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Nuclear quadrupole resonance study of phase transitions and incommensurability in K_2SbF_5

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Abstract
Phase transitions and incommensurability in K_2SbF_5 has been studied by means of ^{123}Sb NQR spectra and spin–lattice relaxation measurements. The phase transitions have been obtained at 117, 135 and 260 K. Line shape and temperature dependence of the spin–lattice relaxation time T_1 in the temperature range from 135 to 260 K are characteristic for the incommensurate state with the plane wave modulation regime. At 117 to 135 K, a distinct fine structure of NQR spectra has been observed. Redistribution of line intensities with the variation of temperature allows us to suggest that this phase exhibits domain structure, and that one of the domains becomes energetically beneficial on cooling and transforms into the low temperature phase at 117 K. The ^{123}Sb NQR measurements in K_2SbF_5 show unusually short values of T_1, which become close to the spin–spin relaxation time T_2 with increasing temperature.

1. Introduction

Potassium pentafluoroantimonate, K_2SbF_5, belongs to a new class of superionic conductors of the M_2SbF_5 family, where M = Na, K, Rb, Cs, Tl and NH_4 [1]. X-ray diffraction study of this compound [2–4] showed that K_2SbF_5 undergoes successive phase transitions at 269, 183, 134 and 119 K, according to the scheme

$$D_{2h}^{17} \xrightarrow{269\ \mathrm{K}} \mathrm{D}_{2h}^{14}(\mathrm{MD}) \xrightarrow{183\ \mathrm{K}} \mathrm{IC} \xrightarrow{134\ \mathrm{K}} \mathrm{C}_{2h}^{5}(\mathrm{MD}) \xrightarrow{119\ \mathrm{K}} \mathrm{C}_{2h}^{5}$$

where MD and IC are commensurate modulated and incommensurate phases, respectively. According to [2–4], the high temperature phase ($T > 269$ K) belongs to the orthorhombic space group D_{2h}^{17}—$Cmcm$. The primary structural units are $[SbF_5E]^{2-}$ anions and K^- cations; here E is a lone pair of $5s^2$ electrons at Sb^{3+}. Each Sb atom is surrounded by five F atoms forming a square pyramid, but, taking into account a stereochemically active lone pair, the coordination

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polyhedron of the Sb atom may be described as an $[SbF_5E]^{2-}$ octahedron, where one of the six apices is occupied by the aforementioned lone pair. The coordination polyhedrons of two nonequivalent K atoms are a square pyramid and a distorted cube, respectively. A fragment of the structure of K_2SbF_5 is shown in figure 1.

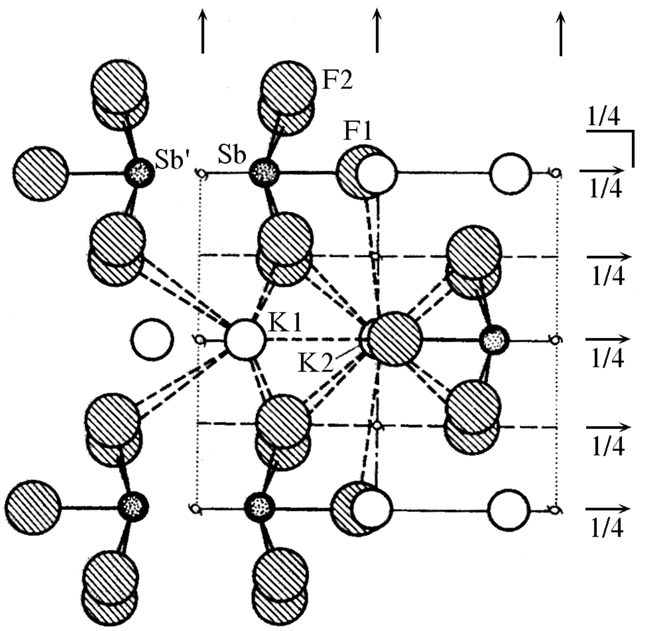

Figure 1. Fragment of the crystal structure of K_2SbF_5.

