraacetates [76].

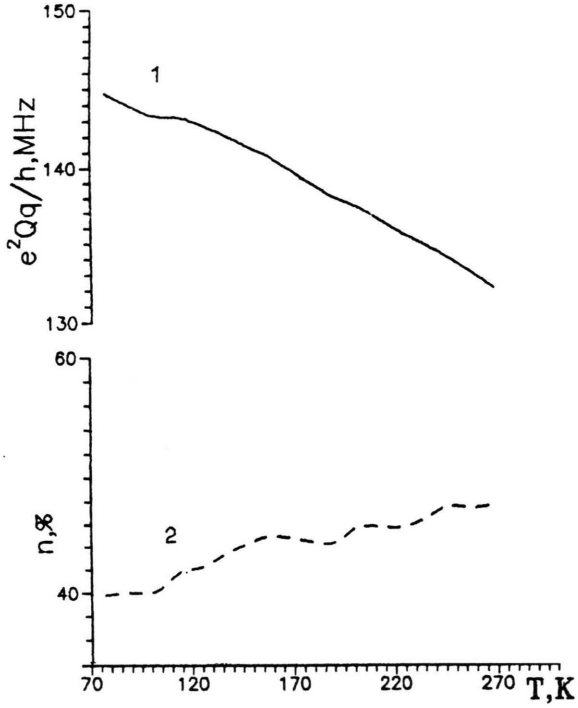


Fig. 9. Temperature dependence of the ^{209}Bi quadrupole coupling constant (1) and asymmetry parameter (2) of K_2BiF_5.

Conclusions

The investigation of complex compounds of antimony(III) and bismuth(III) by NQR spectroscopy on the ^{121,123}Sb and ^{209}Bi nuclei allowed us to obtain information on the structure and properties of these compounds in the temperature range from 77 to about 400 K and to show that many compounds, first of all complex fluorides of antimony(III), have special physical properties related to phase transitions.

[1] T. Deeg and A. Weiss, Ber. Bunsengess. Phys. Chem. **79,** 497 (1975).
[2] K. Yamada and A. Weiss, Ber. Bunsengess. Phys. Chem. **87,** 932 (1983).
[3] L. Ramakrishnan, S. Soundararajan, V. S. S. Sastry, and J. Ramakrishna, Coord. Chem. Rev. **22,** 123 (1977).
[4] H. Chihara and N. Nakamura, Landolt-Bornstein. New Series. III. B.20. Kernquadrupolresonanz-Daten. 1988.
[5] L. Guibé and G. Jugie, in: Molecular Interactions. Edited by H. Ratajczak and W. J. Orville-Thomas, Moscow 1984, p. 344.
[6] G. K. Semin, T. A. Babushkina, and G. G. Yakobson, Primenenie yadernogo kvadrupol'nogo rezonansa v khimii [Application of Nuclear Quadrupole Resonance in Chemistry], Khimiya, Leningrad, 1972 (in Russian).
[7] E. A. Kravchenko, R. L. Davidovich, L. A. Zemnukhova, and Yu. A. Buslaev, Dokl. Akad. Nauk SSSR. **214,** 611 (1974) [Dokl. Chem. **214,** (1974). (Engl. Transl.)].
[8] A. J. Edwards, J. Chem. Soc., A. **17,** 2751 (1970).
[9] E. V. Bryukhova, V. A. Egorov, I. M. Alymov, and G. K. Semin, Izv. Akad. Nauk SSSR. Ser. Khim. 1919 (1974)

