Antimony NQR and Nuclear Magnetic Relaxation in Hexaammonium Dodecafluorotrisulfatotetraantimonate (III), $(NH_4)_6Sb_4(SO_4)_3F_{12}$

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Antimony nuclear quadrupole resonance frequencies in $(NH_4)_6Sb_4(SO_4)_3F_{12}$ crystals were measured as a function of temperature, and no evidence of phase transition was detected between 77 K and room temperature. However, the resonance frequencies do not follow the Bayer type exactly. Such an anomaly is attributed to the effect of rotation of ammonium ions which form hydrogen bonds of types $N-H\cdots F$ and $N-H\cdots O$. In fact, the spin-lattice relaxation time of ^1H and ^{19}F has a minimum which is ascribed to the reorientation of NH_4^+ with an activation energy of 7.14 kJ mol^{-1}. The switch model for the electric field gradient at Sb nuclei was examined.

Introduction

$(NH_4)_6Sb_4(SO_4)_3F_{12}$ is a member of a series of mixed crystals between ammonium sulfate and antimony(III) fluoride with a mixing ratio of 3:4. An early X-ray investigation pointed out that in the crystalline state it belongs probably to a hexagonal system [1]. An infrared spectroscopic study indicated that the SO_4^{2-} groups in this compound coordinate to and bridge the central antimony atoms [2]. A more recent X-ray diffraction study at 300 K revealed that the compound crystallizes in the trigonal system P3 with three formula units in the unit cell [3]. A dielectric study found that it is piezoeletric and anomalies have been reported in both ε' and ε'' between 240 and 260 K due to a probable phase transition in this temperature region [4]. It was noted at the same time that repeated thermal cycling causes the flattening out of the dielectric anomaly. An electron spin resonance experiment on VO^{2+} doped in a single crystal of $(NH_4)_6Sb_4(SO_4)_3F_{12}$ indicated the existence of a phase transition at 256 K [5], while recent dielectric and pyroelectric measurements [6] found that the material undergoes a first-order phase transition between two pyroelectric phases at 92 K but not at 256 K.

Whereas such experimental studies as described above indicate that $(NH_4)_6Sb_4(SO_4)_3F_{12}$ possesses interesting electrical characteristics, different experiments reported different phase transition temperatures and cast some doubt about the very existence of the phase transition(s).

We now attempted to measure the nuclear quadrupole resonance (NQR) frequencies of the antimony isotopes, ^{121}Sb and ^{123}Sb in the compound in order to examine the existence of any phase transition and, if it exists at all, to shed light on its microscopic mechanism. We also measured the nuclear magnetic spin-lattice relaxation times, T_1, of ^1H and ^{19}F, to obtain information on a possible effect of the rotation or reorientation of NH_4^+ on both, the phase transition and the specific electrical properties of $(NH_4)_6Sb_4(SO_4)_3F_{12}$ crystal.

Experimental

Colorless prismatic crystals of $(NH_4)_6Sb_4(SO_4)_3F_{12}$ were obtained according to [6] by slow evaporation at 26 °C from an aqueous solution of $(NH_4)_2SO_4$ and SbF_3 in the molar ratio 3:4 containing a small amount of HF. A powder X-ray diffraction pattern which agrees with the crystal data reported [3] was obtained. Large single crystals with average dimensions of 1 cm × 1 cm × 1.5 cm were used for the antimony NQR experiments; Two superregenerative spectrometers were used to cover the frequency range between 20 and 170 MHz. The uncertainty in the frequency measurements was at most ± 3 kHz at 77 K but increased up to $\pm 10 \sim 15$ kHz at room temperature.

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The measurements of the T_1's for ^1H and ^{19}F were carried out on a powdered specimen sealed into an ampoule with a small amount of He gas for heat exchange. The T_1's were determined with $90°-\tau-90°$ pulse sequences at 10 MHz with an uncertainty of about 10% for ^1H and 20% for ^{19}F. Temperatures were determined using Chromel-P-Constantan thermocouples to within ± 0.2 K.

Results and Discussion

We detected 15 antimony NQR signals at 77 K which correspond to three crystallographically inequivalent antimony sites. At room temperature the signals were so weak that we could measure the frequencies of only six lines due to the ^{121}Sb isotope. The results are listed in Table 1. Our present result may be compared with those reported for other fluorosulfatoantimonates [7].

