Acta Cryst. (1971). A**27**, 65

Nuclear Magnetic Resonance Study of the NaSbF$_6$ Structure*

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(*Received* 7 *March* 1970)

The site symmetry at the antimony in NaSbF$_6$ has been examined by nuclear magnetic resonance. Antimony-123 resonance in polycrystalline NaSbF$_6$ at 12·2 Mc. sec^{-1} and 19°C shows no second-order quadrupole effects. This is a reflection of a negligibly small or zero deformation from O_h symmetry of the surrounding atoms. Because of this and other considerations, NaSbF$_6$ belongs to the space group *Fm*3*m* within the limits established by this work. Antimony-121 resonance in KSbF$_6$, a compound for which the deformation from O_h symmetry is presumably known, exhibits a second order quadrupole effect which leads to a coupling constant e^2qQ/h of $6{\cdot}1 \pm 0{\cdot}6$ Mc. sec^{-1}. A comparison of the data for the two compouds leands to an upper limit for theSbF$_6^-$ deformation of 7×10^{-4} rad in NaSbF$_6$.

Introduction

The structure of NaSbF$_6$ was proposed (Schrewelius, 1938) to be in the crystallographic space group *Pa*3 on the basis of X-ray powder pattern data. In this proposed structure, Sb would have C_{3i} site symmetry with the fluorines in general positions. Teufer (1956) reconsidered the 1938 data and concluded that they are more consistent with the space group *Fm*3*m* which requires O_h site symmetry for the SbF$_6$ ion. Drifford, Rigny & Plurien (1968) have performed electron spin resonance (e.s.r.) experiments on various uranium (V) compounds including the cubic phase of NaUF$_6$. They concluded that the UF$_6$ ion in NaUF$_6$ is distorted along the [111] axis of the cubic unit cell, thereby ruling out the *Fm*3*m* space group. They then extended this conclusion to the SbF$_6$ ion in NaSbF$_6$ because they said that the two compounds belong to the same structure. In this paper, we describe the result of a nuclear magnetic resonance experiment which leads to the conclusion that neither the SbF$_6$ ion itself nor atoms on other ions around the SbF$_6$ can be significantly distorted from O_h symmetry. Therefore, NaSbF$_6$ belongs to the space group F*m*3*m* (or is not significantly different from *Fm*3*m*) in agreement with the conclusion of Teufer (1956).

Theory

In an n.m.r. experiment, transitions between the Zeeman levels of the nucleus are caused by radio-frequency magnetic fields. If the nucleus possesses an electric quadrupole moment as well as a magnetic dipole moment, there can also be an interaction between the nucleus and the electric field gradient (EFG) at the site of the nucleus. The magnitude of this interaction is a sensitive function of the deformation of the surrounding atom positions from those which give rise to no EFG, *i.e.* positions of neighboring atoms that give rise to O_h site symmetry at the nucleus. In this experiment an upper limit is placed on the quadrupolar interaction of the Sb nucleus in NaSbF$_6$. This is accomplished by studying the second-order effects (Cohen & Reif, 1957) of the quadrupolar interaction on the n.m.r. spectrum. For a polycrystalline sample with axially symmetric EFG these second-order shifts are averaged over all orientations of the crystallites with respect to the external static magnetic field. The central peak ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition) in a spectrum for odd-half-integer spin nucleus then becomes a doublet whose peak separation $\Delta\nu$ in absence of dipolar broadening is given by

$$\Delta\nu = (25\nu_Q^2/144\nu_L)\,(a-\tfrac{3}{4}), \qquad (1)$$

where $a = I(I+1)$, $2\pi\nu_L = \gamma H_0$, and $h\nu_Q = 3e^2qQ/2I(2I-1)$. Here I, γ and eQ are the spin, gyromagnetic ratio and the electric quadrupole moment of the nucleus; H_0 is the static magnetic field intensity and eq is the EFG at the nucleus. Thus, if $\Delta\nu$ is measured, eq can be determined, provided that all other parameters are known.

It is, unfortunately, not convenient to relate the magnitude of EFG with structural parameters because of the difficulties in calculating the Sternheimer anti-shielding factor (Das & Hahn, 1958; Slichter, 1963), which is a measure of the electron cloud distortion due to the field gradient external to the cloud. Therefore, we take the following approach.

