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QUADRUPOLE INTERACTIONS AND NMR RELAXATION IN KSbF6

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Potassium hexafluoroantimonate $KSbF_6$ at temperatures below 302 K is assigned cubic syngony, while at higher temperatures it has tetragonal syngony [1]. A specific characteristic of $KSbF_6$ is not only the unusual nature of the change in symmetry but also its tendency toward supercooling: the transition to the low-temperature phase upon cooling the sample occurs at 265 K. This circumstance is possibly the basis for the fact that upon synthesis of $KSbF_6$ either the cubic [2, 3] or the tetragonal [1, 4] phase may be obtained.

In this paper, we focus our primary attention on the study of the physical properties of the low-temperature cubic phase f of $KSbF_6$. We give a change in the temperature dependences of the quadrupole coupling constants at the ¹²¹Sb nuclei, the spin-lattice relaxation time T_1 for the ¹⁹F nuclei, and the dielectric constant $\epsilon(T)$ in polycrystalline samples of $KSbF_6$.

Polycrystals of KSbF_6 were synthesized by two methods. KSbF_6 crystals of cubic syngony are formed upon reaction of KSb(OH)_6 with liquid HF, while crystals of tetragonal syngony are formed upon reaction of KF with SbF_5 in a BrF_3 solution. The samples were monitored using x-ray diffraction powder patterns, which were registered on the DRON-2,0 x-ray diffractometer.

The NMR spectra of the ¹²¹Sb nuclei were recorded using a CW spectrometer at a frequency of 20 MHz. The T_1 measurements at the ¹⁹F nuclei were made using the IS-3 pulse spectrometer at a frequency of 27.2 MHz.

The ¹²¹Sb NMR spectra were analyzed using the technique in [5], allowing us to determine from the powder spectra the values of the quadrupole coupling constants (W) of the ¹²¹Sb nuclei in $KSbF_6$. In Fig. 1, we give the temperature dependences of W obtained on the basis of the NMR spectra. The analysis shows that the dependence obtained is described by the high-temperature approximation of the Bayer law [6]:

$$W = W_0 \left(1 - kT / 8\pi^2 I v_1^2 \right), \tag{1}$$

where W_0 is the asymptotic limit to which W tends when T is lowered; I is the moment of inertia; v_1 is the frequency of the librational motion averaging W. Analysis of the experimental

mo /							
v, MHz r(F-Sb),		Isotrop. reori- ent.	C4	C 3	C2	Experiment	
10 [8]	1,844	11,5	17,5	12,9	33,9	14,1±0,7	
	1,77	9,0	13,7	10,1	25,6		
5,5 [7]	1,844	6,4	9,6	7,1	18,6	- 7±1	
	1,77	5,0	7,5	5,6	14,6		
27,2	1,844	31,4	47,5	35,2	92,4	37±2	
	1,77	24,6	37,2	27,5	72,3		

TABLE 1. Theoretical and Experimental Values of the Spin-Lattice Relaxation Times for the $^{19}{\rm F}$ Nuclei (T₁, ms)

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Fig. 2. Temperature dependence of the dielectric constant in $KSbF_6$ ($\nu = 1 \ kHz$).

data gave the following parameters: for the low-temperature phase, $W_0 = 10.1 \pm 0.3$ MHz and $v_1 = 2.6 \cdot 10^{11}$ Hz; for the high-temperature phase, $W_0 = 15.1 \pm 1$ MHz and $v_1 = 1.9 \cdot 10^{11}$ Hz. The observed change in W_0 with a reduction in temperature may be connected with the increase in symmetry of the crystal, in agreement with the data in [1], since the quantity W_0 is proportional to the deformation of the SbF₆ octahedron, i.e., to the magnitude of the noncubic component of the crystal field at its location. Since in the low-temperature phase of KSbF₆ we obtain $W_0 \neq 0$, the Sb⁵⁺ ions in this phase may not be strictly located at special positions of cubic point symmetry. This conclusion is in agreement with the model of low-temperature phase KSbF₆ discussed previously [1, 7] (space group I23-T³ or I2₁3 T⁵) on the basis of data from x-ray diffraction and Raman studies.

