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On the Symmetry of $Sb^{III}Br_6{}^{3-}$ and $Sb^{V}Br_6{}^{-}$ Ions in the $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ Crystal. A Study of ^{81}Br NQR Zeeman Effect

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The single-crystal Zeeman effect was investigated for the ^{81}Br NQR lines in the mixed-valence compound $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ at room temperature. Comparing with the results of X-ray analysis, it was concluded that the $Sb^{III}Br_6{}^{3-}$ ions possess D_{2d} symmetry and the $Sb^{V}Br_6{}^{-}$ ions possess D_{4h} (nearly O_h) symmetry.

The crystal structure of the mixed-valence compound $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ at room temperature has been solved by Lawton and Jacobson[1] by means of the X-ray diffraction method. The crystals are tetragonal with the space group $I4_1/amd$ and contain two different anions $Sb^{III}Br_6{}^{3-}$ and $Sb^{V}Br_6{}^{-}$. The anions are arranged in an ordered array with like oxidation states of antimony repeating along the a and b directions in the unit cell but alternating along the c direction. The $Sb^{III}Br_6{}^{3-}$ ions are undistorted and possess O_h symmetry, whereas the $Sb^{V}Br_6{}^{-}$ ions are distorted to D_{2d} symmetry. The obvious differences among bond lengths in each anion have not been observed: The mean length is 2.795 ± 0.006 Å for Sb(III)-Br and 2.564 ± 0.006 Å for Sb(V)-Br.

We have found from the ^{81}Br nuclear quadrupole resonance (NQR) investigations[2] that this salt undergoes a structural phase transition at 214 K, and that in both high and low temperature phases each anion yields two ^{81}Br NQR lines. The ^{81}Br NQR frequencies at room temperature and their assignment are listed in Table 1. Since NQR frequencies are very sensitive to charge distributions around the nuclei under consideration, the NQR method makes it possible for us to

Table 1. ^{81}Br NQR frequencies (ν) and asymmetry parameters (η) in $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ at 298 K

Resonance line	ν/MHz$^{a)}$	η	Assignment$^{b)}$
ν_1	153.93	0.015 ± 0.004$^{c)}$	Sb(V)-Br_{xy}
ν_2	152.05	-----	Sb(V)-Br_z
ν_3	61.85	0.015 ± 0.005	Sb(III)-Br_{xy}
ν_4	58.22	-----	Sb(III)-Br_z

a) Ref. 2. b) Br_z and Br_{xy} denote the Br atoms whose bonds are along and perpendicular to the crystallographic c direction, respectively.[2]
c) Average deviation.

distinguish nonequivalent atoms in chemically slightly different situations. Thus the existence of two resonance lines for the $Sb^{III}Br_6{}^{3-}$ ions shows clearly that these anions are also distorted in a rigorous sense to a lower symmetry than O_h, and hence we supposed that the $Sb^{III}Br_6{}^{3-}$ ions would be distorted to D_{2d} symmetry.[2)] In fact, it has been found that, in $Rb_4Sb^{III}Sb^{V}Br_{12}$ belonging to the same space group as the NH_4 salt, both $Sb^{III}Br_6{}^{3-}$ and $Sb^{V}Br_6{}^{-}$ ions are distorted slightly from O_h and possess D_{2d} symmetry.[3)] In the present study we have investigated the ^{81}Br NQR Zeeman effect on a single crystal of $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ at room temperature and tried to obtain more direct information about the symmetry of anions.

A large single crystal was grown in a long glass tube (ca. 38 cm long, diameter 1.6 cm) tapered its one end to a capillary in the following manner. A hot solution of ammonium hexabromoantimonate(III,V) in conc-HBr containing a little bromine was transfered and sealed into the glass tube. The tube was hung in the upper part of a Bridgeman electric furnace which has a steep temperature gradient at the boundary between the upper and the lower parts of the furnace. In the lower part of the furnace no temperature control was done. The solution was brought into saturation remaining seed crystals in the tip of the capillary portion at ca. 110 °C. Then the glass tube was gradually descended down at a speed of ca. 4 mm in a day. A single crystal was obtained with ca. 2 cm long in the glass tube of 1.6 cm diameter. The glass tube containing the single crystal was opened at each end and the crystal was freed from mother liquor in a vacuum desiccator containing KOH.

