# Variations of the shape of $^{123}Sb$ NQR lines in phase transitions in $K_2SbF_5$

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Variations of the shape of $^{123}Sb$ NQR lines in phase transitions in a new ionic conductor, potassium pentafluoroantimonite(III), in the temperature range from 77 to 430 K were studied. The transition from a paraelectric phase to a commensurate phase occurs *via* incommensurate and commensurate-modulated phases.

**Key words:** $^{123}Sb$ nuclear quadrupole resonance spectra, antimony(III), potassium pentafluoroantimonite(III), phase transitions.

The compound $K_2SbF_5$, where a sequence of phase transitions (PT), including transition into the incommensurate phase, has been found,[1—7] is a representative of a new class of ionic conductors of the composition $M_2SbF_5$ where M = Na, K, Rb, Cs, $NH_4$, and Tl.[8]

Since the information on the number of phases and temperatures of phase transitions in $K_2SbF_5$ in previously published works[4—7] is inconsistent, we undertook a reinvestigation of polycrystalline $K_2SbF_5$ by $^{123}Sb$ NQR method. The interest of such an investigation was also due to the fact that the transformation of the NQR line shape with a change in the temperature was never considered previously,[4] while, as a rule, its analysis allows establishing a more precise location of the areas of different phases.[9,10]

## Experimental

Specimens with a maximum signal-to-noise (s/n) ratio at 77 and 298 K (s/n = ~30 at 77 K), sysnthesized following the known procedure,[11] were used for studying the temperature dependence of the NQR frequencies in $K_2SbF_5$. For NQR spectral studies, two specimens were selected from the polycrystalline substance obtained in synthesis. One of the $K_2SbF_5$ specimens was first cooled to 77 K; then, the temperature dependence of the NQR frequencies was studied when it was slowly heated to 430 K. The second specimen was studied after cooling with a specified rate from 298 to 77 K. Only after these procedures were repeated recordings of the spectral lines carried out.

The temperature dependence of the NQR frequencies in $K_2SbF_5$ was studied in the range from 77 to 410 K on an ISSH-1-13 pulsed spectrometer equipped with a temperature control accessory. The accuracy in the temperature measurements was 0.1 K. Measurements of $^{123}Sb$ NQR frequencies (ν) and recordings of the line shape in the spectra were carried out for two transitions: $\nu_1 = \pm(1/2 \leftrightarrow 3/2)$ and $\nu_2 = \pm(3/2 \leftrightarrow 5/2)$ using a procedure analogous to that published previously[4] for the maximum spin-echo intensity with intervals varying from 0.5 to 10 K.

## Results and Discussion

The structural units of $K_2SbF_5$ are anions $[SbEF_5]^{2-}$ and cations $K(1)^+$ and $K(2)^+$ united in layers parallel to the *xz* plane (E is the lone electron pair of $Sb^{3+}$).[5—7]

The phase transitions occurring in the crystalline structure of $K_2SbF_5$ when the temperature is lowered from room temperature to 103 K are not associated with a change in the shape of the antimony coordination polyhedron.[5—8] The transition from the high-temperature phase to the low-temperature phase is accompanied by a change in the environment of potassium atoms from pyramidal to octahedral and results in the formation of two intermediate phases (modulated and incommensurate, ICP) in accordance with the following scheme:[5]

$$D^{17}_{2h} \underset{}{\overset{269\text{ K}}{\rightleftharpoons}} D^{14}_{4h} \overset{183\text{ K}}{\rightleftharpoons} \text{ICP} \overset{134\text{ K}}{\rightleftharpoons} C^5_{2h} \overset{123\text{ K}}{\rightleftharpoons} C^5_{2h}$$

The temperatures of anomalies of $K_2SbF_5$ determined by the different physical methods are listed in Table 1.

The high sensitivity of the NQR method to changes in the electric field gradient (EFG) at the resonant nuclei (in this case at the antimony atoms) allowed us to locate five temperature points[4] at which changes in the NQR spectrum were observed and to make an assumption concerning the existence of seven phases in the temperature range from 77 to 400 K. However, a detailed analysis of the change in the $^{123}Sb$ NQR line shape carried out in this work showed that the transition

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**Table 1.** Sequence of phase transitions in $K_2SbF_5$ obtained by different experimental techniques in the temperature range from 77 to 430 K

| Method | Temperature of PT/K | References |
|---|---|---|
| $^{123}$Sb NQR | 123, 150, 260 | This work |
| $^{123}$Sb NQR | 112.6, 124.8, 135, 140.3, 145.1, 267.2, 280 | 4 |
| Calorimetry | 110.9, 123.0, 137.4, 270, 289, 312 | 4 |
| X-ray analysis | 123, 134, 183, 269 | 5–7 |
| $^{19}$F NMR | 196, 255 | 3,8,12 |
| IR | 160, 200, 250, 300, 320 | 12 |
| ESR | 123, 158–160, 266, 288 | 1,2 |
| Dielectric constant | 250 | 13,14 |

from the high-temperature state of the compound (the paraelectric phase) to the low-temperature state (the commensurate phase) occurs *via* the incommensurate phase; that phase is observed in a wider temperature interval than shown in other works[5–7] and is followed by a commensurate-modulated phase.