[Bull. Acad. Sci. USSR., Div. Chem. Sci. **23** (1974). (Engl. Transl.)].
[10] L. A. Zemnukhova, R. L. Davidovich, S. I Kuznezov, and V. N. Rykovanov, Izv Akad. Nauk. SSSR, Ser. Khim, 1956 (1987) [Bull. Acad. Sci. USSR., Div. Chem. Sci. 1987. (Engl. Transl.)].
[11] V. N. Rykovanov, R. Sh. Lotfullin, L. A. Zemnukhova, A. A. Boguslavskii, and R. L. Davidovich, Phys. stat. sol. (b). **167,** K51, (1991).
[12] H. Chihara, N. Nakamura, and H. Okuda, J. Phys. Soc. Japan. **24,** 306 (1968).
[13] B. Ducourant, R. Fourcade, E. Philippot, and G. Mascherpa, Rev. Chim. Miner. **12,** 553 (1975).
[14] L. A. Zemnukhova and R. L. Davidovich, unpublished results.
[15] R. Fourcade, G. Mascherpa, and E. Philippot, Acta Crystallogr. **B31,** 2322 (1975).
[16] S. H. Mastin and R. R. Ryan, Inorg. Chem. **10,** 1757 (1971).
[17] R. R. Ryan, S. H. Mastin, and A. C. Larson, Inorg. Chem. **10,** 2793 (1971).
[18] L. A. Zemnukhova and R. L. Davidovich, Izv. Akad. Nauk SSSR. Ser. Fiz. **45,** 1764 (1984) (in Russian).
[19] L. A. Zemnukhova, R. L. Davidovich, and G. A. Fedorishcheva, Koord. Khim. **14,** 1641 (1988). [Sov. J. Coord. Chem. **14** (1988) (Engl. Transl.)].
[20] L. A. Zemnukhova, G. A. Fedorishcheva, L. V. Teplukhina, and R. L. Davidovich, Depon. v VININI. N 4818-B89 (1989) (in Russian).
[21] R. L. Davidovich, V. B. Logvinova, L. A. Zemnukhova, and L. V. Teplukhina, Koord. Khim. **17,** 29 (1991). [Sov. J. Coord. Chem. **17** (1991) (Engl. Transl.)].
[22] R. L. Davidovich, V. B. Logvinova, L. A. Zemnukhova, A. A. Udovenko, and I. P. Kondratyuk, Koord. Khim. **17,** 1342 (1991). [Sov. J. Coord. Chem. **17** (1991) (Engl. Transl.)].
[23] R. L. Davidovich, L. A. Zemnukhova, G. A. Fedorishcheva, T. G. Ermakova, and V. A. Lopyrev, Koord. Khim. **16,** 1319 (1990). [Sov. J. Coord. Chem. **16** (1990) (Engl. Transl.)].
[24] V. V. Urbonavicius, Ph. D. Thesis. Vil'nyus. 1985. 18 pp. (in Russian).
[25] N. Habibi, B. Bonnet, and B. Ducourant, J. Fluor. Chem. **12,** 237 (1978).
[26] N. Habibi, B. Ducourant, B. Bonnet, and R. Fourcade, J. Fluor. Chem. **12,** 63 (1978).
[27] V. E. Ovchinnikov, A. A. Udovenko, L. P. Solov'eva, L. M. Volkova, and R. L. Davidovich, Koord. Khim. **8,** 697 (1982). [Sov. J. Coord. Chem. **8** (1982) (Engl. Transl.)].
[27a] V. E. Ovchinnikov, A. A. Udovenko, L. P. Solov'eva, L. M. Volkova, and R. L. Davidovich, Koord. Khim. **8,** 1539 (1982). [Sov. J. Coord. Chem. **8** (1982) (Engl. Transl.)].
[28] A. A. Udovenko, R. L. Davidovich, S. B. Ivanov, M. Yu. Antipin, and Yu. T. Struchkov, Koord. Khim. **16,** 448 (1990). [Sov. J. Coord. Chem. **16** (1990) (Engl. Transl.)].
[29] R. L. Davidovich, P. S. Gordienko, J. Grigas, T. A. Kaidalova, V. Urbonavicius, and L. A. Zemnukhova, Phys. stat. sol. (a). **84,** 387 (1984).
[30] L. A. Zemnukhova, R. L. Davidovich, V. I. Sergienko, V. I. Kostin, and S. I. Kuznezov, Koord. Khim. **11,** 1216 (1985). [Sov. J. Coord. Chem. **11** (1985) (Engl. Transl.)].
[31] L. A. Zemnukhova, R. L. Davidovich, V. N. Rykovanov, and S. I. Kuznezov, Izv. Akad. Nauk. SSSR, Ser. Khim. 544 (1988). [Bull. Acad. Sci. USSR., Div. Chem. Sci. 1988. (Engl. Transl.)].
[32] V. V. Urbonavicius, A. I. Brilingas, R. L. Davidovich, and L. A. Zemnukhova, Thes. dokl. II Vsesoyuznoii konferenzii po fiziko-khimicheskim osnovam teknologii segneto'lektriceskih i rodstvennyh materialov. Zvenigorod. 1983. P. 40 (in Russian).