The X-ray structure analysis indicates that there are six crystallographically inequivalent antimony sites in $(NH_4)_6Sb_4(SO_4)_3F_{12}$ crystal ($Z = 3$) at 300 K [3]: Three antimony atoms occupy special positions on the three-fold axes while nine others are located at three kinds of general positions in the unit cell. As all asymmetry parameters, η, of the three electric field gradient EFG tensors are finite at 77 K, see Table 1, we can assign these three sets of resonance lines to the three kinds of general antimony sites. We did not detect any signal due to the other three antimony atoms at the special positions in the frequency range between 20 and 170 MHz. The signals from these antimony atoms may be very weak for some reason or may appear below 20 MHz due probably to high site symmetry.

The temperature dependence of the resonance frequencies was measured for the three lines corresponding to transitions between $\pm 1/2 \leftrightarrow \pm 3/2$ of ^{121}Sb between 77 and 300 K. The result is shown in Figure 1. We see that all resonance frequencies vary monotonously with temperature and neither show any discontinuous change or change of the temperature coefficient, which usually characterize the existence of a phase transition. Therefore, if $(NH_4)_6Sb_4(SO_4)_3F_{12}$ undergoes any phase transition at 92 K and/or near 256 K as reported in [5, 6], the transition should not accompanied with even a very small change of the EFG at the antimony atoms at the general sites. However, because both of phase transitions reported in

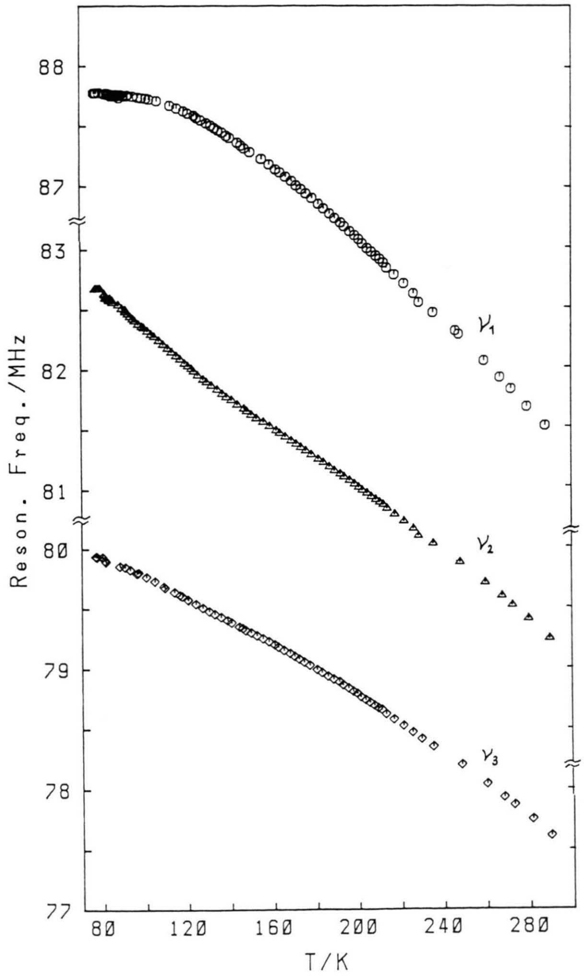

Fig. 1. Temperature dependence of antimony nuclear quadrupole resonance frequencies for the transition between the spin states $\pm 1/2$ and $\pm 3/2$.

Table 1. Antimony NQR parameters in $(NH_4)_6Sb_4(SO_4)_3F_{12}$.

Isotope	Temp.	$\nu\left(\frac{1}{2},\frac{3}{2}\right)$	$\nu\left(\frac{3}{2},\frac{5}{2}\right)$	$\nu\left(\frac{5}{2},\frac{7}{2}\right)$	e^2Qq/h	η
	K	MHz	MHz	MHz	MHz	
^{121}Sb	77	87.774	172.723		577.17	0.113
		82.672	165.216		550.77	0.025
		79.932	159.642		532.25	0.033
	293	84.889	167.41		559.36	0.104
		79.670	159.39		531.13	0.0
		77.560	155.05		516.88	0.018
^{123}Sb	77	54.922	104.388	157.47	735.61	0.113
		50.255	100.280	150.69	702.22	0.023
		48.652	96.872	145.42	678.45	0.033

[5, 6] are associated with a dielectric anomaly, if such a phase change occurs, it must cause some change in the EFG at the antimony sites. Hence the possibility than $(NH_4)_6Sb_4(SO_4)_3F_{12}$ crystal undergoes a phase transition at 92 K or at 256 K is very remote.

