Nuclear Magnetic Resonance of ^{1}H, ^{7}Li, ^{11}B, ^{23}Na and ^{27}Al in Tourmaline (Elbaite)

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Abstract

Nuclear magnetic resonance (NMR) signals of ^{1}H, ^{7}Li, ^{11}B, ^{23}Na and ^{27}Al have been observed in elbaite single crystals. ^{1}H resonance indicates the presence of (OH) groups, but no water molecules. ^{7}Li resonance indicates a quadrupole coupling constant, $|e^2qQ/h| = 0.16$ MHz, and a pseudotetragonal symmetry for the Li$^+$ ion occurring at the $9(b)$ site; the axis of distortion is $\sim 45°$ off the c-axis and coincides approximately with the octahedral O_1-Li-O_3 direction. The ^{11}B resonances clearly show the triangular BO$_3$ coordination with little deviation from three-fold symmetry at the boron site; the quadrupole coupling constant, $|e^2qQ/h| = 2.76 \pm 0.08$ MHz is comparable to values obtained for ^{11}B in BO$_3$ triangles found in other borate minerals. The B-O bond is highly covalent. The ^{23}Na central transitions are unshifted within experimental errors; thus the quadrupole coupling constant is small (<0.2 MHz). The ^{27}Al satellites were broad and overlapping. For ^{27}Al in the distorted octahedral $18(c)$ sites, the quadrupole coupling constant is estimated to be ~ 6 MHz. Weak and broad satellite signals suggest cation disorders or twinned domains for tourmaline.

Introduction

The tourmaline group of minerals represents a compositionally complex series. The recognized end members are: dravite NaMg$_3$Al$_6$B$_3$Si$_6$O$_{27}$(OH,F)$_4$, schorl Na(Fe^{2+})$_3$Al$_6$B$_3$Si$_6$O$_{27}$(OH,F)$_4$, elbaite Na(Li,Al)$_3$Al$_6$B$_3$Si$_6$O$_{27}$(OH,F)$_4$, and buergerite. The recently discovered buergerite, Na(Fe^{3+})$_3$Al$_6$B$_3$Si$_6$O$_{30}$(OH,F) is a variant of schorl, with Fe^{3+} replacing Fe^{2+} and simultaneous reduction in number of (OH, F) ions from four to one.

The broad features of the tourmaline structure were determined by Donnay and Buerger (1950) and by Ito and Sadanaga (1951). Subsequently, Buerger, Burnham and Peacor (1962) have refined the dravite structure; Barton (1969) and Tippe and Hamilton (1971) have refined the buergerite structure by X-ray and neutron diffraction respectively; Barton and Donnay (1971) have refined the elbaite structure by X-ray diffraction. Despite the differences in chemical compositions, the structures are basically similar.

The optical absorption spectra and dichroism in tourmaline have been studied by Wilkins, Farrell and Naiman (1969), by Faye, Manning and Nickel (1968) and by Townsend (1970). These optical studies have clarified the nature of the crystal fields of transition metal ions replacing the Mg, Al, *etc.*, in the octahedral sites. Paramagnetic susceptibility studies of Tsang, Thorpe, Donnay and Senftle (1971) have confirmed the magnetic coupling between nearest neighbor iron atoms and have also indicated different local distortions from octahedral symmetry for the $9(b)$ and $18(c)$ sites.

In this paper, we report nuclear magnetic resonance (NMR) studies on ^{1}H, ^{7}Li, ^{11}B, ^{23}Na and ^{27}Al in a gem quality single crystal of elbaite from Elba (American Museum of Natural History, New York, N.Y.; Specimen No. 12210). The results yield information on the chemical bonding, charge distribution and coordination about these ions in the tourmaline structure, whereas the optical and magnetic properties are related to the environments of the ferric and ferrous ions.

