Incommensurability and Domain Structure of K_2SbF_5

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Phase transitions and incommensurability in K_2SbF_5 have been studied by means of ^{123}Sb NQR spectra and spin-lattice relaxation measurements. The phase transitions occur at 117, 135 and 260 K. The line shape and temperature dependence of the spin-lattice relaxation time T_1 at 135 to 260 K are characteristic for an incommensurate state with a plane wave modulation regime. At 117 to 135 K a distinct fine structure of the NQR spectra has been observed. The X-ray diffraction pattern of this phase is interpreted as a coexistence of two modulation waves along the *a* and *b* axis with wave vectors ($\boldsymbol{a}^*/6 + \boldsymbol{b}^*/6$) and ($\boldsymbol{a}^*/2 + \boldsymbol{b}^*/2$), respectively. The best interpretation that fits our NQR data is a coexistence of two domains, the structures of which are modulated with different periods in such a manner that each domain exhibits only one of the aforementioned modulation waves. Redistribution of line intensities with the variation of temperature shows that one of the domains becomes energetically preferable on cooling and is transformed 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. – Pacs: 61.44.Fw, 64.60, 64.70, 64.70.Rh, 76.60

Key words: NQR; Incommensurate Phases; Phase Transitions; Domain Structure.

Introduction

An X-ray diffraction study of potassium pentafluoroantimonate, K_2SbF_5 [1 - 3], showed that K_2SbF_5 undergoes successive phase transitions at 269, 183, 134, and 119 K, according to the scheme

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

where MD and IC are commensurate modulated and incommensurate phases, respectively. 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 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.

The commensurate (C) modulated phase at 269 - 183 K was found to be modulated along the *a* axis with a period eleven times that of the high temperature phase [1]. 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 coexistence of two modulation waves along the *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 two times that of the high temperature phase [1].

The purpose of the present paper was to study the

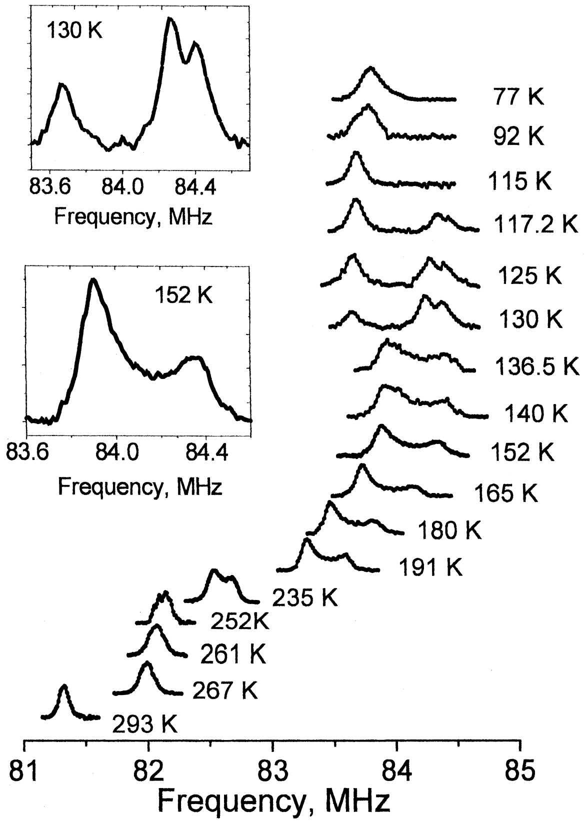

Fig. 1. ^{123}Sb NQR spectra of a powdered K_2SbF_5 sample at 77 to 293 K. Two characteristic spectra are shown in inserts.

phase transitions and incommensurability in K_2SbF_5 by means of the ^{123}Sb NQR spectra and spin-lattice relaxation measurements. Phase transitions have been obtained at 117, 135, and 260 K. The 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 a 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 best interpretation that fits our NQR data is a coexistence of two domains, the structure of which is modulated with different periods in such a manner that each domain exhibits only one of the aforementioned modulation waves. One of the domains, which shows the same structure as the low temperature phase, becomes energetically preferable on cooling and is transformed into the C phase at $T_{p.t.}$ = 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.

