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ZORA DFT Calculation of ^{11}B Electric Field Gradient Tensor for Lithium Borates

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Abstract: ZORA-DFT calculations of ^{11}B EFG (electric field gradient) tensors for lithium borates, LiB_3O_5 (LBO) and $Li_2B_4O_7$ (LTB), were performed. The calculated values of ^{11}B quadrupole coupling constant and asymmetry parameter are in good agreement with the experimental values. The sign of the quadrupole coupling constant for the tetrahedral boron site was deduced from the distortion from the ideal tetrahedral symmetry.

INTRODUCTION

Solid-state ^{11}B NMR spectroscopy has been widely used for structural characterization in borosilicates and minerals.[1-4] Boron-containing amorphous systems possess trigonal (BO_3) and tetrahedral (BO_4) boron sites, which can be distinguished by their ^{11}B quadrupole interaction parameters, quadrupole coupling constant and asymmetry parameter. The ^{11}B quadrupole coupling constants are smaller than 1.0 MHz for BO_4 tetrahedra, whereas BO_3 units possess quadrupole couplings in the range of 2.4 to 3.0 MHz.

The electric field gradient (EFG), eq_{ij}, can be described as a symmetric 3 × 3 traceless tensor with the convention $|eq_{zz}| \geq |eq_{yy}| \geq |eq_{xx}|$. The magnitude of the electric field gradient tensor is given by the quadrupole coupling constant, C_Q . The deviation from axial symmetry is indicated by the asymmetry parameter, η:[5]

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$$C_Q = \frac{e^2 q_{zz} Q}{h} \tag{1}$$

$$\eta = \frac{eq_{yy} - eq_{xx}}{eq_{zz}} \quad (0 \le \eta \le 1) \tag{2}$$

In the principal axis system, the electric field gradient tensor can be reduced to two parameters, eq_{zz} and

$$V^{PA} = \frac{e^2 q_{zz} Q}{4I(2I-1)} \begin{bmatrix} \eta - 1 & 0 & 0 \\ 0 & -\eta - 1 & 0 \\ 0 & 0 & 2 \end{bmatrix} \tag{3}$$

where Q and I are the nuclear quadrupole moment[6] and the nuclear spin number and the values of ^{11}B nucleus are 4.059 fm^2 and 3/2, respectively.

CALCULATIONS

ZORA-DFT (Zeroth-Order Regular Approximation - Density Functional Theory) calculations of ^{11}B EFG tensors for lithium borates were performed using the NMR module of Amsterdam Density Functional (ADF) program[7-10]. Vosko-Wilk-Nusair (VWN) local density approximation with Becke-Perdew generalized gradient approximation (CGA) was used for the exchange-correlation functional. The triple polarized TZ2P Slater-type ZORA basis sets available in the ADF package were also employed. Atomic coordinates for LiB_3O_5[11] and $Li_2B_4O_7$[12] taken from the X-ray crystal structures were used. The main structural units of LiB_3O_5 and $Li_2B_4O_7$ consisting of crystallographically distinct boron-oxygen triangles (BO_3) and boron-oxygen tetrahedrons (BO_4) were considered for the calculation.

RESULTS AND DISCUSSION

The experimental and calculated ^{11}B quadrupole coupling constants (C_Q) and asymmetry parameters (η) for LiB_3O_5 and $Li_2B_4O_7$ are summarized in Table 1. The experimental values for LiB_3O_5 and $Li_2B_4O_7$ were taken from the single crystal ^{11}B NMR works of Ahn *et al.*[13] and Ivanov *et al.*[14]. The sign of quadrupole coupling constants cannot be normally obtained from the solid-state NMR experiments, and it was assumed on the basis of the calculation results. ZORA DFT calculations for ^{11}B EFG tensors were performed under the assumption that (1) only the contributions from the oxygen atoms in BO_3 and BO_4 units are included, (2) the oxygen atoms are negatively charged, and (3) sum of the deviation angles along the 3-fold axis in BO_4 unit is zero. As shown in Table 1, the calculated results are in good agreement with experimental values: the trigonal boron site is associated with a considerably larger value of C_Q, ~2.6 MHz, whereas the tetrahedral boron site has a relatively small value of C_Q, ~±0.5 MHz.

The experimental and calculated components of the ^{11}B EFG tensors for BO_3 and BO_4 structural units are given in Table 1 and depicted in Fig. 1. An important feature in the results is that the value of $e^2q_{zz}Q$ for tetrahedral boron site is nearly smaller in relation to the value of trigonal boron site. The electric field gradient along the z-axis based on the point charge model is seen in

$$q_{zz} = \sum_i K_i \frac{3z_i^2 - r_i^2}{r_i^5} = \sum_i K_i \frac{3\cos^2\theta - 1}{r_i^3} \tag{4}$$

where K_i is the assigned charge of each ith oxygen, r_i is the boron-oxygen bond length, and z is along the 3-fold axis.[15,16] In the case of the ideal tetrahedral symmetry ($\angle$O-B-O = 109.45°), the electric field gradient along the z-axis is zero; therefore quadrupole coupling constant is zero.

