The Temperature Dependences of ^{123}Sb NQR Parameters in the Antimony(III) Complex Compounds XSb_2F_7 ($\text{X} = \text{K}, \text{Cs}, \text{Tl}, \text{CN}_3\text{H}_6$)

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The present paper contains the results of an ^{123}Sb NQR study of the compounds XSb_2F_7 ($\text{X} = \text{K}, \text{Cs}, \text{Tl}$ and CN_3H_6) at 77 - 350 K. The obtained parameters are compared with the corresponding crystal structures.

Key words: Antimony(III); Fluoride Complex Compounds; ^{123}Sb NQR Spectra.

Introduction

The studied group of heptafluoroantimonates(III) XSb_2F_7 contains eleven compounds where $\text{X} = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{Tl}$, and R is an organic base cation: Et_2NH_4^+ (diethylammonium), CN_3H_6^+ (guanidinium), $\text{CNH}(\text{NH}_2)_3^+$ (aminoguanidinium), $\text{C}_2\text{N}_3\text{H}_4^+$ (1,2,4-triazolium), Nic^+ (nicotinamide cation), Bip^+ (2,2'-bipyridine cation) [1]. The complexes with Rb^+ and NH_4^+ cations form an isostructural series. The heptafluoroantimonates(III) properties are little studied. The fluorine sublattice dynamics and electrical conductivity of XSb_2F_7 ($\text{X} = \text{Cs}^+, \text{NH}_4^+$) were studied at 210 - 480 K [2, 3]. The existence of high-temperature modifications β - XSb_2F_7 with high-ionic (superionic) conductivity was discovered above 425 K. The electrical conductivity (σ) of these compounds varies in the range (1.3 - 1.9) $\cdot 10^{-3}$ Sm/cm.

The $^{121,123}\text{Sb}$ NQR spectra of the complex heptafluoroantimonates(III) at 77 K were studied earlier [1]. All the compounds XSb_2F_7 have doublet $^{121,123}\text{Sb}$ NQR spectra, whereas CsSb_2F_7 has a singlet spectrum and TlSb_2F_7 a multiplet six-lines one.

The experimentally obtained ^{123}Sb NQR parameters of XSb_2F_7 ($\text{X} = \text{K}, \text{Cs}, \text{Tl}$ and CN_3H_6) at 77 -

350 K are given and compared with the corresponding crystal structures.

Experimental

The synthesis of the polycrystalline compounds was carried out according to the method described in [4]. The ^{123}Sb NQR spectra were recorded on a ISSh-2-13 spectrometer equipped with a temperature device (to study the $\nu_1 = \pm(1/2 \leftrightarrow 3/2)$ and $\nu_2 = \pm(3/2 \leftrightarrow 5/2)$ transitions) at 77 - 325 K. The quadrupole coupling constant $e^2Qq_{zz} \cdot h^{-1}$ (QCC) and asymmetry parameter of the electric field gradient (EFG) η for ^{123}Sb were calculated from the experimental NQR frequencies [1]. The errors (Δ) of the experimental and calculated data are $\Delta T = \pm 0.1$ K; $\Delta\nu = \pm 0.01$ MHz; $\Delta(\text{QCC}) = \pm 0.1$ MHz; $\Delta\eta = \pm 0.1\%$.

Results and Discussion

The structure of the dimeric Sb_2F_7 groups in XSb_2F_7 ($\text{X} = \text{K}^+$ (a), Cs^+ (b) and Tl^+ (c)) complexes is shown in Figure 1.

The unit cell of KSb_2F_7 has two unequivalent antimony positions [5]. The structure of this complex consists of endless chains formed by the alternating $\text{Sb}(1)\text{EF}_4$ and $\text{Sb}(2)\text{EF}_5$ groups (where E is the lone

Fig. 1. Schemes of Sb_2F_7 dimeric groups in XSb_2F_7 ($\text{X} = \text{K}^+$ (a), Cs^+ (b), Tl^+ (c)) structures [5, 8, 9].

pair) bound with each other by the asymmetric fluorine bridges F(7) and F(2) (Fig. 1a). The structure of KSb_2F_7 clearly contains two types of polyhedra. The ^{123}Sb NQR frequency assignment in this compound was carried out using correlation of the EFG asymmetry parameter values with angular and structural distortions of the antimony polyhedra [6]. According to the $^{121,123}\text{Sb}$ NQR spectrum at 77 K the compound $\text{CN}_3\text{H}_6\text{Sb}_2\text{F}_7$ also has two unequivalent antimony positions [1].