We will derive an expression for a ratio of the observed splittings for two SbF$_6^-$ ions with different amounts of bond angle deformations. Such a ratio should be relatively independent of such parameters as the anti-shielding factor (primarily an atomic property) and covalency effects. We assume that the Sb electrons which are most responsible for the EFG, aside from those which take part in the antishielding, are those which are taking part in the Sb–F bonds. Since a charge e creates an EFG of $e(3\cos^2\theta-1)/r^3$ at a distance r, where θ is the angle between the line

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* This work performed under the auspices of the U.S. Atomic Energy Commission.

joining the two points and the axis of symmetry of EFG (Das & Hahn, 1958; Slichter, 1963), we write

$$eq=A(3\cos^2\theta-1) \qquad (2)$$

for the intraionic contribution to the EFG at the central nucleus in an octahedral ion with a small deformation along a threefold axis. The factor A takes into account those parameters mentioned above which will be common to different SbF_6 ions provided that the bond deformations and the bond lengths are not drastically different and θ is the bond angle with respect to the threefold axis. From equations (1) and (2) it is seen that

$$\Delta\nu_i \propto A^2.(3\cos^2\theta_i-1)^2 \qquad (3)$$

so that

$$\Delta\nu_i/\Delta\nu_j=[(3\cos^2\theta_i-1)/(3\cos^2\theta_j-1)]^2 \qquad (4)$$

for compounds i and j. In addition, if two different isotopes are studied in the two samples, equation (4) must be modified to read

$$\Delta\nu_i/\Delta\nu_j=[(3\cos^2\theta_i-1)/(3\cos^2\theta_j-1)]^2.$$

$$(Q_i/Q_j)^2.(\nu_{Lj}/\nu_{Li}).[(a_i-\tfrac{3}{4})/(a_j-\tfrac{3}{4})] \qquad (5)$$

where $a_i=I_i(I_i+1)$. Therefore, from a measured upper limit for $\Delta\nu_i/\Delta\nu_j$ it is possible to deduce the maximum deviation from octahedral symmetry for compound i if θj and all of the nuclear parameters are known.

Experimental procedure

The powdered $NaSbF_6$ was used in the form as obtained commercially. The X-ray powder pattern agreed with the published patterns (Schrewelius, 1938) except for one line belonging to NaF. The fraction of NaF is estimated to be much less than 10 per cent from the ^{19}F n.m.r. spectrum. (In fact, the NaF signal is unobservable under the $NaSbF_6$ signal.) The powdered $KSbF_6$ was also obtained commercially.

The Sb spectra in both the sodium and the potassium compounds are quite insensitive to the presence of NaF or KF as verified by experiments on various samples prepared in this laboratory.

The n.m.r. measurements were made with a *cw* induction apparatus (Fukushima & Mastin, 1969).

Results and discussion

Potassium hexafluoroantimonate is taken to be the compound with a known deformation of the SbF_6^- group. Based on a powder pattern study (Bode & Voss, 1951), it is reported to be in the space group $Ia3$ so that SbF_6 is a slightly deformed octahedron with threefold symmetry. The angle between the threefold axis and the Sb–F bond is 56·89° in contrast to the regular octahedral angle of 54·74°. This deformation gives rise to a value for $(3\cos^2\theta-1)^2$ of $1{\cdot}10\times10^{-2}$.

There are two naturally occurring antimony isotopes: ^{121}Sb which is 57·25% abundant with $I=\frac{5}{2}$, $\gamma/2\pi=10{\cdot}19\times10^2G^{-1}sec^{-1}$, and $eQ=-0{\cdot}53b$; ^{123}Sb which is 42·75% abundant with $I=\frac{7}{2}$, $\gamma/2\pi=5{\cdot}518\times10^2G^{-1}sec^{-1}$ and $eQ=-0{\cdot}68b$.

Fig. 1 is a plot of the room-temperature second-order splitting of the ^{121}Sb central transition in $KSbF_6$ *vs.* the reciprocal of the Larmor frequency. The inset shows the derivative of the absorption spectrum at a frequency of 21·8 Mc.sec^{-1}. The coupling constant e^2qQ/h can be obtained directly from the slope of Fig. 1 or by an alternate method which involves a plot of the derivative extrema separation (Casabella, 1964). The coupling constants obtained by the two methods are 5·9 and 6·3 Mc.sec^{-1} with 10% uncertainties.

The Sb resonances in $NaSbF_6$ were obtained at several frequencies, also at room temperature. Fig. 2 shows the ^{123}Sb resonance at 12·2 Mc.sec^{-1} (the lowest Larmor frequency used). The doublet is not evident, which indicates that the intra-molecular and inter-molecular contributions to the EFG must be very small or zero at the Sb site.

From a comparison of Fig. 2 with the inset of Fig. 1, a generous upper limit of 10^{-2} for the ratio $\Delta\nu_{NaSbF_6}/\Delta\nu_{KSbF_6}$ is obtained. Equation (5), together with the value of $(3\cos^2\theta-1)^2$ for $KSbF_6$, yields about 7×10^{-4}