The commensurate (C) modulated phase at 269–183 K was suggested to keep orthorhombic symmetry, belonging to the space group D_{2h}^{14}—$Pbcn$; the structure was found to be modulated along the a-axis with a period 11 times that of the high temperature phase [2]. At temperatures from 183 to 134 K the crystal shows an incommensurate (IC) structure modulated along the a and b axes. The x-ray pattern at 134 to 119 K was interpreted as a commensurate phase showing a coexistence of two modulation waves along a and b axes with wave vectors $(\boldsymbol{a}^*/6 + \boldsymbol{b}^*/6)$ and $(\boldsymbol{a}^*/2 + \boldsymbol{b}^*/2)$, respectively. The low temperature phase ($T < 119$ K) belongs to the monoclinic space group C_{2h}^5—$P2_1/c$, with a period along the a and b axes twice that of the high temperature phase [2]. The period along the c-axis is almost the same over the whole temperature range, 98–323 K, studied by means of x-ray diffraction. It was concluded [3] that the Sb polyhedron is not changed significantly with temperature, and the phase transitions result from a transformation of the environment of one of the K atoms from the apical KF_5 pyramid to an octahedral KF_6 coordination, when one of the fluorine atoms from the second coordination sphere (r(K–F) = 3.385 Å) moves to the first coordination sphere (r(K–F) = 2.823 Å) of the K atom.

Specific heat measurements of K_2SbF_5 [5] showed anomalies at 110.9, 123.0, 134.7, 270, 289 and 312 K. The dielectric permittivity displays an anomaly at $T \sim 260$ K and a jump with the onset at 118 K, lasting up to ∼136 K [5]. Recently published nuclear quadrupole resonance (NQR) spectra [6] supported the existence of IC and commensurate modulated phases, but in the temperature ranges 260 to ∼150 K and ∼150 to 123 K, respectively. Thus there are some discrepancies in the phase transition temperatures and in the nature of the phases established by means of different methods. The objective of the present paper was to study phase transitions and incommensurability in K_2SbF_5 by means of the ^{123}Sb NQR spectra and spin–lattice relaxation measurements. The phase transitions have been obtained at 117, 135 and 260 K. The line shape and temperature dependence of spin–lattice relaxation time T_1 in the temperature range from 135 to 260 K are characteristic for the incommensurate state with the plane wave modulation regime. The features of the IC state are discussed in the paper. At 117 to 135 K, a distinct fine structure of NQR spectra has been observed. An important feature of these spectra is a redistribution of the line intensities with the variation of temperature. Two scenarios of this transformation (existence of domain structure and quasi-soliton lattice) are discussed. The model that fits the NQR data is that this phase consists of commensurate domains having different structure, and that one of the domains, which shows the same structure as the low temperature phase, becomes energetically beneficial on cooling and is transformed into the C phase at $T_{\mathrm{p.t.}} = 117$ K. The ^{123}Sb NQR measurements in K_2SbF_5 show unusually short values of T_1, which become close to the spin–spin relaxation time T_2 with increasing temperature.

2. Experiment

The transparent colourless K_2SbF_5 crystals were grown from a 2:1 saturated solution of KF and SbF_3 by slow evaporation and then were identified by means of x-ray diffraction. A powder K_2SbF_5 sample prepared from the ground crystals was put into a 5 mm outer diameter quartz ampoule and used for the NQR measurements.

The ^{123}Sb NQR measurements in the temperature range from 77 to 293 K have been carried out using a Tecmag pulse spectrometer and an Oxford Instruments cryostat. The $\pm(3/2 \leftrightarrow 5/2)$ ^{123}Sb NQR transition was observed. The NQR spectra cover a range of several hundred kHz, which is too broad to be excited by a radio frequency (rf) $\pi/2$ pulse. Therefore the spectra were obtained using a computer-controlled point-by-point frequency sweep (with the step from 10 to 20 kHz) and acquisition of solid echo amplitudes at each specified frequency. These measurements have been made using rather long, 'soft' rf pulses (with pulse duration of 15.6 μs equal to the duration of the $3\pi/2$ pulse) to excite only a small portion of the NQR line, ~4 kHz. The obtained echo amplitude represents the intensity of the actual NQR line at the specified frequency. The number of scans was from 16 000 to 640 000 depending on the temperature and signal intensity. The repetition time was $5T_1$. The ^{123}Sb NQR spin–lattice relaxation time T_1 has been measured using a π–τ–$\pi/2$ inversion recovery sequence.