Fig. 2 shows the values of quadrupole coupling constant calculated as the function of the largest deviation angle from the ideal tetrahedral angle. It was calculated with 1.47 Å bond distance between boron and oxygen atoms, with a relative error less than 5 %.

Table 1. Experimental and calculated ^{11}B quadrupole coupling constants, asymmetry parameters, and principal EFG tensor components for LiB_3O_5 and $Li_2B_4O_7$.

Compound	Site [a]	C_Q	η	$e^2q_{xx}Q$	$e^2q_{yy}Q$	$e^2q_{zz}Q$
		(a) Experimental [b]				
LiB_3O_5	T	0.176	0.584	-0.006	-0.023	0.029
	Δ_1	2.615	0.266	-0.160	-0.276	0.436
	Δ_2	2.690	0.204	-0.178	-0.270	0.448
$Li_2B_4O_7$	T	-0.513	0.51	0.021	0.064	-0.085
	Δ	2.551	0.18	-0.174	-0.251	0.425
		(b) Calculated [c]				
LiB_3O_5	T	0.315	0.534	-0.012	-0.040	0.053
	Δ_1	2.678	0.288	-0.159	-0.287	0.446
	Δ_2	2.588	0.279	-0.155	-0.276	0.431
$Li_2B_4O_7$	T	-0.522	0.555	0.019	0.068	-0.087
	Δ	2.659	0.147	-0.189	-0.254	0.443

[a] Tetrahedral (T) and trigonal (Δ) coordinated boron site. [b] Obtained from a single crystal ^{11}B NMR. The signs of the quadrupole coupling constant and the EFG tensor components were assumed on the basis of the calculation. [c] Obtained from ZORA DFT calculation. [b, c] EFG tensor components are expressed in MHz.

As required by the ideal tetrahedral symmetry, the value of C_Q is zero. In addition, the distorted structure in which the largest deviation angle is negative shows a negative value of C_Q, and vice versa. Therefore, it is possible to deduce a negative sign of the quadrupole coupling constant for tetrahedral boron site in $Li_2B_4O_7$ conforms to the X-ray structural data. The deviation angles along the 3-fold axis are 2.33, -7.27, 5.43 ° for $Li_2B_4O_7$ and -1.04, 3.47, -0.88 ° for LiB_3O_5.

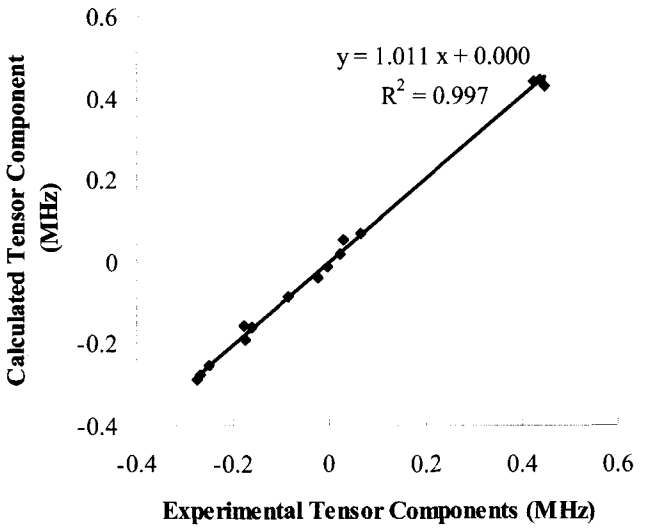

Fig. 1. Correlation between the experimental and calculated principal ^{11}B EFG tensor components.

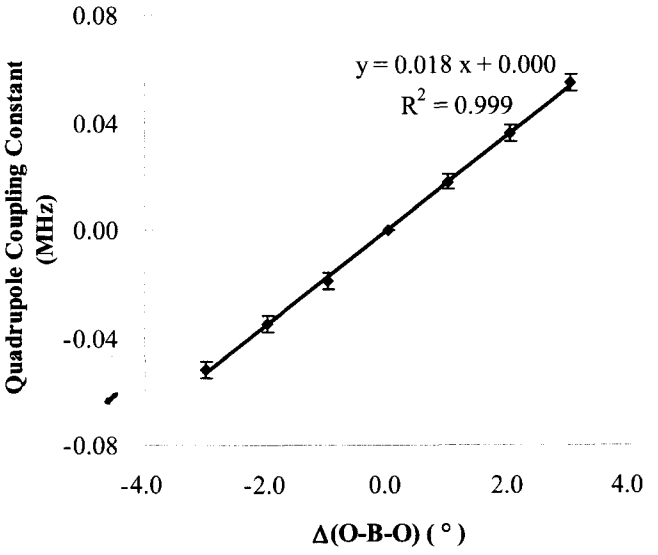

Fig. 2. Quadrupole coupling constants in tetrahedral boron sites as a function of the largest deviation from the tetrahedral angle.

CONCLUSIONS

^{11}B EFG tensors of the trigonal (BO_3) and tetrahedral (BO_4) boron sites in lithium borates determined using ZORA DFT calculation are in good agreement with the experimental NMR results. The sign of quadrupole coupling constant of the tetrahedral boron site can be deduced from the distortion from the ideal tetrahedral angle.

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