Crystal Structure

The tourmaline structure has rhombohedral symmetry, with space group $R3m$. The cell dimensions of elbaite are $a_0 = 15.838$ Å and $c_0 = 7.103$ Å (Barton and Donnay, 1971). The structure consists of linked sheets of island units. The tetrahedral sheet is formed by sixfold rings of nearly regular SiO$_4$

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tetrahedra pointing in the same direction parallel to the *c*-axis. The Na^+ ions occupy the $3(a)$ position on the threefold axis at the center of the six-membered ring as shown in Figure 1 (top diagram). The Na-O bond lengths within the NaO_9 polyhedron of dravite are 2.45, 2.71 and 2.83 Å, each occurring three times. The second sheet unit consists of three components: (1) Li or Al occupying the $9(b)$ position forming a cluster of three octahedra of four oxygen and two (OH,F) ions sharing a common corner, (2) Six outer AlO_5OH octahedra, sharing edges with (Li,Al) octahedra and with Al in $18(c)$ position, and (3) B-atoms in $9(b)$ positions, forming BO_3 triangles which connect corners of two AlO_5OH octahedra and a common corner of two $(Li,Al)O_4(OH)_2$ octahedra (see bottom diagram of Figure 1). The outer AlO_5OH octahedrons, with the Al atoms in $18(c)$ positions, form spiral chains along the *c*-axis by sharing edges with two similar octahedra related by the 3_1 screw axis. The (Li,Al) octahedra have two hydroxyl groups at opposite corners.

Experimental

Certain nuclei, such as ^1H, ^7Li, *etc.*, have intrinsic spins and associated intrinsic magnetic moments. For an isolated nucleus of spin S within a magnetic field **H**, there will be $2S + 1$ magnetic or Zeeman sublevels labelled by the magnetic quantum number $m = S, S - 1, \cdots, -S + 1, -S$. These sublevels are separated by equal energy differences, γH, where γ is a constant factor characteristic of the nucleus. Radiofrequency waves with frequency ν and photon energy $h\nu = \gamma H$ (h is the Planck's constant) will induce transitions between neighboring magnetic levels. Energy is absorbed when the resonance condition $h\nu = \gamma H$ occurs. Since the sublevels are equally spaced, resonance absorption occurs only at a single magnetic field. Further splittings, however, may occur in solids:

(1) For nuclei with spin $S \geqq 1$, such as ^7Li, ^{23}Na and ^{27}Al, nuclear electric quadrupole moments may also be present. It is necessary to consider the interactions of the nuclear quadrupole moment with the electron cloud surrounding the nucleus in the solid. This quadrupole interaction is usually small and may be treated as a perturbation on the Zeeman energy levels. The single resonance line from the free nuclei now splits into several components, because the Zeeman sublevels $m = S, S - 1, \cdots, -S$ are no longer equally spaced. The $m = -\frac{1}{2} \leftrightarrow \frac{1}{2}$ central transition remains sharp and intense, because the energy shifts are small (from second order and higher order perturbations only). The transitions $m = \pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ (and also $m = \pm\frac{3}{2} \leftrightarrow \pm\frac{5}{2}$ for ^{27}Al) will be shifted in pairs, toward the low field side and toward the high field side respectively. Following the standard conventions of Cohen and Reif (1957), the interactions are characterized by two parameters, the quadrupole coupling constant e^2qQ/h and the asymmetry parameter η.
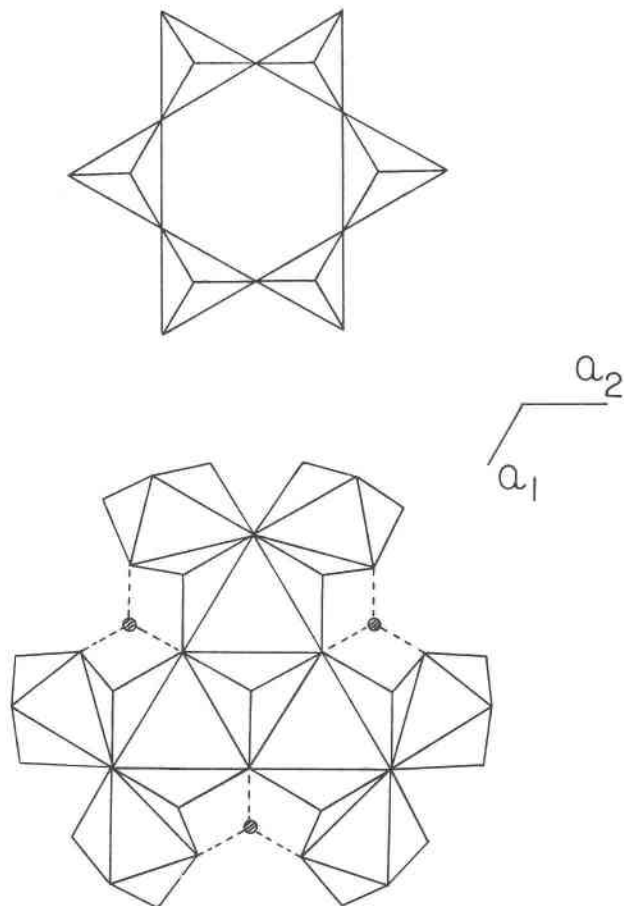