The temperature was measured by a copper–constantan thermocouple with an accuracy of 1 K. Temperature stability during the experiment was ± 0.3 K.

3. Results and discussion

Some characteristic NQR spectra of the K_2SbF_5 powder sample in the temperature range from 77 to 293 K are given in figure 2. The temperature dependence of the NQR frequencies is given in figure 3. From drastic changes in the line shape and multiplicity, four different regions are clearly seen in figures 2 and 3, corresponding to the four different phases and three phase transitions between them at 117, 135 and 260 K.

At $293 > T > 260$ K, the high temperature phase I shows a single Gaussian-like resonance. Its line width $\Delta\omega$ increases from ~80 to 110 kHz when the temperature decreases from 293 to 260 K. Between 260 K and 135 K (phase II), the NQR spectra are characterized by a quasi-continuous distribution of the resonance frequencies (figure 2). Such line shape

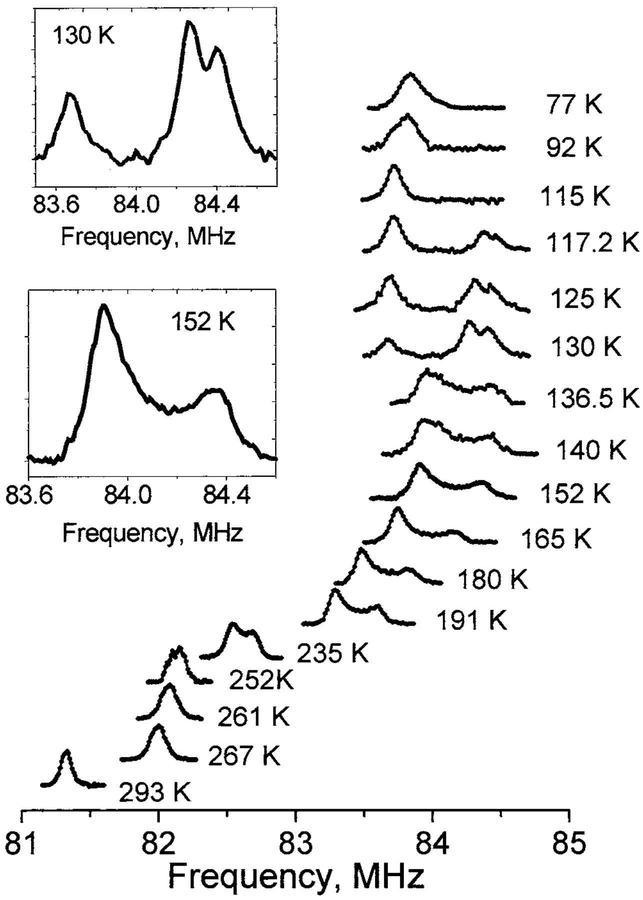

Figure 2. [123]Sb NQR spectra of powder K_2SbF_5 sample in the temperature interval from 77 to 293 K. Two characteristic spectra are shown in the insets.

with two edge singularities is typical for the incommensurate systems, in which the resonance frequency varies in space and reflects the spatial variation of the incommensurate modulation [7–9]. The line shape is characteristic for the plane wave modulation regime. One can see that the obtained resonance shape is not symmetric and the amplitudes of two singularities are not equal. Such line shape with non-equal weight of shoulders occurs when both linear and quadratic terms in the expansion of the resonance frequency in powers,

$$\nu = \nu_0 + \nu_1 \cos\varphi(x) + (1/2)\nu_2 \cos^2\varphi(x) \tag{1}$$

are taken into account [8]. Here $\nu_0 = \text{const}$, ν_1 and ν_2 concern the first and second order terms of the incommensurate modulation, respectively, $\varphi(x)$ is the phase of the incommensurate modulation and x is a displacement along the axis of the modulation.

