Brief Communications

Temperature dependence of ^{121}Sb nuclear quadrupole resonance frequencies in the spectra of $M_2Sb_2SO_4F_6$ (M = K, Rb, NH_4)

L. A. Zemnukhova, R. L. Davidovich, and G. A. Fedorischeva*

Institute of Chemistry, Far-Eastern Branch of the Russian Academy of Sciences,
159 prosp. 100-Letiya Vladivostoka, 690022 Vladivostok, Russian Federation.
Fax: +7 (423) 231 1889

The temperature dependence of the frequencies of ^{121}Sb nuclear quadrupole resonance in the spectra of $M_2Sb_2SO_4F_6$ (M = K, Rb, NH_4) was studied in the temperature range from 77 to 340 K. A secondary phase transition was found above 320 K for $(NH_4)_2SO_4F_6$.

Key words: ^{121}Sb nuclear quadrupole resonance spectra, antimony(III), sulfatofluorodiantimonates(III), temperature measurements, nuclear quadrupole resonance frequency.

A characteristic feature of the stereochemistry of Sb^{III} fluorine-containing complexes is the low-symmetry of the crystal lattices of these complexes, which results in various anisotropic properties and phase transitions. Some phase transitions have been revealed previously for a number of sulfatofluoroantimonates(III).[1–3]

The high sensitivity of nuclear quadrupole resonance (NQR) spectral parameters toward the dynamics of molecules or their fragments in a crystal makes this method highly informative in studies of compounds containing quadrupole nuclei, which include compounds of antimony.[4]

In this paper potassium, rubidium, and ammonium sulfatohexafluorodiantimonates(III) have been studied by NQR at 77–340 K.

Experimental

The compounds $M_2Sb_2SO_4F_6$ (M = K, Rb, NH_4) were synthesized according to known procedures.[5] NQR spectra of polycrystaline samples were obtained on a wide-band ISSh 1-13 pulsed spectrometer equipped with a thermostatic system. ^{121}Sb NQR frequencies for the $\pm(1/2 \rightleftharpoons 3/2)$ transition were measured. The temperature was determined from a calibration plot for $KClO_3$ within ±1 K. Experimental results are shown in Figs. 1 and 2.

Results and Discussion

Our early results of X-ray, IR, and NQR spectral data for $M_2Sb_2SO_4F_6$ [5–7] suggest isomorphism of these compounds at 77 K and at room temperature. The IR spectra indicate a nearly ionic state of the SO_4^{2-}-group in $M_2Sb_2SO_4F_6$ at room temperature, while the NQR spectra reveal two nonequivalent crystallographic positions of the Sb_1 and Sb_2 atoms in the unit cell at 77 K.

The structure of $K_2Sb_2SO_4$ has been determined,[8] and the crystals are monoclinic. The coordination polyhedrons of antimony in $K_2Sb_2SO_4F_6$ are of two types: the distorted octahedron SbX_5E and the single-cap distorted octahedron Sb_6E, where E is a lone electron pair. Simi-

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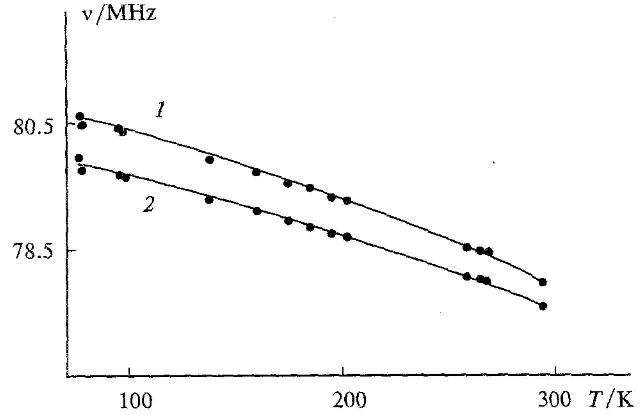

Fig. 1. Temperature dependence of ^{121}Sb NQR frequencies for the transition $\pm(1/2 \rightleftharpoons 3/2)$ for $K_2Sb_2SO_4F_6$.