The temperature dependence of the $^{123}$Sb NQR frequencies and intensities ($I$) of the spin-echo signals are shown in Fig. 1. The recorded shape of the NQR line for

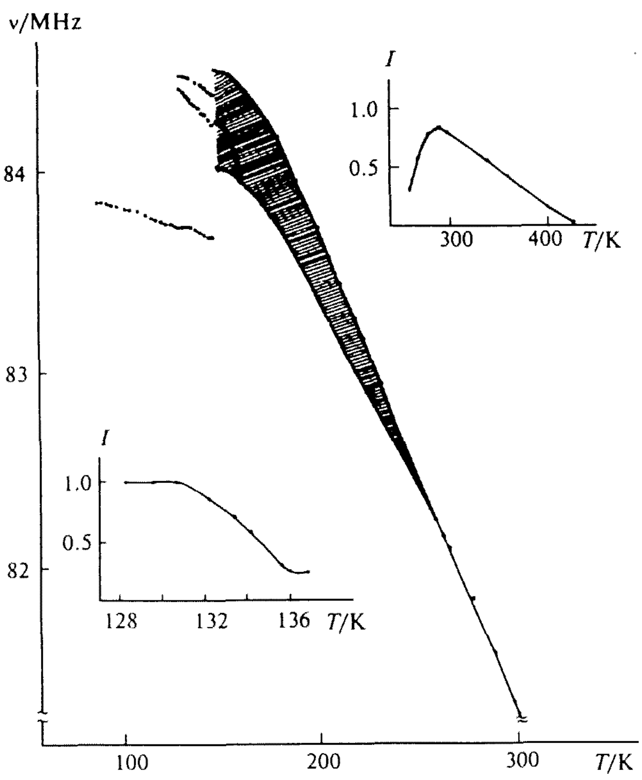


**Fig. 1.** Changes in the $^{123}$Sb NQR frequency (ν) and the intensity of the spin-echo signal ($I$) for the transition $\pm(3/2 \leftrightarrow 5/2)$ in $K_2SbF_5$ as functions of temperature.

**Table 2.** Temperature changes in frequency (ν) and intensities ($I$) of the $^{123}$Sb NQR signal in phase transitions in $K_2SbF_5$

| The region of existence of the phase, $T$/K | $T$/K | ν $^{123}$Sb $\pm(3/2 \leftrightarrow 5/2)$ /MHz | | | $I$(rel.unit ) |
|---|---|---|---|---|---|
| 430–260(290?) | 261.5 | | 82.19 | | 6.6 |
| | 251.8 | 82.50 | | 82.39 | 1.6 : 3 |
| | 213.7 | 83.43 | | 83.14 | 1 : 3.3 |
| | 192.1 | 83.86 | | 83.50 | 1 : 3.6 |
| | 169.4 | 84.30 | | 83.87 | 1.6 : 6 |
| 260–(145?)150 | 161.3 | 84.42 | | 83.95 | 3 : 5 |
| | 159.4 | 84.43 | 84.05 | 83.98 | 3 : 2.5 : 4.3 |
| | 155.6 | 84.46 | 84.13 | 84.00 | 3 : 2 : 3 |
| | 153.2 | 84.50 | 84.20 | 84.03 | 3 : 2 : 2.5 |
| | 150.2 | 84.52 | 84.25 | 84.04 | 2.6 : 2 : 1 |
| | 148.6 | 84.38 | 84.22 | 83.71 | 6 : 7.3 : 4.3 |
| | 146 | 84.11 | 84.26 | 83.73 | 9.3 : 10.6 : 9.3 |
| 150–(130?)123 | 133 | 84.46 | 84.36 | 83.73 | 6.6 : 8 : 11.3 |
| | 130 | 84.48 | 84.37 | 83.73 | 1 : 1.3 : 16.6 |
| 123–77 | 110 | | 83.76 | | 20.6 |

the $\nu_2$ transition in the temperature range from 77 to 430 K is shown in Fig. 2. The values of the NQR frequencies are listed in Table 2.

The NQR spectrum in the interval from 430 to 260 K is characterized by a narrow singlet of medium intensity, which is evidence of the crystallographic equivalence of all antimony atoms in the crystal lattice of $K_2SbF_5$. The intensity of the singlet increases as the temperature decreases from 430 to 290 K (in accordance with the Bayer theory[15]) and reaches its maximum at 290 K. In the temperature range from 290 to 260 K, the