The data from measurements of the minimum values of T_1 for NMR relaxation at the ¹⁹F nuclei in KSbF₆ are given in Table 1 together with the previously obtained values from [7, 8]. A theoretical analysis was carried out using the technique for calculating T_1^{min} in [9] for several probable mechanisms for reorientation of an almost ideal octahedral SbF₆ anion about the fixed C₄, C₂, and C₃ axes, and also upon isotropic reorientation. In the calculation we used the intramolecular distances r(Sb-F) known from x-ray diffraction data, 1.844 Å [10] and 1.77 Å [3]. As is evident from Table 1, agreement between the experimental and calculated data is obtained for the model of anisotropic reorientation of the octahedral SbF₆ anion either about the C₃ axis or about the C₄ axis. In the calculation, we determined the value of the pre-exponential factor for the Arrhenius equation in [11] as $v_0 \approx 10^{15}$ Hz. From comparison with the value $v_1 \approx 10^{11}$ Hz obtained above, we may conclude that relaxation and averaging of the quadrupole interaction are connected with different types of motion. Furthermore, the too-high value of v_0 may also be due to the contribution of the entropy factor [12].

The strong anisotropy in the reorientation of the almost regular SbF_6^- octahedron may be interpreted within the framework of a model according to which the antimony ions are shifted from the centers of symmetry for the SbF_6^- anions, and the anisotropy of the reorientation is due to the existence of electric dipole moments for the SbF_6^- anions. Such an hypothesis is consistent with measurements of the dielectric constant $\varepsilon(T)$ for KSbF_6 (Fig. 2). The nature of the behavior of $\varepsilon(T)$ in the phase transition region may indicate that the phase transition in KSbF_6 is an improper ferroelectric phase transition, analogous to that described in [13]. Thus, the results obtained are found to be in agreement with the assumptions of [7], in which the low-temperature phase is classified as piezoelectric and optically active.

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REFINEMENT OF THE STRUCTURE AND COMPOSITION OF THE TETRAHYDRATE

OF HAFNIUM HEXASODIUM SULFATE

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We earlier described the structure of a compound whose formula was represented as $Hf(SO_{4})_{2} \cdot 3Na_{2}SO_{4} \cdot H_{2}O[1]$. This formula has been assumed on the basis of chemical analysis [2]; trusting these data, we did not continue to look for H_2O molecules in the structure after locating the molecule involved in the hafnium polyhedron. A later investigation of the thermal properties of this compound, and also a study of the composition of the analogous zirconium sulfate, has shown that it contains a greater amount of water and corresponds to the formula $Na_6Hf(SO_4)_5 \cdot 4H_2O$. Such an H_2O content follows from the TG curves given in [3], although in that paper the compound is considered as the monohydrate.

Atom	x	V .	z	Atom	x	¥	z
Hf	0.2219	0	0.2747	0	0,384	0,027	0,645
Na.	0.058	0.324	0.497	044	0,178	0,179	0,645
Na	0,531	0,692	0,979	041	0,969	0,016	0,255
Na	0,592	0,974	0,535	012	0,803	0,994	0,418
Na	0,189	0,473	0,953	· 043	0,704	0,093	0,220
Nas	0,694	0,327	0,271	0,1	0,898	0,191	0,367
Nas	0,970	0.066	0,775	051	0,126	0,924	0,093
S,	0,3051	0,7738	0,3837	0 ₅₂	0,379	0,006	0,114
S,	0,2468	0,3049	0,2220	0 ₅₃	0,213	0,031	0,911
S _a	0,2209	0,0616	0,5964	O ₅₄	0,315	0,836	0,969
S_4	0,8437	0,0769	0,3202	0 _{w1}	0,460	0,083	0,349
S ₅	0,2604	0,9480	0,0148	0 _{w2}	0,073	0,656	0,028
011	0,391	0,851	0,304	O _{wa}	0,409	0,570	0,107
O ₁₂	0,150	0,840	0,374	O _{w4}	0,332	0,313	0,856
0 ₁₃	0,388	0,768	0,515	H,	0,47	0,61	0,57
014	0,279	0,656	0,327	H,	0,44	0,58	0,69
021	0,183	0,178	0,200	Ha	0,04	. 0,18	0,02
0.22	0,253	0,338	0,358	H	0,08	0,74	0,01
0 ₂₃	0,138	0,383	0,140	H ₅	0,50	0,53	0,19
024	0,408	0,309	0,187	H ₆	0,29	0,57	0,12
031	0,208	0,074	0,454	H ₇	0,25	0,31	0,76
O ₃₂	0,110	0,967	0,627	H_8	0,42	0,26	0,79

TABLE 1. Atomic Coordinates

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