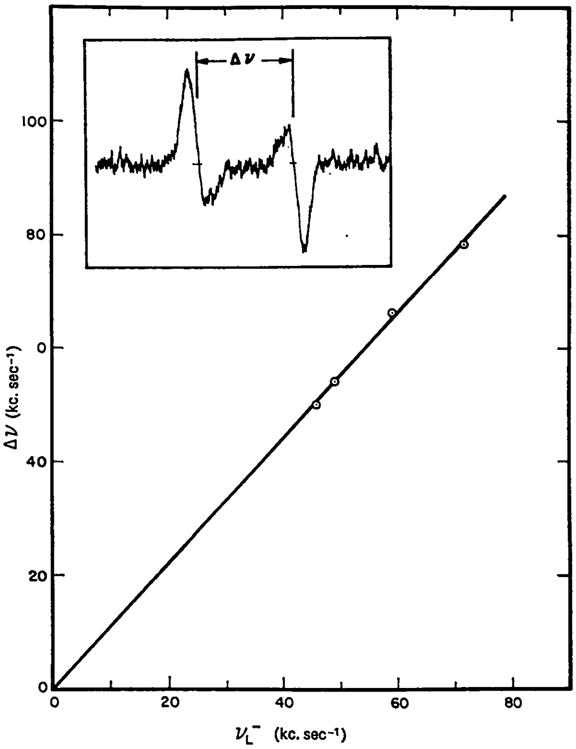

Fig. 1. Room-temperature second-order splitting of the ^{121}Sb $-\frac{1}{2}\leftrightarrow\frac{1}{2}$ transition in polycrystalline $KSbF_6$ *vs.* reciprocal of Larmor frequency. The inset shows the derivative absorption spectrum at 21·8 Mc.sec^{-1} where Δ_ν is 50 kc.sec^{-1}.

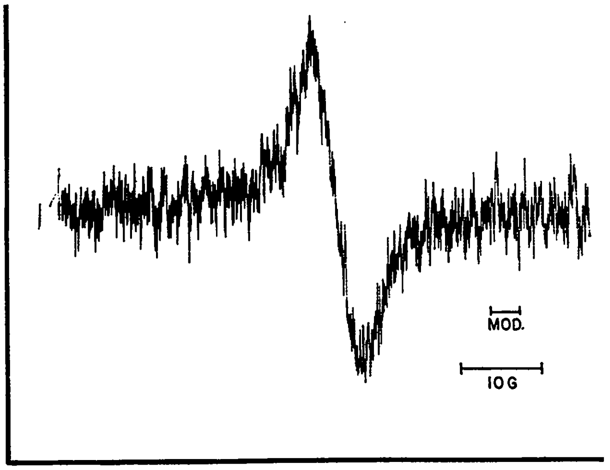

Fig. 2. Room temperature ^{123}Sb resonance in NaSbF$_6$ at 12·2 Mc.sec^{-1}.

rad for the maximum bond angle deviation from that of a regular octahedron for SbF_6^-.

The octahedral symmetry of SbF_6^- in itself does not require the elimination of $Pa3$ as a possible structure, but the lack of interionic EFG at Sb does. The n.m.r. experiment is less sensitive, however, to the interionic contribution because of distance considerations. Therefore, we also examined the ^{23}Na resonance in NaSbF$_6$ and found no detectable second order effects. This indicates that the Na site symmetry is also O_h in agreement with the lack of observable interionic EFG for Sb.

Room-temperature single-crystal X-ray measurements performed in this laboratory (Ryan, 1969) also are consistent with the assignment of the space group $Fm3m$.

The relation between NaSbF$_6$ and NaUF$_6$

We now examine the conclusion of Drifford, Rigny & Plurien (1968) on the structure determination of NaSbF$_6$ from their experiment on NaUF$_6$. Penneman, Sturgeon & Asprey (1964) characterized NaUF$_6$ from its X-ray powder pattern as f.c.c. with $a_0 = 8{\cdot}608$ Å. In a subsequent paper (Sturgeon, Penneman, Kruse & Asprey, 1965) it is mentioned that '...cubic NaUF$_6$ shows the NaSbF$_6$ structure type reported for a number of other NaB$^{\mathrm{V}}$F$_6$ compounds...'. No single-crystal X-ray work has been reported for these compounds, to our knowledge, and we have not found any other original references concerning the possible similarities of these compounds. The e.s.r. results (Drifford *et al.*, 1968) show that UF_6^- in cubic NaUF$_6$ is indeed a deformed octahedron but an extension of this result to conclude that SbF_6^- in NaSbF$_6$ is also distorted is not justified. Indeed, the present work establishes that, at 19 °C, NaSbF$_6$ belongs in $Fm3m$, a space group which is definitely ruled out for NaUF$_6$.

I wish to thank R. A. Penneman and R. R. Ryan* for valuable discussions and S. H. Mastin for preparing several samples.

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* At the suggestion of R. R. Ryan we have recently examined the ^{121}Sb resonance in polycrystalline LiSbF$_6$, prepared by L. B. Asprey, which is known to belong to the space group $R\bar{3}$ from single-crystal X-ray work of Burns (1962). Because the Sb site symmetry due to the six nearest fluorine atoms is O_h, the EFG contribution, if any, will be entirely interionic in origin. The measured e^2qQ/h of 4·5 Mc.sec^{-1} in LiSbF$_6$ confirms the previous conclusion regarding the impossibility of $Pa3$ being the correct space group for NaSbF$_6$. Furthermore, the final result no longer depends only on the correctness of the KSbF$_6$ structure which was derived on the basis of powder pattern work.