11B and 23Na solid-state NMR and density functional
theory studies of electric field gradients at boron sites in
ulexite

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Nuclear magnetic resonance (NMR) parameters of 11B in borates and borosilicates, unlike those of many other
nuclei such as 29Si and 27Al, vary only over limited ranges and have been thought to be insensitive to local
structural environments. High-resolution NMR spectroscopy at high (14 T) and ultrahigh (21 T) fields yield precise
11B and 23Na NMR parameters for ulexite, which contains the pentaborate polyanion ([B5O6(OH)6]3−) as the fun-
damental building block (FBB). These NMR parameters are compared with ab initio theoretical calculations as
implemented in WIEN2K, including optimization of the ulexite structure, determination of the electric field gradi-
ents (EFG) and consequently the nuclear quadrupole interaction (QI) parameters at the five distinct B sites, and cal-
culations of the density of states (DOS). These calculations show that the magnitudes and signs of the EFG for 11B
and 23B are determined by multiple factors, including the electron distributions in the B 2pz orbitals and their in-
teractions with Ca-3p/O-2s orbitals. Most importantly, the calculated B 2pz orbitals at all B sites in ulexite are predom-
inantly affected by the atoms within the fundamental building block, resulting in the insensitivity of the 11B QI
parameters to the weak interunit interactions among FBB. Calculations with the water molecules removed from
the ulexite structure provide further support for the strong intraunit interactions in FBB as a cause for the poor sen-
sitivity of 11B NMR parameters to local structural environments, including hydrogen bonding, in borates.

1. Introduction

Ulexite ([NaCa[B5O6(OH)6]·5H2O]) is a common hydrated calcium and sodium borate of economic significance in
boron deposits and saline lake sediments.1 The fundamental building block (FBB) in ulexite is the pentaborate polyanion
([B5O6(OH)6]3−) with five distinct boron sites: three four-coordinate ([4]B) and two three-coordinate ([3]B) species, in the
form of two hexagonal soroborate rings connected via oxygen atoms (Fig. 1). The isolated FBB in ulexite is cross-linked by
chains of hydrated Na- and Ca-coordination polyhedra via hydrogen bonds.1

Solid-state nuclear magnetic resonance (NMR) is a power-
ful technique for probing subtle structural differences and disorder in minerals and other materials.2,3 For example, 29Si
described by the quadrupole coupling constant (\(Q\)) and the asymmetry parameter (\(\eta\)). These nuclear quadrupole interaction (QI) parameters can be investigated by using several spectroscopic methods, including NMR, to provide detailed information about the local structural environments of nuclei. This is due to the EFG being highly sensitive to the electronic charge distribution at the nucleus and its surroundings. Specifically, the QI parameters are related to the principal elements of the EFG tensor at the site as (Slichter 1992):

\[
C_Q = eV_{zz}Q/h
\]

(1)

\[
\eta = |V_{xx} - V_{yy}|/V_{zz}
\]

(2)

where \(V_{zz}, V_{xy}\), and \(V_{xx}\) are the EFG components in the principal axis system (PAS) and fulfill the condition \(|V_{xx}| \geq |V_{yy}| \geq |V_{zz}|\), \(e\) is the electron charge, \(h\) is Planck’s constant, and \(Q\) is the quadrupole moment. The recommended quadrupole moment of 0.0409 x 10^{-28} m^2 for the bare boron atom was determined from multiconfigurational Hartree–Fock calculations of the EFG, derived from the hyperfine structure of B(\(^2P\)) states, combined with the experimental nuclear quadrupole coupling constant obtained from atomic-beam magnetic resonance measurements. The quadrupole moment for \(^{\text{23}}\text{Na}\) is 0.0102 x 10^{-28} m^2.

In addition to spectroscopic experiments, ab initio theoretical calculations have gained popularity for quantitatively predicting the EFG of nuclei in crystalline solids. For example, Full Potential Linear Augmented Plane Wave (FP LAPW) modeling has been widely used for theoretical calculations and the prediction of electronic and other properties, including EFG, for solids with periodic boundary conditions. For this full-potential and all-electron method, the electronic potential in the unit cell is partitioned into non-overlapping atom-centered spheres and an interstitial area between the spheres (Muffin-Tin partition), no approximation to either the potential or charge density is made, and the exchange and correlation effects are treated in the density functional theory (DFT) using the generalized gradient approximation (GGA). A linear combination of the products of radial functions and spherical harmonics is then used inside the atomic spheres and a plane wave expansion is used in the interstitial area as the basis sets. Finally, the Kohn–Sham equations and thus the crystal wavefunctions are solved by a linear variation of LAPW, and thus the electronic structure can be obtained. These calculations are implemented in the computer package WIEN2k. FP LAPW calculations have proven to be very sensitive to atomic positions, because small differences in structural data exert significant effects on the calculated EFG values.