Experimental

The ^{123}Sb NQR measurements at 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 radio frequency (*rf*) $\pi/2$ pulse. Therefore the spectra were obtained using a computer-controlled point-by-point frequency sweep (with steps from 10 to 20 kHz) and acquisition of solid echo amplitudes at each specified frequency, which represents an intensity of the actual NQR line at a specified frequency. The number of scans was from 16000 to 640000, depending on the temperature and signal intensity. Repetition time was $5T_1$. The ^{123}Sb NQR spin-lattice relaxation time T_1 has been measured using the π-τ-$\pi/2$ inversion recovery sequence.

Results and Discussion

Some characteristic NQR spectra of the powdered K_2SbF_5 sample at 77 to 293 K are given in Figure 1. The temperature dependence of the NQR frequencies is given in Figure 2. From drastic changes in the line shape and multiplicity, four different regions are clearly seen in Figs. 1 and 2, corresponding to the four different phases and three phase transitions at 117, 135 and 260 K.

At 293 > T > 260 K, the high temperature phase I shows a single Gaussian-like resonance. Between 260 and 135 K (phase II), the NQR spectra are characterized by a quasi-continuous distribution of the resonance frequencies (Fig. 1). Such a line shape with two edge singularities is typical for incommensurate systems, in which the resonance frequency varies in space and reflects the spatial variation of the incommensurate modulation [4 - 6]. 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 the linear and quadratic

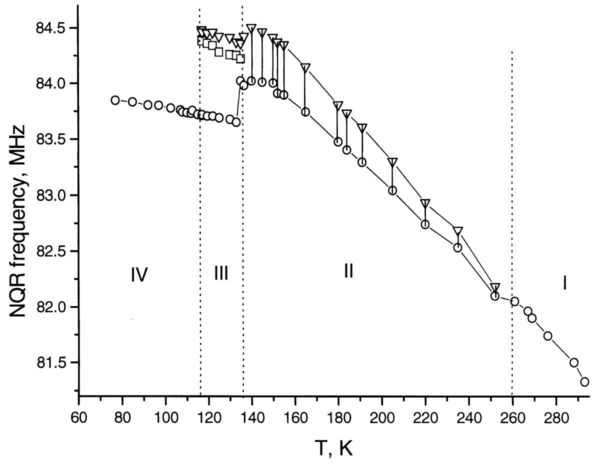

Fig. 2. Temperature dependence of ^{123}Sb NQR frequencies of powdered K_2SbF_5 at 77 to 293 K. At temperatures from 135 to 260 K, the two curves shown in the figure correspond to the low and high frequency singularities of the broad resonance. Open circles, squares and triangles correspond to low, medium and high frequency peaks, respectively. Vertical dotted lines show phase transition temperatures.

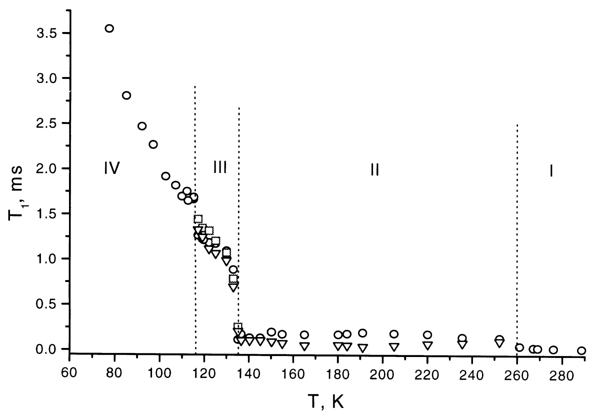

Fig. 3. Temperature dependence of ^{123}Sb NQR spin-lattice relaxation time T_1 in powdered K_2SbF_5 at 77 - 293 K. Open circles, squares and triangles correspond to low, medium and high frequency peaks, respectively. Vertical dotted lines show phase transition temperatures.