The resonance frequencies in Fig. 1 vary with temperature in an anomalous manner in the sense that they do not show the Bayer-type behavior [8]; the temperature coefficient of the highest frequency line, ν_1, is almost constant near 77 K and the middle line (ν_2) is convex to the temperature axis over the temperature range 100–180 K. The lowest frequency line (ν_3) appears to behave normally.

Such a type of anomalous behavior of the resonance frequencies has been encountered in the NQR studies on several ammonium salts such as NH_4HgCl_3, NH_4ReO_4, and NH_4I_3, in which $N-H\cdots X$ type hydrogen bonds exist [9–11]. For these compounds we interpreted the anomalies in the NQR frequencies as the effect of the reorientation of the NH_4^+ ions on the EFG at the resonant nuclei. Usually the formation of a hydrogen bond contributes to the EFG at the resonant nucleus that is directly or indirectly involved in the bond to some extent; when the reorientation of NH_4^+ sets in, the average resident time, τ_r, during which the hydrogen bond is formed decreases, and so the EFG at the resonant nucleus undergoes a change synchronized with the reorientation. In such a case, the averaged NQR frequency $\nu_Q(T)$ is given by

$$\nu_Q(T) = \nu_0(T) + [\nu_r \tau_r(T) + \nu_t \tau_t]/[\tau_r(T) + \tau_t], \quad (1)$$

where $\nu_0(T)$ represents the normal temperature dependence due to the Bayer effect, and ν_r and ν_t are the contribution of the NH_4^+ ion with and without hydrogen bonding to the NQR frequency, respectively. τ_t is the transition time during which the NH_4^+ ion is moving. Usually the resident time τ_r is successfully represented by the correlation time τ_c of the reorientation of the NH_4^+ ion.

In the present material, the formation of hydrogen bonding of $N-H\cdots F$ and $N-H\cdots O$ type was suggested [3]. Therefore, we may attribute the anomalous behavior of the resonance frequencies to the rotational effect of the NH_4^+ ions. In order to analyze the NQR data using (1), one needs τ_r (or τ_c) is necessary at each temperature. We measured T_1 of ^1H and ^{19}F at 10 MHz to obtain these values. The results are shown in Figure 2. These data were analyzed according to the standard relaxation theory with cross relaxation between ^1H and ^{19}F [12, 13], assuming the Arrhenius activation process,

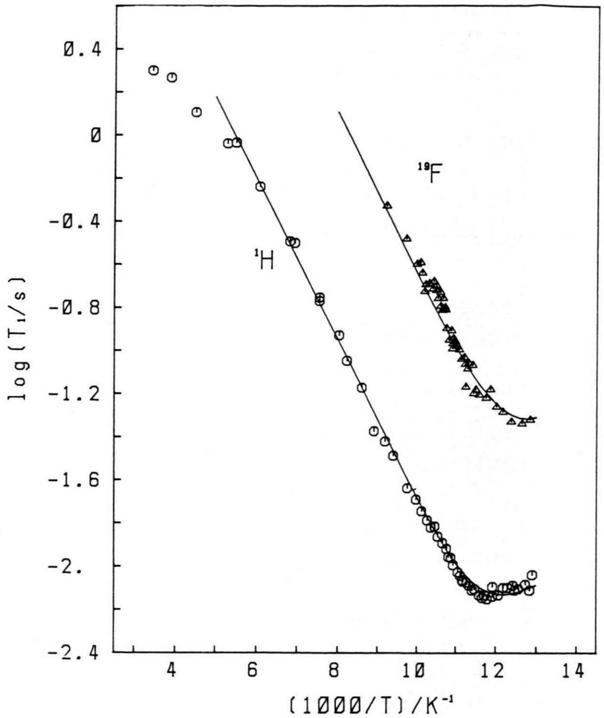

Fig. 2. ^1H and ^{19}F spin-lattice relaxation times at 10 MHz. Solid lines represent the theoretical T_1's.