In this contribution, aspects of the electronic structure of ulexite such as the origin of the EFG, the anisotropy of the electron density distribution, the p-orbital occupation and charge transfer at the B sites, have been investigated by ab initio density of states (DOS) calculations combined with high-resolution \(^{\text{11}}\text{B}\) and \(^{\text{23}}\text{Na}\) MAS NMR spectroscopy at high (14 T) and ultrahigh (21 T) fields. These theoretical results shed new light on the interpretation of \(^{\text{11}}\text{B}\) and \(^{\text{23}}\text{Na}\) NMR parameters in borates, especially possible causes for the insensitivity of \(^{\text{11}}\text{B}\) QI parameters to local structural environment. Together, the experimental and theoretical values suggest a refinement to the hydrogen positions in ulexite obtained from X-ray diffraction.

2. Experiments and theoretical calculations

2.1. Material and characterization

A ulexite sample from Tibet was provided by Prof. Miaping Zheng of the Chinese Academy of Geological Sciences. Small crystals of ulexite in this sample were visually separated and ground into a fine powder using an agate mortar and pestle. The identity of this sample was verified by powder X-ray diffraction (PXRD) analysis, using a PANalytical X’Pert Pro Bragg–Brentano X-ray diffractometer. Analytical conditions included the Bragg–Brentano geometry, a Cu Ko radiation source (\(\lambda = 0.15418 \text{ nm}\)), an X’Celerator detector, and a Ni-filter diffracted beam. Data were acquired at room temperature with a 2\(\theta\) range of 10° to 110° at an increment of 0.017° and 305.5 seconds per step. The PXRD pattern confirms that ulexite is the dominant phase in this sample.

2.2. Nuclear magnetic resonance

All NMR spectra were regulated at 298 K using variable-temperature cooling gas to account for frictional heating. The magic angle was adjusted by optimizing the \(^{\text{11}}\text{B}\) and \(^{\text{23}}\text{Na}\) NMR parameters in borates, especially possible causes for the insensitivity of \(^{\text{11}}\text{B}\) QI parameters to local structural environment. Together, the experimental and theoretical values suggest a refinement to the hydrogen positions in ulexite obtained from X-ray diffraction.
cycles were set at 5 Å. The convergent conditions of the self-consistent calculations were run in a non-spin-polarized mode and the overlapping of two typical second-order quadrupolar lineshapes (Fig. 2b). The NMR parameters from simulations of the spectra are given in Table 1.

The highly symmetrical octahedral sodium site in ulexite gives a narrow Na MAS NMR resonance at 7.1 ppm. A low intensity broad resonance at ~6 ppm is interpreted as arising from an impurity (Fig. 2c) that may be a sodium borate such as Na2O·4B2O3 (ref. 31) or Na2B4O5(OH)4 which was not detected in the PXRD pattern. The estimated abundance of this impurity phase at ~3% would not be expected to exert a significant impact on the 11B spectrum of ulexite. The narrow Gaussian-like central transition (CT) lineshape Na MAS NMR resonance at 7.1 ppm indicates a small C\text{\textsubscript{Q}}. Slow spinning MAS experiments performed to determine C\text{\textsubscript{Q}} from the spinning sideband manifold of the satellite transitions yielded a value of 70(5) kHz (Fig. 2c), which deviates from theoretical calculations (Table 1). Bonhomme et al. suggested that discrepancies between calculated and experimental data may indicate the presence of local motions such
as exchange, reorientation, vibration, libration or even hopping of Na$^+$ and its coordinated water molecules. In ulexite, such motions may result in partial averaging of the quadrupolar interaction. The small QI of $^{23}$Na in ulexite corresponds to a second-order quadrupolar shift of about 2 Hz and allows the center of gravity shift at 7.1 ppm (Fig. 2b) to be taken as the isotropic chemical shift.