The temperature dependence for XSb_2F_7 ($\text{X} = \text{K}^+$, CN_3H_6^+) showed that ^{123}Sb nuclei signals can be observed in the range 77 - 290 K. No structural phase transitions were found in this temperature range. The NQR signals of the lower transition (ν_1) in KSb_2F_7 fade at lower temperature (230 K) than those for the higher one (ν_2). Therefore the changes of QCC and η were calculated at the range 77 - 230 K. Figure 2 shows the changes of the ^{123}Sb NQR parameters (QCC and η) for XSb_2F_7 ($\text{X} = \text{K}^+$, CN_3H_6^+). According to Bayer's theory [7] the antimony atom temperature coefficients $\partial e^2Qq_{zz}h^{-1}/\partial T$ (Fig. 2) are comparable between each other for the both compounds XSb_2F_7 ($\text{X} = \text{K}^+$, CN_3H_6^+). The temperature coefficients of the antimony atoms $\partial\eta/\partial T$ in these complexes (Fig. 2) vary more slightly and depend upon the cation nature. The opposite signs of the $\partial\eta/\partial T$ coefficient found in $\text{CN}_3\text{H}_6\text{Sb}_2\text{F}_7$ for Sb(2) at 120 -

290 K (Fig. 2) can be due to more stable H-bonds. The explanation of small changes of the value and sign of the $\partial\eta/\partial T$ coefficient for Sb(2) atoms (Fig. 2, line 8) requires first of all knowledge about changes of the crystal thermal expansion coefficient.

The structure of CsSb_2F_7 contains Sb_2F_7^- symmetric dimeric complex anions (Fig. 1b) formed by unification of the two SbF_3 molecules by means of the bridge fluorine atom [8]. SbEF_4 trigonal bipyramid is the antimony coordination polyhedron in this case.

The ^{123}Sb NQR spectrum of CsSb_2F_7 is observed in the range 77 - 322 K. It is singlet according to its structure. The temperature coefficient $\partial e^2Qq_{zz}h^{-1}/\partial T$ and $\partial\eta/\partial T$ have usual negative values (Fig. 2). In the range 220 - 270 K the crystals show slight piezoelectric properties discovered by typical piezoelectric noises in the radio-frequency field. The temperature range with the piezoelectric phase correlates to the slight changes of the temperature coefficients $\partial e^2Qq_{zz}h^{-1}/\partial T$ (from -71.6 in the range 77 - 220 K to $-118 \text{ kHz}\cdot\text{K}^{-1}$ in the range 270 - 322 K) and $\partial\eta/\partial T$ (from $-6.0\cdot 10^{-3}$ to $-4.7\cdot 10^{-3} \text{ K}^{-1}$) that can be a result of Sb_2F_7 groups reorientation vibrations appearance.

The compound TlSb_2F_7 has the most complex structure among the heptafluoroantimonates(III). The six-nuclear cyclic anions $[\text{Sb}_6\text{F}_{21}]^{3-}$ formed by Sb_2F_7 dimeric groups bound by their common apexes were discovered in this complex (Fig. 1c) [9]. The structure TlSb_2F_7 contains six antimony atoms which are independent from the crystallographic point of view. SbEF_5 octahedra are the coordination polyhedra of Sb(1,3,5) and SbEF_4 trigonal bipyramids are those for Sb(2,4,6). The distortions of these polyhedra are typical for this type of the polyhedra with the stereochemically active lone pair.

