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Fig. 1

Figure 1: Fig. 1

**Abstract****Full Text**

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**QUADRUPOLE SPLITTING AND DISORDER OF  $\text{Li}^7$  IN AMBLYGONITE  $\text{LiAlPO}_4(\text{OH},\text{F})$** *(Presented by Academician N. V. Belov on 31 XII 1964)*

Quadrupole splitting of nuclear magnetic resonance (n.m.r.) lines has been used in structural studies of crystals to establish coordination, to trace order-disorder phenomena, and to determine local intracrystalline electric fields at the sites of nuclei possessing quadrupole moments. In a series of works in recent years on n.m.r. of  $\text{B}^{11}$  ((1) and others), Volkov's method (2) was very effectively applied to distinguish tetrahedral and trigonal groupings of boron in borates and borosilicates. In n.m.r. studies of  $\text{Al}^{27}$  in disordered spinels (3) and feldspars (4), this method could not be applied because of the broadening and disappearance of the satellites. In the case of amblygonite, a distinct splitting of the satellites and of the central transition is observed. This makes it possible to use, in full measure, the effect of quadrupole interaction in nuclear magnetic resonance to study the disorder of the distribution of  $\text{Li}^7$  atoms in the structure of amblygonite.

**Fig. 1.** Structure of amblygonite in projection onto the plane (102) of the doubled lattice. The numbers show the heights of the atoms relative to the projection plane in angstroms.

The X-ray structural analysis of amblygonite was carried out twice: by V. I. Simonov and N. V. Belov (5), and then by V. Bauer (6). With identity of the general structural motif, the data on the position of  $\text{Li}^7$  proved to be different. In the crystal studied by V. I. Simonov and N. V. Belov, Li is distributed statistically over two positions; in Bauer's sample Li occupies only one position, coinciding with one of the positions established by V. I. Simonov and N. V. Belov. Amblygonite is triclinic,  $P\bar{1} = C_i^1$ . Various choices of crystallographic axes are possible. Figure 1 shows a projection of the structure (without oxygen atoms—nonmagnetic) onto the plane (102) in the setting with a doubled lattice. This plane is readily determined morphologically as the plane of the most perfect cleavage, and it is convenient to use it for orienting the crystal when recording n.m.r. spectra. The atomic coordinates were recalculated for this setting from the data of V. I. Simonov and N. V. Belov (5). The elementary cell in Bauer's

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

setting <sup>(6)</sup>, containing  $2\text{LiAlPO}_4(\text{OH},\text{F})$ , is also shown here. The (102) plane of the doubled cell corresponds to (100) in Bauer's setting. The doubled lattice is close to orthorhombic:

$\alpha = 86^\circ 30'$ ,  $\beta = 88^\circ 20'$ ,  $\gamma = 89^\circ 20'$ ,  $a = 7.71 \text{ \AA}$ ,  $b = 6.99 \text{ \AA}$ ,  $c = 11.90 \text{ \AA}$  <sup>(5)</sup>. The dimensions of the unit cell according to <sup>(5)</sup> in the setting <sup>(6)</sup>, also shown in Fig. 1, are:  $\alpha = 113^\circ 12'$ ,  $\beta = 97^\circ 54'$ ,  $\gamma = 67^\circ 31'$ ,  $a = 5.16 \text{ \AA}$ ,  $b = 7.21 \text{ \AA}$ ,  $c = 5.06 \text{ \AA}$ .

Owing to its small size, the Li atom occupies only one of the halves (but not both simultaneously) of the distorted oxygen octahedron, so that its coordination polyhedron is a five-vertex polyhedron. Therefore the 2 Li atoms belonging to the unit cell can occupy 4 different positions. These positions (I and II in Fig. 1) are pairwise related by a center of symmetry.