In the temperature dependence of the ^{123}Sb resonance frequency given in figure 3, two curves correspond to the low- and high-frequency peaks of the broad resonance, of which the width reaches the value of 480 kHz at 140 K. The obtained dependence, which shows that the NQR frequencies of both singularities in the IC phase increase with decreasing temperature, is characteristic for the case when a quadratic term is present in the expansion of the frequency of equation (1) [8]. The difference between the two singularities is proportional to the order

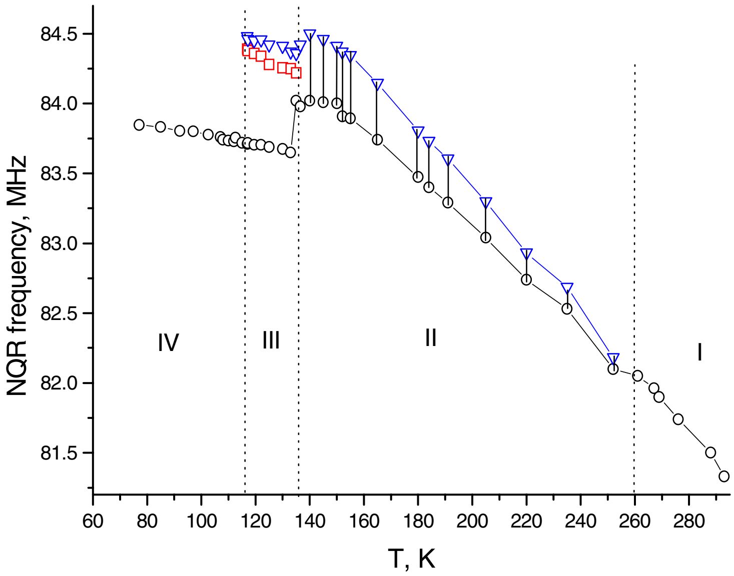

Figure 3. Temperature dependence of the [123]Sb NQR frequencies of powder K_2SbF_5 in the region from 77 to 293 K. At temperatures from 260 to 136 K, two curves shown in the figure correspond to the low and high frequency singularities of the broad resonance. Open circles, squares and triangles correspond to the low-, medium- and high-frequency peaks, respectively. Vertical dotted lines show the phase transition temperatures.

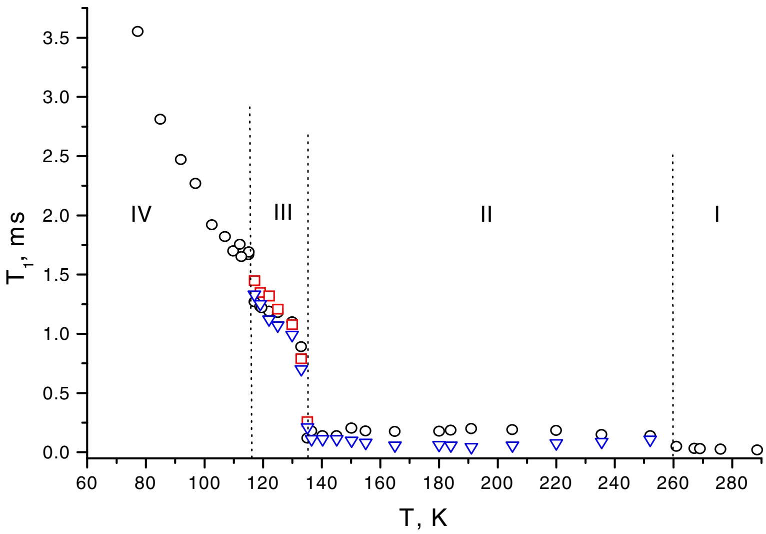

Figure 4. Temperature dependence of the [123]Sb NQR spin–lattice relaxation time T_1 in powder K_2SbF_5 at 77–293 K. Open circles, squares and triangles correspond to the low-, medium- and high-frequency peaks, respectively. Vertical dotted lines show the phase transition temperatures.

parameter [8] and increases with decreasing temperature in the same way as the amplitude of the IC modulation. We note that similar line shape and temperature dependence of the NQR frequencies was obtained in the [14]N NQR study of the IC phase in $NaNO_2$ [10, 8].