We are the first who studied the $^{121,123}\text{Sb}$ NQR spectrum of TlSb_2F_7 at 77 K with six different antimony atom positions in the unit cell [10]. The frequency assignments were made according to correlation of the EFG asymmetry parameter values with the angular distortions of the antimony polyhedra in TlSb_2F_7 structure [6]. In [1] we described the ^{121}Sb NQR frequency variations of $\nu_1 = \pm(1/2 \leftrightarrow 3/2)$ transitions for the six unequivalent antimony atoms in the range 77 - 345 K. These variations reflect the two independent phase transitions of the second type in TlSb_2F_7 crystals at 270 and 340 K. The paper [11] informs about the phase transition in TlSb_2F_7 with the superionic phase appearance at 240 K. So far as the X-ray analysis of TlSb_2F_7 [9] crystals showed the

Fig. 2. Temperature dependence of the quadrupole coupling constants (e^2Qq/h , MHz) and asymmetry parameters (η , %) for ^{123}Sb in XSb_2F_7 ($X = \text{K}, \text{CN}_3\text{H}_6, \text{Cs}$). The experimental points are connected by lines belonging to KSb_2F_7 (1 and 9 for Sb(1)), 3 and 8 for Sb(2)), $\text{CN}_3\text{H}_6\text{Sb}_2\text{F}_7$ (5 and 7 for Sb(1), 2 and 10 for Sb(2)), and CsSb_2F_7 (4 and 6).

Fig. 3. Temperature dependence of the quadrupole coupling constants (e^2Qq/h , MHz) and asymmetry parameters (η , %) for ^{123}Sb in TlSb_2F_7 . Lines 5 and 11 correspond to antimony atoms Sb(1), lines 2 and 8 to Sb(2), 4 and 9 to Sb(3), 1 and 10 to Sb(4), 3 and 12 to Sb(5), 6 and 7 to Sb(6).

Table 1. The $\partial e^2Qq_{zz}h^{-1}/\partial T$ and $\partial\eta/\partial T$ parameters for ^{123}Sb in TiSb_2F_7 .

— Type of Sb polyhedron —					
— SbEF_5 —			— SbEF_4 —		
Atom	$\partial e^2Qq_{zz}h^{-1}/\partial T$ $\text{MHz}\cdot\text{K}^{-1}$	$\partial\eta/\partial T$ K^{-1}	Atom	$\partial e^2Qq_{zz}h^{-1}/\partial T$ $\text{MHz}\cdot\text{K}^{-1}$	$\partial\eta/\partial T$ K^{-1}
Sb(1)	−0.137	10.1	Sb(2)	−0.138	7.39
Sb(3)	−0.152	−4.28	Sb(4)	−0.151	−6.30
Sb(5)	−0.167	8.27	Sb(6)	−0.188	9.36

presence of six different antimony atom positions at ~ 298 K we carried out the repeated study of its ^{123}Sb NQR spectrum change in the range 77 - 345 K and calculated QCC and η values.

The NQR signals of (ν_2) transition in TiSb_2F_7 fade above 280 K therefore the changes of $e^2Qq_{zz} \cdot h^{-1}$ and η were calculated in the range 77 - 280 K (Fig. 3, Table 1). The results obtained show preservation of the six unequivalent positions of the antimony atoms in this temperature range although QCC lines for Sb(1) and Sb(3) unite practically together above 270 K (Fig. 3). The temperature coefficients $\partial e^2Qq_{zz}h^{-1}/\partial T$ for all the antimony atoms have the usual negative values. The $\partial\eta/\partial T$ coefficients have the negative values only for Sb(3) and Sb(4) (Fig. 3). The symmetry of the EFG tensor in the Sb(1), Sb(5) and Sb(6) localization sphere lowers with the temperature growth on

the contrary to Sb(3) and Sb(4). It can be proved by positive values of their $\partial\eta/\partial T$ coefficients (Fig. 3). The asymmetry parameter value for Sb(2) practically does not change in the range 100 - 280 K (Fig. 3).

Conclusions

Thus, the study of the ^{123}Sb NQR parameters temperature changes of XSb_2F_7 ($\text{X} = \text{K}^+, \text{Cs}^+, \text{Ti}^+$ and CN_3H_6^+) shows that $\partial e^2Qq_{zz}h^{-1}/\partial T$ coefficients have usually negative values that in turn shows the absence of structural phase transitions in the temperature ranges studied. Positive $\partial\eta/\partial T$ coefficients in the compounds with K^+ , CN_3H_6^+ , and Ti^+ cations which structures are built of unequivalent antimony polyhedra in Sb_2F_7 groups show that these compounds have a more rigid crystal lattice as compared with CsSb_2F_7 crystals where the antimony atoms are in equivalent positions.

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