In the measurement of Zeeman effect, the goniometer with a Helmholtz coil as described elsewhere[4)] was employed. The observation of signals was carried out on an oscilloscope screen by using a super-regenerative oscillator as described by Herlach[5)] but modified to a frequency-modulated type. For all of three single crystals prepared, the ν_1 and ν_3 lines had intensities enough for the Zeeman experiment but the ν_2 and ν_4 lines had not. This is presumably because that crystals are easy to grow along the crystallographic c direction. The Zeeman experiment was therefore achieved only for the ν_1 and ν_3 lines. This is sufficient for the present purpose to investigate an angular distortion in each anion, because the parallelism of respective Sb(V)-Br_z and Sb(III)-Br_z bonds to the c direction is demanded crystallographically.[1)] Zero-splitting cones were searched by applying magnetic fields up to 2×10^{-2} T in the temperature range of 291 K to 298 K.

The zero-splitting patterns obtained for the ν_1 and ν_3 lines are shown in Figs. 1 and 2, respectively. Unexpectedly, only two zero-splitting loci were obtained for the ν_1 line, while four loci consisting of a pair of two closely overlapped loci were obtained for the ν_3 line. Four nonequivalent orientations of the maximum or z components of the EFG (electric field gradient) tensor for the Br atoms ascribed to ν_3 make us possible to obtain the directions of all crystallographic axes.[6)] The angles between the z-axes of EFG and the crystallographic axes are listed in Table 2. It was found that (1) 1A and 1B, the z-axes of EFG for the Br_{xy} atoms forming Sb(V)-Br_{xy} bonds, are well coincident with the crystallographic a and b directions, respectively, and (2) 3A, 3B, 3C, and 3D, those for the Br_{xy} atoms forming Sb(III)-Br_{xy} bonds, deviate by 4.89 ± 0.01° above or below from the a or b

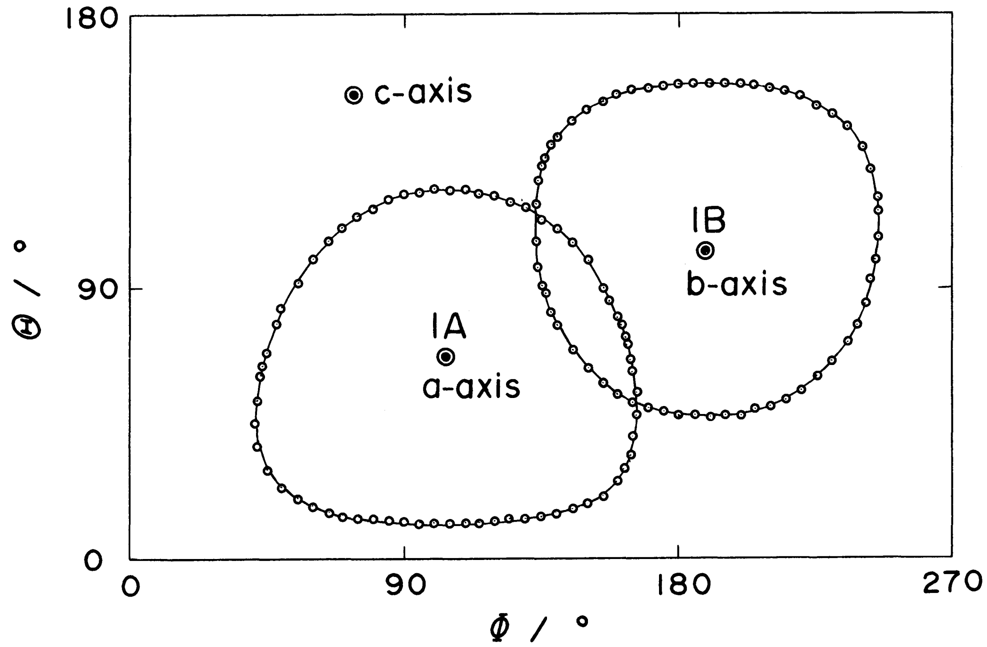

Fig. 1. Zero-splitting patterns for the ν_1 line. 1A and 1B denote the z-axes of EFG in crystallographic nonequivalence.