3.2. DFT structural optimization

Our DFT structural optimizations resulted in the forces acting on each of the atoms in ulexite to decrease from the average values of 737 mRy per a.u. (and a maximum of 2031 mRy per a.u.) to only 1 mRy per a.u. Fig. 3 shows that the calculated total energy is the lowest, when the volume of the unit cell is reduced by 6% from the original X-ray structure. This volume reduction is at least partially attributable to the fact that theoretical calculations are done at 0 K, whereas the XRD data were obtained at room temperature.

The optimized fractional atomic coordinates as well as the original XRD data for ulexite are listed in Table 2. The changes in the coordinates of the 16 H atoms in ulexite after structural optimizations are more dramatic than those of the O, B and Na atoms, with the maximum change of 21.2% for the $z$-coordinate of H14 (Table 3). The positions of the B, Na and O atoms in ulexite are almost unchanged (less than 1%). The non-hydrogen bond distances from XRD and optimized structures are compared in Table 3. The largest deviation in the bond distance is Ca–O4 at 0.0309 Å (Table 3). The deviations in the bond distance is Ca–O4 at 0.0309 Å (Table 3).

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**Table 1** Experimental and calculated NMR results using WIEN2k for ulexite (uncertainties for the experimental parameters are listed in parentheses)

<table>
<thead>
<tr>
<th>Experimental</th>
<th>Theoretical calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{11}$B(2)</td>
<td>$C_Q$, MHz</td>
</tr>
<tr>
<td>18.0</td>
<td>2.57</td>
</tr>
<tr>
<td>$^{11}$B(5)</td>
<td>18.9</td>
</tr>
<tr>
<td>$^{14}$B(1)</td>
<td>1.2$^{d}$</td>
</tr>
<tr>
<td>$^{14}$B(3)</td>
<td>-0.46</td>
</tr>
<tr>
<td>$^{14}$B(4)</td>
<td>-0.38</td>
</tr>
<tr>
<td>$^{23}$Na</td>
<td>7.1</td>
</tr>
</tbody>
</table>

$^a$ Calculated results from the XRD structure using WIEN2k.
$^b$ Calculated results from the structure with all atoms optimized using WIEN2k.
$^c$ Calculated results from the structure with lattice parameters and all atoms optimized using WIEN2k; the optimized unit cell parameters are: $a = 8.8015$ Å; $b = 12.8488$ Å and $c = 6.6670$ Å. $^d$ Average value of three $^{14}$B sites; the uncertainty in $\eta$ is 0.15.

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tions of the B–O bond lengths after DFT optimizations are less than 0.02 Å for both BO$_4$ and BO$_3$ sites, and the average B–O bond distances in the optimized structure are systematically ~0.01 Å longer than those from the XRD experiment.

The atomic coordinates that changed most after DFT optimizations are the H atoms (Table 4). This is attributable to the large uncertainty in the location of H atoms by XRD due to the non-spherical electron density and the small diffraction coefficient of the H atom.$^{5,34-36}$ Other contributing factors may be the dynamic or static disorder of H atoms in the crystal structure, which cause XRD to give only average H positions, especially those in the water molecules. The inaccuracy of H positions from XRD is shown by the significantly shorter O–H bond distances from XRD data than those determined by neutron diffraction techniques.$^{33,35}$ The optimized O–H distances in ulexite (Table 4) in this study are in agreement with values reported by neutron diffraction of

\[
\text{borates.}^{37,18,6}
\]

The structural optimization for ulexite leads to systematically longer donor (D)–H distances by ~0.2 Å (with the largest variation of 0.313 Å between OW1–H7), and the donor–acceptor (A) distances are shorter by 0.04 Å (with the largest variation of 0.1029 Å between OW4 and O–H2) (Table 4). This is similar to the optimization of borate dimorphs, kunkanovite and inderite.$^{24}$ These results suggest that the water molecules in ulexite exert a greater influence on the structure than suggested by previous XRD data. It is noteworthy that the calculated D–A and D–H values from the two structural optimization methods (i.e., with and without changing the unit cell parameters) are very close, differing only by less than 0.03 Å.