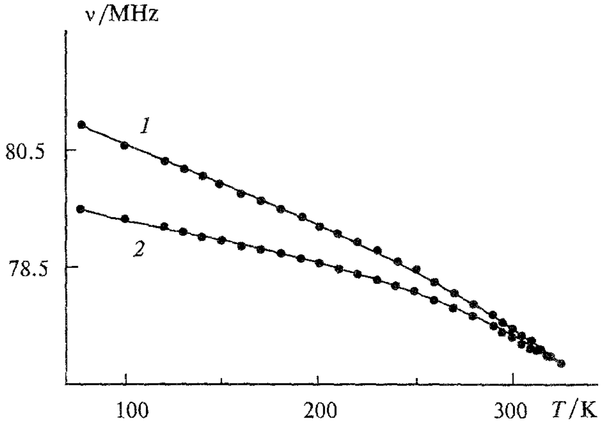

Fig. 2. Temperature dependence of ^{121}Sb NQR frequencies for the transition $\pm(1/2 \rightleftharpoons 3/2)$ for $(NH_4)_2Sb_2SO_4F_6$.

lar to the SbF_3 structure, each antimony atom has, in its closest surroundings, three fluorine atoms arranged at a distance of 1.91—1.97 Å.[9] The Sb—O bonds are relatively weak (2.43—2.59 Å) in the polyhedrons. The antimony polyhedrons are linked into chains along the Y-axis. The chains form layers, which are parallel to [102] plane and connected by K^+ cations.

The temperature dependences of the NQR frequencies for $M_2Sb_2SO_4F_6$ with K^+ and Rb^+ are similar, and differ from that for $(NH_4)_2Sb_2SO_4F_6$. According to NQR data the antimony atoms in the $M_2Sb_2SO_4F_6$ (M = K, Rb) lattice retain two equivalent positions in the unit cell in the temperature range 77—320 K. The relative intensity of the $^{121}Sb_{1,2}$ signals gradually decreases as the temperature increase, and at temperatures above 320 K for $K_2Sb_2SO_4F_6$ and 310 K for $Rb_2Sb_2SO_4F_6$ the signals are not detected. The monotonic decrease in the resonance frequencies as the temperature increases is in accordance with the predictions of the Bayer—Kushida theory.[4] The temperature factors $d\nu/dT$ for Sb_1 and Sb_2 in $K_2Sb_2SO_4F_6$ are slightly different: $-11.3 \cdot 10^{-3}$ and $-12.6 \cdot 10^{-3}$ MHz deg^{-1}, respectively. The frequency difference $\Delta\nu$ decreases from 0.68 MHz at 77 K to 0.39 MHz at 320 K. The linearity of the $\nu(T)$ plot suggests preservation of local symmetry around the resonance antimony atoms for $M_2Sb_2SO_4F_6$ (M = K, Rb) at these temperatures. Extrapolation of the plots (see Fig. 1) shows that the frequency variations merge together at 400—410 K.

The NQR spectrum of $(NH_4)_2Sb_2SO_4F_6$ (see Fig. 2) reveals two nonequivalent positions of the Sb_1 and Sb_2 atoms at 77—314 K. The temperature factors $d\nu/dT$ are $-5.7 \cdot 10^{-3}$ MHz deg^{-1} and $-18.3 \cdot 10^{-3}$ MHz deg^{-1} for Sb_1 and Sb_2, respectively. There is one NQR line for the studied transition above 320 K. Such $\nu(T)$ dependence is typical for secondary phase transitions.[10] A change in the multiplicity of the NQR spectrum was detected at temperatures between 229 and 258 K. We observed weak $^{121}Sb_3$ NQR signals whose frequencies were the mean values between those for Sb_1 and Sb_2. This effect is explained by partial disordering of the crystal lattice in the temperature range indicated above.

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