[33] R. Fourcade, G. Mascherpa, E. Philippot, and M. Maurin, Rev. Chim. Miner. **11,** 481 (1974).
[34] A. Bystrom and K.-A. Wilhelmi, Arkiv Kemi **3,** 461 (1951).
[35] A. A. Udovenko, M. F. Eiberman, S. B. Ivanov, A. N. Levin, and S. S. Sergienko, Kristallografiya. **37,** 729 (1992) [Sov. Phys. Crystallogr. **37** (1992) (Engl. Transl.)].
[36] I. P. Makarova, L. A. Muradyan, V. E. Zavodnik, A. V. Tovbas, and I. V. Oberladze, Kristallografiya. **29,** 445 (1984) [Sov. Phys.-Crystallogr. **29** (1984) (Engl. Transl.)].
[37] A. A. Udovenko, L. M. Volkova, P. S. Gordienko, R. L. Davidovich, M. Yu. Antipin, and Yu. T. Struchkov, Koord. Khim. **13,** 558 (1987) [Sov. J. Coord. Chem. **13** (1987) (Engl. Transl.)].
[38] N. Nakamura, Z. Naturforsch. **41a,** 243 (1986).
[39] L. M. Avkhutskii, R. L. Davidovich, L. A. Zemnukhova, P. S. Gordienko, V. Urbonavicius, and J. Grigas, Phys. stat. sol. (b) **116,** 483 (1983).
[40] L. A. Zemnukhova, R. L. Davidovich, P. S. Gordienko, J. Grigas, A. N. Kovrianov. S. I. Kuznetsov, T. A. Kaidalova, and V. Urbonavicius, Phys. stat. sol. (a). **80,** 553 (1983).
[41] L. A. Zemnukhova, R. L. Davidovich, and S. I. Kuznetsov, Izv. Akad. Nauk. SSSR, Ser. Khim. 561 (1985) [Bull. Acad. Sci. USSR., Div. Chem. Sci. (1985) (Engl. Transl.)].
[42] Yu. N. Moskvich, B. I. Cherkasov, A. M. Polyakov, A. A. Sukhovskii, and R. L. Davidovich. Phys. stat. solidi, (b) **156,** 615 (1989).
[43] L. A. Zemnukhova, R. L. Davidovich, and G. A. Fedorishcheva, Russian J. Inorg. Chem. **40,** 1608 (1995) (Engl. Transl.).
[44] R. L. Davidovich, L. A. Zemnukhova, and N. I. Sigula, Russian J. Inorg. Chem. **19,** 2529 (1974) (Engl. Transl.).
[45] D. R. Schroeder and R. A. Jacobson, Inorg. Chem. **12,** 515 (1973).
[46] A. A. Udovenko, L. M. Volkova, R. L. Davidovich, and M. A. Simonov, Koord. Khim. **5,** 133 (1979) [Sov. J. Coord. Chem. **5** (1979) (Engl. Transl.)].
[47] A. A. Udovenko, L. M. Volkova, R. L. Davidovich, and L. A. Zemnukhova, Koord. Khim. **5,** 595 (1979) [Sov. J. Coord. Chem. **5** (1979) (Engl. Transl.)].
[48] L. A. Zemnukhova and R. L. Davidovich, Izv. Akad. Nauk. SSSR, Ser. Khim. 2545 (1975) [Bull. Acad. Sci. USSR., Div. Chem. Sci. 1975 (Engl. Transl.)].
[49] R. L. Davidovich, L. A. Zemnukhova, and N. I. Sigula, Russian J. Inorg. Chem. **18,** 144 (1973) (Engl. Transl.).
[50] A. A. Udovenko, V. N. Butenko, R. L. Davidovich, V. G. Andrianov, M. Yu. Antipin, and A. I. Yanovskii, Kristallografiya. **26,** 488 (1981) [Sov. Phys. Crystallogr. **26** (1981) (Engl. Transl.)].
[51] R. L. Davidovich, L. A. Zemnukhova, and E. A. Kravchenko, Russian J. Inorg. Chem. **18,** 144 (1973) (Engl. Transl.).
[52] H. Cihihara and N. Nakamura, Z. Naturforsch **45a,** 541 (1990).
[53] V. V. Tkachev, I. O. Atovmyan, L. A. Zemnukhova, A. A. Udovenko, and R. L. Davidovich, Koord. Khim. **19,** 25 (1993) [Sov. J. Coord. Chem. **19** (1993) (Engl. Transl.)].
[54] R. L. Davidovich, L. A. Zemnukhova, A. A. Udovenko, and N. I. Sigula, Koord. Khim. **9,** 787 (1983) [Sov. J. Coord. Chem. **9** (1983) (Engl. Transl.)].
[55] L. A. Zemnukhova, R. L. Davidovich, V. N. Rykovanov, and S. I. Kuznetsov, Izv. Akad. Nauk. SSSR, Ser. Khim. 1136 (1987) [Bull. Acad. Sci. USSR., Div. Chem. Sci. (1987) (Engl. Transl.)].