$$\tau_c = \tau_0 \exp(E_a/RT), \quad (2)$$

and determined the activation parameters for the reorientation of the NH_4^+ ions as $E_a = 7.14 \text{ kJ mol}^{-1}$ and $\tau_0 = 3.25 \cdot 10^{-13}$ s. The solid lines in Fig. 2 represent the calculated T_1's evaluated from these parameters. As there are six inequivalent NH_4^+ ions in the unit cell and also two kinds of hydrogen bonds, $N-H\cdots F$ and $N-H\cdots O$ in a ratio of 2 to 1 [3], the activation parameters derived must be regarded as averaged ones for the reorientation of these six ammonium ions.

When the high temperature approximation can be used for the Bayer-type theory, we can put

$$\nu_0(T) = a + bT + c/T,$$

and so (1) is rewritten as

$$\nu_Q(T) = a' + b\,T + c/T + \Delta\nu\,\tau_t/(\tau_r + \tau_t) \quad (3)$$

with $\Delta\nu = \nu_t - \nu_r$ and $a' = a + \nu_r$. We attempted to fit (3) to experimental resonance data in Fig. 1 by the use of the non-linear least squares method and determined the parameters a', b, c, $\Delta\nu$, and τ_t as shown in

Table 2. Fitting parameters in (3) for three resonance lines.

Parameter	ν_1	ν_2	ν_3
a'/MHz	90.256	84.181	81.822
b/MHz K^{-1}	−0.01470	−0.01725	−0.01482
c/MHz K	−105.1	−12.85	−132.4
$\Delta\nu$/MHz	1.507	−0.8933	0.4254
τ_t/ps	4.603	14.24	2639
S.D.	0.01844	0.007757	0.007143

Table 2 together with the standard deviations. If we attempt to fit the data to a simple Bayer type behavior using only a', b, and c, the standard deviations would be 3–5 fold larger. Hence the last term, $[\Delta\nu(T)]$, in (3) works significantly, i.e., the rotation of the ammonium ions affects to some extent on the NQR frequencies in $(NH_4)_6Sb_4(SO_4)_3F_{12}$. The fact that the values of c are large and negative indicates that the high temperature approximation does not hold in the lowest temperature region of the experiments. The τ_t's obtained here are very long compared with the values for other ammonium salts [10]: Especially, the value $2.6 \cdot 10^{-9}$ s for ν_3 is too long to accept it as the transition time for rotation of NH_4^+ ions.

Such a long τ_t was derived for ν_3 because ν_3 nearly follows the Bayer type of behavior. In other words, we are dealing with a temperature range where only a small deviations from the Bayer behavior can be seen in contrast to other ammonium salts [9]. If measurements could be made below 77 K, where one would see a substantial deviation from the Bayer behavior, a more realistic set of parameters would be obtained. This means that, in applying the "switch" model, a proper assessment of the "normal" temperature dependence is necessary in order to separate the anomalous contribution. Note that the switch effect of the ammonium reorientation can be real even though the parameters derived do not conform to the common sense.

There remain some problems for future study on $(NH_4)_6Sb_4(SO_4)_3F_{12}$ crystal: We failed to detect the NQR signals due to three antimony atoms at special position. Search for those signals will be useful because some change in crystal symmetry usually occurs at a structural phase transition, and it will be possible to answer the question of the existence of a phase transition by examining if any symmetry element is lost by observing NQR of the atoms at the special positions. Next we recognized that in some freshly prepared specimens many strong piezoelectric signals was observed and prevented the observation of the NQR lines. However, after repeating the thermal cycling between room and liquid nitrogen temperature, most of these piezoeletric signals disappeared, making the observation of the NQR signal possible. This fact may be closely related to the experience cited in [4] that the repeated thermal cycling caused a flattening out of the dielectric anomaly between 240–260 K. Although we did not find any evidence of phase transition in our specimens which experienced the thermal cycling, the possibility that the virgin samples undergo some phase transition can not be ruled out.

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