We also note that an additional weak peak in the central part of the NQR line was observed at temperatures 150–160 K by the authors of [6]. In our measurements, however, no evidence of such a peak was obtained.

The temperature dependence of the spin–lattice relaxation time T_1 at 77–293 K is given in figure 4. One can see that in the temperature range from 260 to 136 K, T_1 is almost temperature independent. Such behaviour is a characteristic property of the classical IC state. The values of T_1 are somewhat different for the two shoulders of the spectra (figure 3), showing larger T_1 for the low frequency singularity. We noted above that the phase transition at 183 K was obtained by the x-ray measurements. One can see in figure 4 that the temperature dependence of T_1 shows slightly different slopes of $T_1(T)$ for the regions below and above $T \sim 190$ K, namely at 135–190 and 190–260 K. However, the variations of the $T_1(T)$ slope are small and smooth and thus cannot be considered as an evidence of a phase transition. We would like to remark that no phase transition at 183 K was obtained also by specific heat and dielectric permittivity measurements [5].

We note that the values of the ^{123}Sb NQR spin–lattice relaxation time T_1 in the IC phase of K_2SbF_5 are unusually short and are close to the spin–spin relaxation time T_2. In fact, very fast spin–lattice relaxation of quadrupolar nuclei is typical for IC phases [7–9]. We note, however, that the T_1 values in the low temperature phase IV (see below) are also not long and show values of several milliseconds. One can speculate about some contribution of the interaction of nuclei with the $5s^2$ lone pair of Sb to the NQR relaxation. We note that ESR measurement shows that the sample under study is ESR silent and thus short T_1 values can not be attributed to an influence of paramagnetic centres.

When temperature is lowered to $T = 135$ K, the line shape is changed (figures 2, 3), showing a phase transition. Between 117 and 135 K (phase III), a broad resonance with three overlapping peaks is observed. The intensities of the peaks are temperature dependent. Spectrum multiplicity disappears at 117 K, being transformed into a single resonance at lower temperatures.

The phase transition at 135 K is readily seen in the temperature dependent T_1 measurements (figure 4). In the temperature range from 117 to 135 K the values of spin–lattice relaxation time increase with decreasing temperature for all lines. Such temperature dependence is characteristic for the C phase and is usually caused by thermal fluctuations of electric field gradient (EFG) due to torsional vibrations [11, 12]. To explain the spectra and relaxation at 135–117 K, two interpretations can be suggested. As known, an IC structure exists in a certain temperature interval between T_i and T_c, where T_i corresponds to a normal–incommensurate transition, and T_c to an IC–C 'lock-in' transition, where a three-dimensional translational periodicity of the crystal lattice is restored. In some cases, the changes in the line shape below T_i follow the scenario of the evolution of the incommensurate modulation from the plane wave limit, which is a good approximation of the structure of the IC phase below T_i, to the multi-soliton lattice which becomes increasingly important on approaching the IC–C lock-in phase transition temperature T_c [7–9, 13]. The occurrence of such a lattice is usually accompanied by the appearance of additional NQR peaks, which correspond to commensurate regions without modulation. At first sight, our data are in accordance with this scheme, and the observed spectra may be attributed to a quasi-soliton lattice, in which three C phases are separated by IC phases (phase solitons). However, usually, when such a lattice is formed, the phase solitons become narrower on approaching T_c and almost the whole intensity of the spectrum concentrates in the C peaks. The frequencies of these peaks continuously move through the transition temperature into the low temperature phase. However, the spectrum transformation observed in our experiment does not exactly follow this scenario. An important feature of the spectra of the phase III (between 117 and 135 K) is a redistribution of the line intensities with the variation of temperature. Reduced temperature yields an increase in intensity of the low-frequency resonance, while the other two lines are gradually decreased and finally disappear. The single NQR resonance at the low-temperature C phase IV ($T < 117$ K) appears at the same frequency as the low-frequency line of phase III; only this frequency continues from phase III to the low-temperature phase IV. One can suggest that phase III consists of commensurate domains having different structure, and that one of the domains, which shows the same structure that the low-temperature phase, becomes energetically beneficial on cooling and is transformed into the C phase IV at $T_{\mathrm{p.t.}} = 117$ K. The temperature dependences of spin–lattice relaxation time T_1 in the phases III and IV are similar, supporting the aforementioned proposition.