FIG. 1. Tourmaline structure (Buerger, Burnham, and Peacor, 1962). Top diagram: layer of six nearly regular SiO_4 tetrahedra. Bottom diagram: octahedral layer, with three larger central octahedra containing Mg, Li or Fe, six smaller peripheral octahedra containing Al or Fe, and three boron atoms (shaded circles).

With the principal axes (X, Y, Z) directions, these parameters may be evaluated from the angular dependence of the resonance line positions. The quadrupole coupling constant e^2qQ/h is related to the maximum deviation from perfect octahedral or cubic symmetry, whereas the asymmetry parameter η is a measure of the deviation from cylindrical symmetry about the principal Z-axis.

(2) Resonance lines may also be split by nearby magnetic nuclei because of interactions between two magnetic moments. Thus for water of hydration in crystals, the proton resonance lines occur in pairs. The pair spectra has been observed, for example, in gypsum (Pake, 1948), beryl (Sugitani, Nagashima, and Fujiwara, 1966) and cordierite (Tsang and Ghose, 1972b). Therefore, measurements of the NMR line splittings at various orientations of H with respect to the crystal will yield information about nearest neighbor environments of the various magnetic nuclei.

The NMR signals were observed at room temperature near 14 MHz (megahertz) using a conventional crossed-coil spectrometer in the dispersion mode. A strong ($\sim 10^4$

gauss) and slowly varying magnetic field **H** was applied to the tourmaline sample. A small (~ 1 gauss) modulating field was used at 40 Hz. The crystal was glued onto a glass rod and mounted in a single-circle goniometer, the glass rod being perpendicular to **H**. Various orientations of **H** with respect to the crystal were used, with **H** being either perpendicular to one of the a-axes or within one of the ac-planes.

Results

The satellite resonance lines from ^{11}B, ^{7}Li and ^{27}Al have been observed in several different elbaite crystals. Compared to their central lines, the satellite lines were always weak, broad and hard to detect. The resonance spectra for **H** $\parallel c$ are shown in Figure 2, the $-\frac{1}{2} \longleftrightarrow \frac{1}{2}$ transition being the central line. The total scans in magnetic field are 2400, 120, 2400 and 24 gauss for ^{27}Al, ^{7}Li, ^{11}B and ^{1}H respectively (Fig. 2). In our elbaite samples, the ^{19}F signals have also been observed, which are much weaker than the proton signals, indicating a high OH:F ratio.

(A) ^{11}B resonance

The splitting between the two satellites reached its maximum value for **H** $\parallel c$. For **H** $\perp a$-axis, the splittings at various orientations are shown in Figure 3. Our data are in satisfactory agreement with the curve $1010(3 \cos^2 \theta - 1)$, where θ is the angle between **H** and the crystallographic c-axis. The experimental data and the calculated curve are shown in Figure 3. Following the notation of Cohen and Reif (1957),
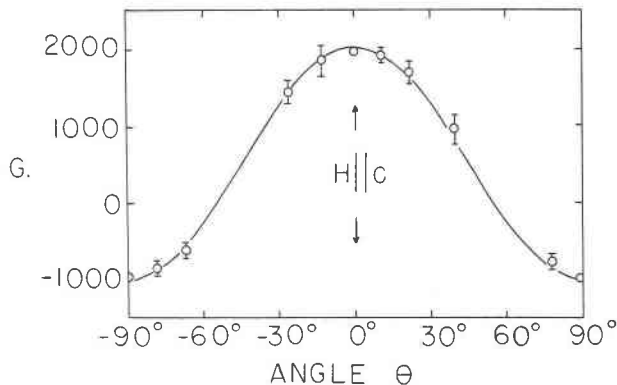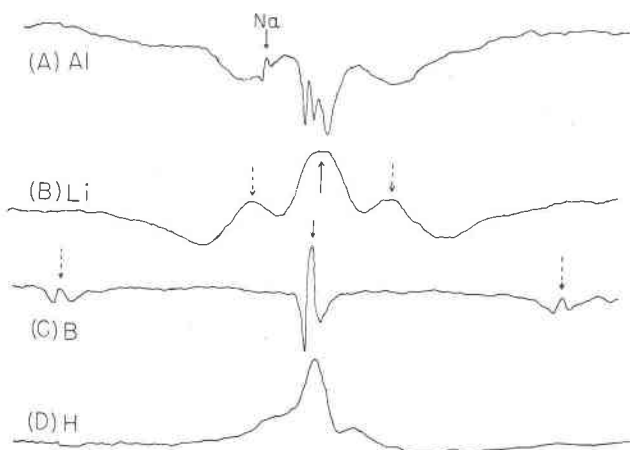
FIG. 2. Tourmaline NMR spectra for **H** $\parallel c$. (A) ^{27}Al, total magnetic field scan is 2400 gauss. The arrow indicates ^{23}Na central transition. (B) ^{7}Li, total scan is 120 gauss. (C) ^{11}B, total scan is 2400 gauss. (D) ^{1}H, total scan is 24 gauss. The central transitions ($-1/2 \longleftrightarrow 1/2$) and the satellites ($\pm 1/2 \longleftrightarrow \pm 3/2$) are shown as solid and dashed arrows.