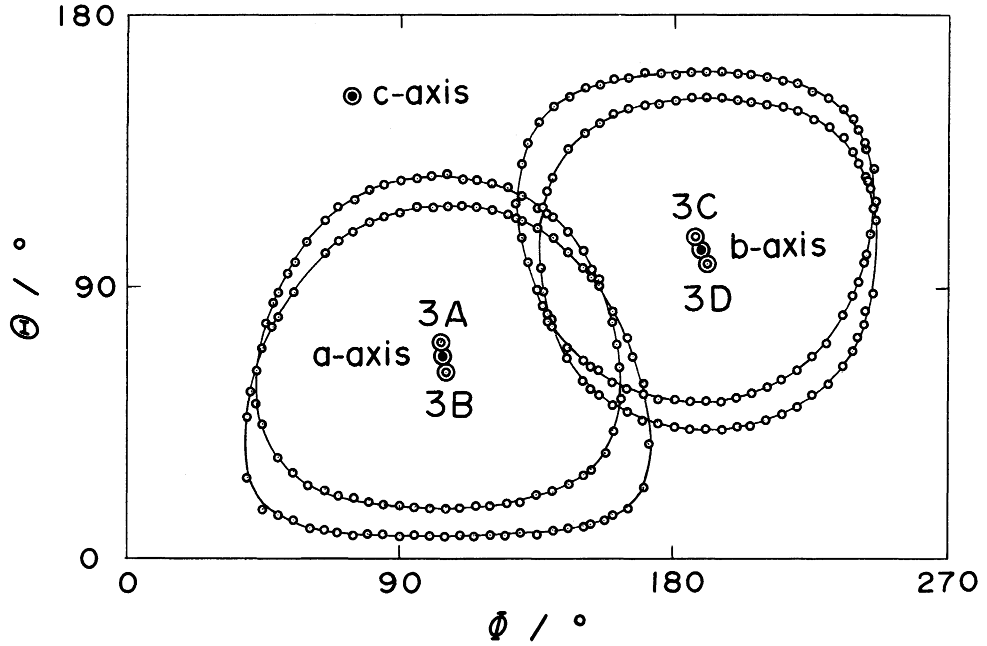

Fig. 2. Zero-splitting patterns for the ν_3 line. 3A, 3B, 3C, and 3D denote the z-axes of EFG in crystallographic nonequivalence.

axis in the a(or b)-c plane. Since the asymmetry parameters (η) obtained from zero-splitting loci are quite small (Table 1), indicating the almost cylindrically symmetric arrangement of charges around the Sb(V)-Br_{xy} and Sb(III)-Br_{xy} bonds, it is expected that the directions of the z-axes of EFG are well coincident with the Sb-Br bond directions. Then we estimate the bond angles in respective anions from the

Table 2. Angles between z-axes of the EFG and crystallographic axes (in degrees)

Axis	1A	1B	3A	3B	3C	3D	a	b
1B	90.07							
3A	4.83	90.00						
3B	4.97	90.01	9.80					
3C	90.06	4.89	89.58	90.42				
3D	90.08	4.87	90.42	89.59	9.76			
a	0.11	90.00	4.90	4.90	89.99	89.99		
b	90.07	0.00	90.00	90.01	4.89	4.87	90.00	
c	89.92	89.99	85.10	94.89	85.10	94.87	89.99	89.99

angles between the z-axes of EFG. The values are listed in Table 3, together with the X-ray results.1)

In conclusion, the present results show that the $\mathrm{Sb^{V}Br_6^-}$ ions possess D_{4h} (nearly O_h) symmetry and the $\mathrm{Sb^{III}Br_6^{3-}}$ ions possess D_{2d} symmetry. These results are different from the X-ray results:1) D_{2d} symmetry for the $\mathrm{Sb^{V}Br_6^-}$ ions and O_h symmetry for the $\mathrm{Sb^{III}Br_6^{3-}}$ ions. We deduced previously2) that the $\mathrm{Sb^{III}Br_6^{3-}}$ ions interact strongly with $\mathrm{NH_4^+}$ ions through the hydrogen bonds, Br···H-N, even in the high temperature phase of the $\mathrm{NH_4}$ salt, whereas $\mathrm{Sb^{V}Br_6^-}$ ions do not. Probably, this predominant interaction of $\mathrm{Sb^{III}Br_6^{3-}}$ ions with the cations produces the angular distortion of these ions, whereas the $\mathrm{Sb^{V}Br_6^-}$ ions are free from the distortion.

Table 3. Bond angles in anions

Bond angle	Zeeman NQR a)	X-Ray b)
($\mathrm{Sb^{V}Br_6^-}$ Ion)		
$\mathrm{Br_z}$-Sb-$\mathrm{Br_{xy}}$	90.00 ± 0.05° c)	93.67 ± 0.15° d)
$\mathrm{Br_{xy}}$-Sb-$\mathrm{Br_{xy}}$	90.07 ± 0.05°	90.23 ± 0.02°
($\mathrm{Sb^{III}Br_6^{3-}}$ Ion)		
$\mathrm{Br_z}$-Sb-$\mathrm{Br_{xy}}$	94.89 ± 0.01°	90.32 ± 0.13°
$\mathrm{Br_{xy}}$-Sb-$\mathrm{Br_{xy}}$	90.42 ± 0.01°	90.002 ± 0.002°

a) This work. b) Ref. 1. c) Average deviation. d) Standard deviation.

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