We note that the x-ray diffraction pattern of the phase III was interpreted [2, 4] as a coexistence of two modulation waves along a and b axes with the wave vectors $(\boldsymbol{a}^*/6 + \boldsymbol{b}^*/6)$ and $(\boldsymbol{a}^*/2 + \boldsymbol{b}^*/2)$, respectively. The amplitude of the former wave becomes smaller on cooling and disappears at phase transition temperature, while the amplitude of the latter grows in intensity. The low-temperature phase IV shows a period along the a and b axes twice that of the high temperature phase [2, 4]. In principle, if two modulation waves are present over the whole lattice simultaneously, they can yield inequivalent Sb positions reflected in the NQR spectra. However, the values of the corresponding EFGs should depend on the amplitude of displacement, yielding the shift of the NQR frequencies with varying temperature. This was not observed in the experiment, and therefore such a scenario seems to be unlikely from the point of view of NQR. At the same time, x-ray data might be interpreted as coexistence of two domains, when each of them shows only one of the aforementioned modulation waves. Such an interpretation fits the NQR data.

We note that x-ray study [2] showed the transition between phases III and IV is blurred and occurred in some temperature interval down to 119 K. Some discrepancies in the phase transition temperature between ours and x-ray studies might result from the significant error in measuring the temperature in the x-ray study, ± 3 K [2].

As seen from figure 2, phase transition at 117 K is accompanied by a drastic change in line multiplicity, and the low-temperature phase IV ($T < 117$ K) shows a single NQR resonance characteristic for the C phase. It has a Gaussian-like shape, and the line width $\Delta\omega$ increases from $\sim$110 to 180 kHz with the temperature decrease from 115 to 77 K. Though x-ray diffraction study showed that the unit cell parameters a and b of phase IV are two times that of the high-temperature phase [2], no additional NQR lines appear in the experiment. The reason is that, according to the x-ray diffraction data, the Sb polyhedron is not changed significantly with temperature, and the phase transitions result from a transformation of the environment of one of the K atoms [3]. Therefore, one can suggest that the splitting between the lines corresponding to inequivalent Sb atoms (if they exist) is smaller than the line width and is not reflected in the NQR spectra.

One can see in figure 4 that the spin–lattice relaxation time in the low temperature phase is reduced rather sharply with increasing temperature up to $T_{p.t.} = 117$ K. The dielectric permittivity displays a jumplike anomaly rather than a λ-type anomaly at this temperature [5]. A decrease in the dielectric permittivity ε under transition from phase III to phase IV is characteristic for a transition to an antiferroelectric state. One could therefore speculate that K_2SbF_5 undergoes successive phase transitions from the paraelectric, non-polar high-temperature phase (D_{2h}^{17}—$Cmcm$) to the antiferroelectric low-temperature phase through IC and MD phases. The space group of the low-temperature phase, C_{2h}^5—$P2_1/c$, allows an antiferroelectric state. However, the authors of [5], who studied the dielectric permittivity, doubted a transition to an electrically ordered state at low temperature.

According to the x-ray study, structural changes in K_2SbF_5 were attributed to the displacement-type phase transitions [2–4]. However, concerning the nature of the phase transition at 260 K, we note that the ^{19}F NMR study showed the ^{19}F line narrowing around this temperature [1]. This behaviour was attributed to the anisotropic reorientation of the $[SbF_5E]^{2-}$ octahedron around its C_4 symmetry axis [1]. One can suggest that such a rotation leads to an effective increase in symmetry and therefore removes the incommensurability of the crystal lattice. Moreover, the ^{19}F NMR study showed that temperatures upper than 365 K yield a transformation from the anisotropic reorientation to an isotropic rotation of the $[SbF_5E]^{2-}$ octahedron around random axes. Finally, along with the octahedron rotation, F^- anions diffusion was observed at 472–610 K. However, the aforementioned temperature range was beyond of the scope of our paper.

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