FIG. 3. Separations in gauss between ^{11}B satellites ($\pm 1/2 \longleftrightarrow \pm 3/2$ transitions) *vs* orientations of magnetic field **H** for **H** $\perp a$-axis. The calculated separations, $1010 (3\cos^2\theta - 1)$, are based on axial symmetry about c, θ being the angle between **H** and crystallographic c-axis.

we get $|e^2qQ/h| = 2.76 \pm 0.08$ MHz and $\eta \ll 1$ with $Z \parallel c$.

We have also observed the central transition ($-\frac{1}{2} \longleftrightarrow \frac{1}{2}$) for **H** in the ac-plane near 8 MHz. Within experimental errors, the shift is proportional to $\sin^2\theta(9 \cos^2 \theta - 1)$, the expected behavior for axial ($\eta = 0$) distortion along c. From our data, we get $|e^2qQ/h| = 2.7 \pm 0.1$ MHz.

Our NMR results, $|e^2qQ/h| = 2.76 \pm 0.08$ MHz, $\eta \sim 0$ and $Z \parallel c$, show that the nearest neighbor environments about boron atoms are almost axially symmetric, although the boron atoms are located at general positions in the tourmaline structure. The satellite resonance lines from various boron sites very nearly coalesce. Our $|e^2qQ/h|$ value also agrees well with measurements on other borate minerals containing BO_3 triangles (Holuj and Petch, 1960; Pennington and Petch, 1960, 1962; Kriz and Bray, 1971).

(B) ^{23}Na resonance

Unfortunately, the nearby ^{27}Al resonances interfered with measurements on ^{23}Na. The central transition of ^{23}Na could be clearly seen at either 8 or 14 MHz; within experimental error (± 1 gauss), the field strengths at resonance remain unchanged for various orientations of the crystal with respect to **H**. Our results give an upper limit for the quadrupole coupling constant: $|e^2qQ/h| < 0.2$ MHz.

The small quadrupole coupling constant implies that the nearest neighbor coordination symmetries about Na ions are not too different from being cubic.

(C) ^{7}Li resonance

The Li$^+$ ions are located on the $9(b)$-sites, with mirror plane symmetry. The a-axis, which is perpen-

dicular to the mirror plane, must be one of the principal axes of the quadrupole coupling tensor (Cohen and Reif, 1957). The various sites are related to each other via 120° rotations about the c-axis.

We have observed the ^{7}Li resonance for **H** in the ac-plane and for **H** $\perp$ a-axis. There are three unknowns, $|e^2qQ/h|$, η and α, where α is the angle between the principal Z-axis and the crystallographic c-axis. The value of $|e^2qQ/h|$ may be derived directly from the maximum observed satellite splittings.