**Fig. 2.** Nuclear magnetic resonance spectra of  $\text{Li}^7$  in amblygonite

**Fig. 3.** Angular dependence of the distance between quadrupole satellites upon rotation about the  $X, Y, Z$  axes for  $\text{Li}^{\text{I}}$  and  $\text{Li}^{\text{II}}$

Since NMR does not distinguish centrosymmetric positions, 2 Li atoms related by a center of symmetry (an ordered distribution of Li over one structural position) should give one NMR spectrum, whereas 2 Li atoms not related by a center of symmetry should give two superposed spectra.

Observation of the NMR spectra of different amblygonite crystals showed that both ordered and disordered varieties exist.

Amblygonite from Kazakhstan with an  $\text{F} : \text{OH} \approx 1 : 1$  ratio ( $2\nu = -89^\circ$ ), containing only 0.015% Na, was studied in more detail. From a large single-crystalline block of amblygonite, a cylindrical specimen about 2 cm in diameter and height was prepared, cut in such a way that  $\perp (102)_4$  was the axis of rotation. Optical examination of the specimen (after the spectra had been recorded) showed the absence of twins in it.

The measurements were carried out on an NMR spectrometer for broad lines, built on the basis of an electromagnet <sup>(7)</sup>. The maximum value of the polarizing field was 10,000 Oe. The adjustment limits were from 200 to 1000 Oe. Sweep range: 1-1000 Oe. Sweep time: 0.1 s-3 h. An autodyne with stabilization and amplitude adjustment served as the NMR signal detector. The operating frequency was 9 MHz.

The components of the quadrupole-interaction tensor were determined from the results of measuring the angular dependence of the distance between quadrupole satellites upon successive rotation of the crystal about three mutually perpendicular axes  $X, Y, Z$  <sup>(2)</sup>.

The distance between the satellites  $\nu''_m - \nu'_m$  depends on the rotation angle  $\theta$ :

$$\nu''_m - \nu'_m = \frac{1}{2}(2m - 1)(a + b \cos 2\theta + c \sin 2\theta).$$

Fourier analysis of the experimental curves gives the coefficients  $a, b, c$ , with which the components of the quadrupole-interaction tensor in the system  $X, Y, Z$  are related:

$$a_X = \frac{1}{2}k(\Phi_{YY} + \Phi_{ZZ}) = -\frac{1}{2}k\Phi_{XX}, \quad b_X = \frac{1}{2}k(\Phi_{YY} - \Phi_{ZZ}),$$

$$c_X = -k\Phi_{ZZ}.$$

By cyclic permutation, similar relations are obtained for rotation about the axes  $Y$  and  $Z$ . The resulting tensor  $k\Phi_{ij}$  is obtained by diagonalization in the standard way.

The quadrupole-interaction tensor is usually described by means of its largest component, called the quadrupole-interaction constant  $eQq/h$  ( $q = \Phi_{zz}$ ), and by the ratio of the difference between the smallest and the intermediate components of the tensor to the largest component, called the asymmetry parameter,  $\eta = (\Phi_{xx} - \Phi_{yy})/\Phi_{zz}$ .

**Table 1**

Experimental values of the Fourier coefficients (in kHz) for the splitting curves  $\nu''_m - \nu'_m$  of the satellite lines  $\text{Li}^{\text{I}}$  and  $\text{Li}^{\text{II}}$  in amblygonite

Fourier coeff.	$\text{Li}^{\text{I}} X$	$\text{Li}^{\text{I}} Y$	$\text{Li}^{\text{I}} Z$	$\text{Li}^{\text{II}} X$	$\text{Li}^{\text{II}} Y$	$\text{Li}^{\text{II}} Z$
$a$	-85, 14	+39, 14	+46, 44	-46, 44	+15, 48	+15, 48
$b$	+6, 88	-131, 15	+125, 84	+15, 48	-67, 40	+61, 92
$c$	-70, 00	+2, 00	-22, 00	-12, 04	-1, 72	+29, 24