[56] L. A. Zemnukhova, R. L. Davidovich, and T. A. Semenova, Russian J. Phys. Chem. **53,** 48 (1979) (in Russian).
[57] L. A. Zemnukhova, R. L. Davidovich, V. N. Rykovanov, S. I. Kuznetsov, S. K. Shcherbakova, and G. K. Semin, Izv. Akad. Nauk. SSSR, Ser. Khim. 1501 (1987) [Bull. Acad. Sci. USSR., Div. Chem. Sci. (1987) (Engl. Transl.)].
[58] R. L. Davidovich, L. A. Zemnukhova, G. A. Fedorishcheva, T. A. Kaidalova, and S. B. Ivanov, Koord. Khim. **16,** 177 (1990) [Sov. J. Coord. Chem. **17** (1990) (Engl. Transl.)].
[59] R. L. Davidovich, L. A. Zemnukhova, and T. L. Semenova, Koord. Khim. **3,** 1373 (1977) [Sov. J. Coord. Chem. **3** (1977) (Engl. Transl.)].
[60] V. N. Rykovanov, R. Sh. Lotfullin, L. A. Zemnukhova, A. A. Boguslavskii, and R. L. Davidovich, Phys. stat. sol. (b). **165,** K13 (1991).
[61] A. A. Udovenko, L. M. Volkova, R. L. Davidovich, and L. A. Zemnukhova, Koord. Khim. **3,** 259 (1977) [Sov. J. Coord. Chem. **3** (1977) (Engl. Transl.)].
[62] L. A. Zemnukhova, G. A. Fedorishcheva, S. I. Kuznetsov, and R. L. Davidovich, Izv. Akad. Nauk. SSSR, Ser. Khim. 382 (1996) [Bull. Acad. Sci. USSR., Div. Chem. Sci. (1996) (Engl. Transl.)].
[63] Yu. A. Buslaev and R. L. Davidovich, Koord. Khim. **15,** 1444 (1989) [Sov. J. Coord. Chem. **15** (1989) (Engl. Transl.)].
[64] L. A. Zemnukhova, R. L. Davidovich, and T. L. Semenova, Koord. Khim. **9,** 1369 (1983) [Sov. J. Coord. Chem. **9** (1983) (Engl. Transl.)].
[65] A. Astrom and S. Andersson, J. Solid. State Chem **6,** 191 (1973).
[66] A. A. Udovenko, L. M. Volkova, R. L. Davidovich, L. A. Zemnukhova, and E. S. Panin, Koord. Khim. **11,** 1132 (1985) [Sov. J. Coord. Chem. **11** (1985) (Engl. Transl.)].
[67] R. L. Davidovich, L. A. Zemnukhova, A. A. Udovenko and L. V. Samarets, Koord. Khim. **8,** 374 (1982) [Sov. J. Coord. Chem. **8** (1982) (Engl. Transl.)].
[68] R. L. Davidovich and L. A. Zemnukhova, Koord. Khim. **8,** 1572 (1982) [Sov. J. Coord. Chem. **8** (1982) (Engl. Transl.)].
[69] M. Bourgault, R. Fourcade, and G. Mascherpa, J. Solid State Chem. **36,** 214 (1981).
[70] R. L. Davidovich, L. A. Zemnukhova, G. A. Fedorishcheva, A. A. Udovenko, and M. F. Eibermann, Koord. Khim. **16,** 926 (1990) [Sov. J. Coord. Chem. **16** (1990) (Engl. Transl.)].
[71] R. L. Davidovich, M. A. Medkov, E. B. Bogomolova, and L. A. Zemnukhova, Izv. Akad. Nauk. SSSR, Ser. Khim. 973 (1984) [Bull. Acad. Sci. USSR., Div. Chem. Sci. (1984) (Engl. Transl.)].
[72] A. A. Udovenko, L. M. Volkova, R. L. Davidovich, and S. S. Sergienko, Koord. Khim. **14,** 834 (1988) [Sov. J. Coord. Chem. **14** (1988) (Engl. Transl.)].
[73] A. A. Udovenko and R. L. Davidovich, Koord. Khim. **17,** 1354 (1991) [Sov. J. Coord. Chem. **17** (1991) (Engl. Transl.)].
[74] L. M. Volkova, A. A. Udovenko, A. N. Levin, R. L. Davidovich, and M. A. Medkov, Koord. Khim. **11,** 689 (1985) [Sov. J. Coord. Chem. **11** (1985) (Engl. Transl.)].
[75] R. Fourcade, M. Bourgault, B. Bonnet, and B. Ducourant, J. Solid State Chem. **43,** 81 (1982).
[76] R. L. Davidovich, L. A. Zemnukhova, V. N. Rykovanov, and N. M. Dyatlova, Izv. Akad. Nauk. SSSR, Ser. Khim. 1915 (1989) [Bull. Acad. Sci. USSR., Div. Chem. Sci. (1989) (Engl. Transl.)].