For **H** $\parallel$ c, the satellites from Li-sites are degenerate, and therefore may be readily observed. The satellite resonance lines are broad (see Fig. 2). For other orientations, often only the faraway satellite lines can be observed because of interference. The results are shown in Figure 4. The curves are calculated from $|e^2qQ/h| = 0.16$ MHz, $\eta = 0$ and $\alpha = 45°$. The general agreement with the experimental results is satisfactory. Our calculations give very small satellite splittings if the magnetic field **H** is oriented 70-80° away from the c-axis in the ac-plane. Experimentally, a single intense resonance line (superposition of satellites and central $-\frac{1}{2} \longleftrightarrow \frac{1}{2}$ transition) was observed at these orientations, thus confirming our calculations.

Our quadrupole coupling constant, $|e^2qQ/h|$, which is a direct measure of the maximum axial distortion, is somewhat larger than previous results on octahedrally coordinated lithium atoms (Pound, 1950; Brun and Derighetti, 1961).

(D) *Proton resonance*

For various orientations of **H** with respect to the tourmaline crystal, a narrow and strong proton resonance line was always observed. For chemically-bonded water molecules in crystals such as beryl and cordierite, the proton resonance lines occur in pairs because of the intramolecular proton-proton dipolar interactions (Sugitani, Nagashima, and Fujiwara, 1966; Tsang and Ghose 1972b). For tourmaline, the narrow line widths (<4 gauss) indicate the absence of a nearby magnetic nucleus, and are consistent with the structural evidence of the presence of hydroxyl groups (the ^{16}O nucleus is nonmagnetic with zero spin).

(E) ^{27}Al *resonance*

Both 18(c) and 9(b) sites, with distorted octahedral coordinations, are occupied by aluminum atoms. The ^{27}Al satellites are broad and overlapping. Because of the absence of individual lines, it is only possible to derive an approximate value of e^2qQ/h

for ^{27}Al in the more distorted 18(c) sites. From the observed maximum inner satellite splitting of 1600 gauss, we get $|e^2qQ/h| \sim 6$ MHz. The maximum variation of the positions of central transitions was 60 gauss at 14 MHz; this gives $|e^2qQ/h| \sim 6$ MHz also.

Discussion

Even though gem elbaite crystals were investigated for NMR signals, no sharp resonance lines have been found. The X-ray, neutron diffraction and magnetic susceptibility experiments (Barton, 1969; Tippe and Hamilton, 1971; Tsang, Thorpe, Donnay, and Senftle, 1971) suggest that the distribution of cations on the various cation sites in tourmaline may be somewhat random. Therefore the satellite resonance lines would broaden, because the magnitudes and directions of the electric field gradients at various atomic sites may have some random variations. (If Li, Al were ordered in elbaite, then the periodicity along the c-axis would be doubled. This has not been observed. Furthermore, the possibility of $Li^+ - Al^{3+}$ ordering is ruled out by Pauling's rule of local neutralization of charge in silicates).
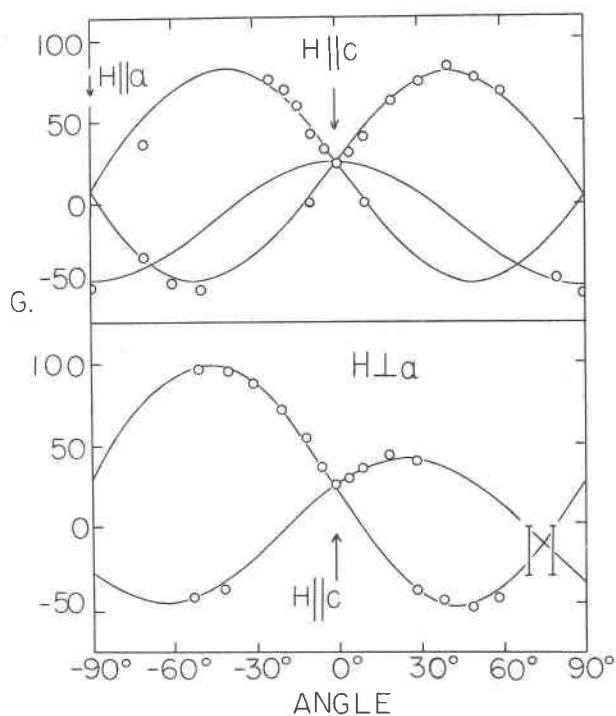
Among various Al and Na bearing minerals, some

FIG. 4. Separations in gauss between ^{7}Li satellites ($\pm 1/2$ $\longleftrightarrow$ $\pm 3/2$ transition) vs orientations of **H**. Top diagram, **H** in ac-plane; bottom diagram, **H** $\perp$ a-axis.