**Table 2**

Components of the tensor (in kHz)  $\Psi_{ij} = eQ\Phi_{ij}/h$  in the coordinate system  $X, Y, Z$  for  $\text{Li}^{\text{I}}$  and  $\text{Li}^{\text{II}}$  in amblygonite

	$\Psi_{XX}$	$\Psi_{YY}$	$\Psi_{ZZ}$	$\Psi_{XY}$	$\Psi_{YZ}$	$\Psi_{ZX}$
$\text{Li}^{\text{I}}$	+175, 28	-78, 26	-92, 88	+18, 92	-1, 72	+60, 20
$\text{Li}^{\text{II}}$	+92, 88	-30, 96	-72, 96	-29, 24	+1, 72	+12, 04

Figure 2 shows the NMR spectrum of  $\text{Li}^7$  in amblygonite. In accordance with the nuclear spin of  $\text{Li}^7$ ,  $I = 3/2$ , and the presence of two nonequivalent positions, two lines from the central transitions and two pairs of satellites are observed.

Figure 3 shows the angular dependence of the distance between satellites for both positions. The axes  $X, Y, Z$  were chosen as follows: the  $Z$  axis is perpendicular to  $(102)_4$ ,  $Y = b_4$  (the line of intersection of the two cleavage systems along  $102_4$  and  $10\bar{2}_4$ ), and  $X$  lies in the plane  $(102)_4$ , perpendicular to  $Y$  and  $Z$ .

Table 1 gives the Fourier coefficients\*, Table 2 gives the components of the quadrupole-interaction tensor obtained from them, Table 3 gives the values of  $eQq/h$  and  $\eta$  for both positions  $\text{Li}^{\text{I}}$  and  $\text{Li}^{\text{II}}$ , and Table 4 gives the direction cosines of the angles between the principal axes of the tensor and the axes  $X, Y, Z$ .

**Table 3**

Quadrupole-interaction constant  $eQq/h$  (in kHz) and asymmetry parameter  $\eta$  for  $\text{Li}^{\text{I}}$  and  $\text{Li}^{\text{II}}$  in amblygonite

	$eQq/h$	$\eta$
$\text{Li}^{\text{I}}$	44.24	0.620
$\text{Li}^{\text{II}}$	32.44	0.359

**Table 4**

Cosines of the angles of the principal axes  $x, y, z$  of the quadrupole-interaction tensor for  $\text{Li}^{\text{I}}$  and  $\text{Li}^{\text{II}}$  relative to the axes  $X, Y, Z$  in amblygonite

		$X$	$Y$	$Z$
$\text{Li}^{\text{I}}$	$x$	+0.0597	+0.0701	+0.0533
$\text{Li}^{\text{I}}$	$y$	-0.6285	-0.8164	-0.4588
$\text{Li}^{\text{I}}$	$z$	-0.7753	-0.6065	-0.8860
$\text{Li}^{\text{II}}$	$x$	-0.1089	-0.1560	-0.0815
$\text{Li}^{\text{II}}$	$y$	-0.3817	-0.5159	-0.2139
$\text{Li}^{\text{II}}$	$z$	-0.9220	-0.8434	-0.9725

The measurements show that the two positions  $\text{Li}^{\text{I}}$  and  $\text{Li}^{\text{II}}$  in amblygonite are characterized by close, but clearly different, values of the quadrupole-interaction constants and asymmetry parameters.

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\* The displacement of the midpoint between each pair of satellites  $\bar{\nu}_m$  from the unperturbed frequency  $\nu_0$  depends <sup>(2)</sup> on the rotation angle  $\theta$ :

$$\bar{\nu}_m - \nu_0 = n + p \cos 2\theta + r \sin 2\theta + u \cos 4\theta + v \sin 4\theta.$$

The calculated coefficients  $n, p, r, u, v$  proved to be negligibly small.

*Note: Figure translations are in progress. See original paper for figures.*

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