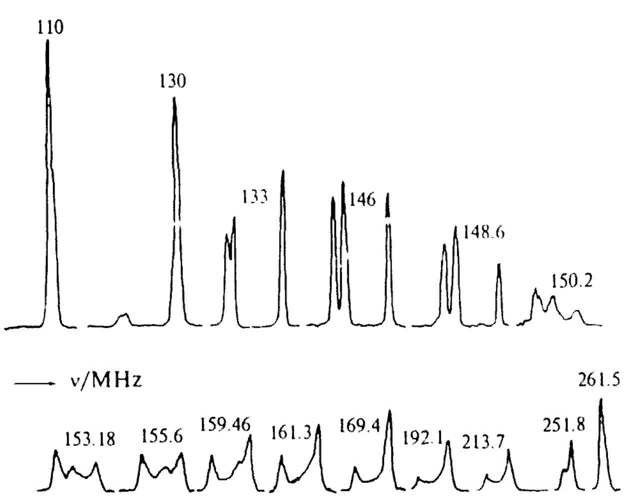


**Fig. 2.** Changes in the $^{123}$Sb NQR line shape for transition $\pm(3/2 \leftrightarrow 5/2)$ in $K_2SbF_5$ as functions of temperature.

intensity of the line drops, which contradicts that theory. Two strong effects were observed on the temperature curve of the specific heat of $K_2SbF_5$[4] at 312 and 289 K. The nature of the abnormal change in the intensity of the NQR signal at 290 K is still unknown; it could be associated with the onset of the phase transition. Repeated recordings of the temperature dependence of the NQR spectrum of $K_2SbF_5$ demonstrated good reproducibility of the results in the range from 430 to 260 K. No hysteresis phenomena were observed in that interval.

The intensity of the NQR signals in the spectrum of $K_2SbF_5$ decreases and the multiplicity of the $^{123}Sb$ lines smoothly changes below 260 K, which is a typical indication of a second-order phase transition. The phase formed exists in the region from 260 to 150 K (see Fig. 1). The change in the shape of the NQR spectral line in this region (see Fig. 2) is a radiospectroscopic manifestation of the incommensurate modulation[9,10,16] caused by the second-order phase transition; in this case the values of the electric field gradient at the resonant nuclei of antimony are continuously distributed in the interval whose width increases in moving away from the phase transition (see Figs. 1 and 2). The third intermediate line, poorly resolved and weak, which appears in the narrow temperature interval (159—150 K) of the NQR spectrum of $K_2SbF_5$, is also typical of the NQR spectra of compounds in the incommensurate state.

The jump-like change in the $K_2SbF_5$ spectrum at ~150 K corresponds to a first-order phase transition. In this case, three well-resolved lines appear in the spectrum (with an intensity ratio of 1 : 1.6 : 1.3), which is evidence of the periodic crystal lattice of the substance. The temperature hysteresis (~0.7 K) also confirms the existence of a first-order phase transition in the region of 150 K.

The new phase is observed in the narrower temperature interval (150—123 K) than the preceding phase. In this case, the behavior of resonance frequencies (see Fig. 1) by and large corresponds to a conventional temperature dependence of the NQR parameters[15]; however, the intensity of each of the three spectral lines changes differently as the temperature decreases: smooth redistribution of the amplitude of the signals occurs, so that only one intense narrow line remains in the NQR spectrum near 123 K (see Fig. 2).

The third phase transition, observed at 123 K, results in a state of the substance that is stable up to 77 K and is characterized by new periodicity of the crystal lattice parameters. The temperature hysteresis is insignificant in this region (~0.3—0.5 K); nevertheless, good reproducibility of the results obtained for different $K_2SbF_5$ specimens, as well as a sharp change in the multiplicity of the spectrum, point to the existence of a first-order phase transition at 123 K.

It should be noted that in repeatedly recorded NQR spectra of $K_2SbF_5$ for specimens obtained by different synthetic procedures, the temperature of the phase transition (260 K) remains unchanged (the value of 267 K reported in Ref. 4 can be explained by a larger temperature increment in the studies of the temperature behavior of the spectra), whereas the temperatures of two succeeding transitions exhibit scattering. Thus, the second and third phase transitions are observed in the regions from 150 to 145 K and from 130 to 123 K, respectively.

The NQR parameters (the quadrupole coupling constant, $e^2Qq/h$, and the asymmetry parameter of the electric field gradient, $\eta$), calculated using the $^{123}Sb$ frequencies measured in this work, are the same as those reported previously.[4] Analysis of the $\eta$ values showed that the electric field symmetry around the antimony atoms in potassium pentafluoroantimonite(III) is lower for the low-temperature phase ($\eta$ = 8.3—8.8%) than for the paraelectric phase ($\eta$ = 6.0—5.7%), which is in agreement with the results obtained in the known works.[5—7] However, a detailed comparison of the NQR and X-ray[5—7] data reveals essential discrepancies in locating the points of phase transitions in the range from 260 to 123 K. The reason for such discrepancies could be associated with a difference in the studied specimens of $K_2SbF_5$: the NQR study was carried out on polycrystalline specimens, while for the X-ray study only twin crystals were selected from crystals of two types.[5]

Thus, the study performed showed that the transition from the paraelectric phase (existing in the temperature range from 430 to 260 K) to the commensurate phase (the temperature interval from (130—123) to 77 K) occurs first *via* the incommensurate phase (the temperature range from 260 to (145—150 K)) and then *via* the commensurate-modulated phase (the temperature interval from (150—145) to (130—123) K).

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