of them, such as zoisite (Brinkmann, Staehli, and Ghose, 1969), andalusite (Hafner, Raymond, and Ghose, 1970), topaz (Tsang and Ghose, 1972a), and cordierite (Tsang and Ghose, 1972b), gave sharp satellite NMR signals. On the other hand, rather broad satellite signals have been observed for ^{23}Na and ^{27}Al nuclei in nepheline (Brinkmann, Ghose, and Laves, 1972). In nepheline, there is partial Al-Si disorder in the tetrahedral sites. The nepheline sample showing the highest degree of Al-Si order yielded ^{23}Na satellites but no detectable ^{27}Al satellites. This behavior of nepheline was interpreted in terms of a domain structure. The individual domain symmetry is lower than hexagonal. However, threefold twinning of these domains gives pseudohexagonal symmetry to nepheline. This postulate was corroborated by the existence of a curious threefold disorder of one oxygen atom, a feature which persists in the structural refinement in spite of very low R-factor (Dollase, 1970; Foreman and Peacor, 1970). Such cases of pseudosymmetry may be fairly common among silicate structures of high symmetries, such as garnets, analcime, scapolite, melilite, idocrase, chabazite, *etc.* Indeed, such a twinned domain model has been proposed for the structure of the melilite, gehlenite (Louisnathan, 1971).

In the refinement of the buergerite structure, Barton (1969) and also Tippe and Hamilton (1971) have observed unusually large thermal vibrations of the Na atoms at the $3(a)$ sites. The large temperature factor for Na was explained by Barton (1969) as probable positional disorder, that is, the occurrence of the Na atoms slightly off the threefold axes. This evidence is not conclusive, but the possibility of twinned domain structure in tourmaline is suggested. On the other hand, the tourmaline texture variations (Wagner, Pollard, Young, and Donnay, 1971) have shown no evidence for domain twinning. In case twinned domains are present in tourmaline, they must be on a scale below X-ray resolution.

In the crystal structure of tourmaline, the boron atoms occupy general positions. However, the nearest neighbor symmetry at the boron site within the BO_3 triangle is almost trigonal about the crystallographic c-axis. Our ^{11}B resonance results, $|e^2qQ/h| = 2.76 \pm 0.08$ MHz, $\eta \ll 1$, are in general agreement with values obtained for ^{11}B in triangular coordination in other borate minerals. It appears that the electric field gradient at the boron nuclear site is determined primarily by the B-O bonds only, indicating a strong covalent B-O bond within the BO_3 triangle.

It is conceivable that within the six-membered ring, water molecules or H_3O^+ ions sometimes occur in place of the Na. However, the proton resonance indicates the absence of water molecules, confirming the neutron diffraction results (Tippe and Hamilton, 1971).

The lithium ions occupy the larger octahedrally coordinated $9(b)$-positions. Our ^7Li resonance results, $\eta \sim 0$ and $\alpha \sim 45°$, indicate that the site symmetry is close to pseudotetragonal, with the axis of distortion being $\sim 45°$ off the crystallographic c-axis. From structural studies (Buerger, Burnham, and Peacor, 1962; Barton, 1969), the axis of distortion would be approximately along the O_1-Li-O_3 direction, and thus $\sim 60°$ off the c-axis, in satisfactory agreement with our NMR data. The pseudotetragonal symmetry was previously noted by Wilkins, Farrell, and Naiman (1969) from their optical as well as pre-existing structural data.

In many varieties of tourmaline, magnetic ions such as Fe^{2+} or Fe^{3+} may occupy the $9(b)$ and/or $18(c)$ sites. Whereas the magnetic susceptibility may be noticeably anisotropic for individual Fe^{2+} ions on $9(b)$-sites, the experimental anisotropy (differences between susceptibilities for $H \parallel c$ and for $H \perp c$) would be much reduced for $\alpha \sim 45°$, since the observed value is the average over various sites related by $120°$ rotations about the c-axis. The experimental susceptibilities of ferrous tourmalines have been found to be almost isotropic for Fe^{2+} ions on $9(b)$-sites, but noticeably anisotropic for Fe^{2+} on $18(c)$-sites (Tsang, Thorpe, Donnay, and Senftle, 1971), thus confirming our NMR results. Because of the ^6S electronic configuration, the susceptibilities of ferric tourmalines are almost isotropic.

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