terms in the expansion of the resonance frequency in powers,

$$\nu = \nu_0 + \nu_1 \cos\varphi(x) + \frac{1}{2}\nu_2 \cos^2\varphi(x), \qquad (1)$$

are taken into account [5]. Here ν_0 = const, ν_1 and ν_2 correspond to 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 Fig. 2, the two curves correspond to the low and high frequency peaks of the broad resonance, the width of which reaches 480 kHz at 140 K. The observed dependence, which shows that the NQR frequencies of both singularities in the IC phase increase with decreasing temperature, is characteristic for the case when the quadratic term in (1) presents in the expansion of the frequency [5]. The difference between the two singularities is proportional to the order parameter [5] and increases with decreasing temperature in the same way as the amplitude of the IC modulation. We note that a similar line shape and temperature dependence of the NQR frequencies was obtained in the ^{14}N NQR study of the IC phase in $NaNO_2$ [7, 5].

The temperature dependence of T_1 at 77 - 293 K is given in Figure 3. One can see that at 260 to 136 K, T_1 is almost temperature independent. Such behavior is a characteristic property of the classical IC state. The values of T_1 are somewhat different for the two shoulders of the spectrum, showing a 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 Fig. 3, 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 can not be considered as evidence of a phase transition. We would like to remark that no phase transition at 183 K was observed also by specific heat and dielectric permittivity measurements [8].

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 [4 - 6]. We note, however, that the T_1's 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.

When the temperature is lowered to 135 K, the line shape is changed (Figs. 1 and 2), 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. Spectra multiplicity disappears at 117 K, being transformed into a single resonance at lower temperatures.

Between 117 to 135 K, for all lines T_1 increases with decreasing temperature. Such temperature dependence is characteristic for C phase and is usually caused by thermal fluctuations of the electric field gradient (EFG) due to torsional vibrations [9, 10]. 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 [4 - 6, 11]. Occurrence of such a lattice is usually accompanied by the appearance of additional NQR peaks, which correspond to commensurate regions without modulation. At first glance, 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 spectra transformation observed in our experiment does not exactly follow this scenario. An important feature of the spectra of 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 gradually decrease 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 as the low temperature phase, becomes energetically preferred on cooling and is transformed into the C phase IV at $T_{p.t.} = 117$ K. The temperature dependences of T_1 in the phases III and IV are similar, supporting the aforementioned proposition.

We note that the x-ray diffraction pattern of phase III was interpreted [1, 3] as a coexistence of two modulation waves along the 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 the 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 two times that of the high temperature phase [1, 3]. 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 EFG's should depend on the amplitude of displacement, yielding a 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 reinterpreted as coexistence of two domains, when each of them shows only one of the aforementioned modulation waves. Such an interpretation fits the NQR data.

As it is seen from Fig. 1, a 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 the 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 [1], no additional NQR lines appear in the experiment. The reason is that, according to the X-ray diffraction data, the Sb polyhedron does not change significantly with temperature, and the phase transitions result from a transformation of the environment of one of the K atoms [2]. Therefore, one can suggest that the splitting between the lines corresponding to inequivalent Sb atoms (if these exist) is smaller than the line width and is not seen in the NQR spectra.

Figure 3 shows that the spin-lattice relaxation time in the low temperature phase is reduced rather sharply with increasing temperature up to $T_{\mathrm{p.t.}}$ = 117 K. The dielectric permittivity displays a jump-like anomaly rather then a λ-type anomaly at this temperature [8]. The 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 a 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 [8], who studied the dielectric permittivity, doubted the presence of a transition to an electrically ordered state at low temperature.

Summary

In summary, our ^{123}Sb NQR study shows that K_2SbF_5 exhibits phase transitions at 260, 135, and 117 K between the high temperature and low temperature commensurate phases via the incommensurate phase in the temperature range from 135 to 260 K, the modulated phase having domain structure at 117 to 135 K.

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