### 3.3. DFT calculations of QI parameters

The calculated $Q_0$ and $\eta$ values at the $[^{31}B]$ and $[^{33}B]$ sites from the XRD and optimized structures of ulexite are also listed in Table 1. Thermal vibrations do not alter the calculated EFG values significantly; especially for sp-hybridized atoms, such effects are expected to be negligible.$^{39}$ However, if the atomic
positions are not determined accurately, agreement between theoretical and experimental EFGs (particularly for η) is not expected.\textsuperscript{40} Table 1 shows that the $C_Q$ parameters for the $[3]B$ sites calculated from the optimized structures are in better agreement with the experimental values than those from the XRD structure. Usually the $^{11}B$ $C_Q$ and η change little with geometric distortion,\textsuperscript{41,27,28} therefore, the slightly better agreements between the experimental $C_Q$ values for the $[3]B$ sites and those calculated from the optimized structure are significant. The calculated average $^{11}B$ $C_Q$ values of 0.43 MHz and 0.41 MHz for the $[4]B$ sites with and without structural optimization, respectively, are both in agreement with the experimental value of 0.42 MHz. The η values at the $[4]B$ sites are poorly constrained by theoretical calculations owing to the very small and similar EFG tensor components (see eqn (2)).

Table 5 shows the calculated EFG results from the “dehydrated” ulexite structures with different numbers of water molecules removed. The calculated $C_Q$ values for both Na and Ca sites that coordinate directly with water molecules are changed not only in amplitude (up to ~3 times) but also in sign. On the other hand, the calculated $C_Q$ values for the $[3]B$ sites decrease by <0.1 MHz (i.e., $B(2)$, 2.51 to 2.42 MHz; $B(5)$, 2.50 to 2.47 MHz) after the removal of all five water molecules. Similarly, the calculated $C_Q$ values for the $[4]B$ sites increase only marginally (Table 5). These results demonstrate that the H$_2$O molecules and hydrogen bonds in ulexite do not exert a significant influence on the EFG at the B sites.

The EFG at the B atoms in borates results mainly from the anisotropy and distortion of the valence electron distribution, therefore, even slightly different occupations in the p$_x$, p$_y$ and p$_z$ orbitals due to polarization effects and chemical bonding with neighboring atoms are expected to have a significant effect on EFG.\textsuperscript{42,6} The non-cubic oxygen atom environment surrounding the B sites and B sp$^3$/sp$^2$ hybridizations lead to different occupations in p$_x$, p$_y$ and p$_z$ orbitals, thus causing anisotropic B-2p charge distribution around the B nucleus. The degree of such anisotropy of the p electron density, which is proportional to $V_{zz}$, can be described by eqn (3):\textsuperscript{42}

$$\Delta \eta_p = \frac{1}{3} (p_x + p_y) - p_z$$

and the sign for $V_{zz}$ (thus the sign for $C_Q$) is also determined by this equation. The calculated $\Delta \eta_p$ values for the

Table 5 | The calculated $C_Q$ (MHz) and η values for ulexite with different numbers of H$_2$O molecules

<table>
<thead>
<tr>
<th>Water\textsuperscript{a}</th>
<th>Ca</th>
<th>Na</th>
<th>$^{[3]}B(1)$</th>
<th>$^{[4]}B(2)$</th>
<th>$^{[4]}B(3)$</th>
<th>$^{[4]}B(4)$</th>
<th>$^{[4]}B(5)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_Q$</td>
<td>η</td>
<td>$C_Q$</td>
<td>η</td>
<td>$C_Q$</td>
<td>η</td>
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<td>η</td>
</tr>
<tr>
<td>None</td>
<td>1.35</td>
<td>0.52</td>
<td>1.18</td>
<td>0.85</td>
<td>-0.37</td>
<td>0.39</td>
<td>2.51</td>
</tr>
<tr>
<td>1</td>
<td>3.35</td>
<td>0.41</td>
<td>-1.54</td>
<td>0.76</td>
<td>-0.32</td>
<td>0.84</td>
<td>2.49</td>
</tr>
<tr>
<td>4</td>
<td>1.35</td>
<td>0.52</td>
<td>2.42</td>
<td>0.45</td>
<td>-0.36</td>
<td>0.34</td>
<td>2.51</td>
</tr>
<tr>
<td>3</td>
<td>1.42</td>
<td>0.56</td>
<td>-4.78</td>
<td>0.37</td>
<td>-0.43</td>
<td>0.51</td>
<td>2.50</td>
</tr>
<tr>
<td>3, 2</td>
<td>3.66</td>
<td>0.23</td>
<td>-4.76</td>
<td>0.37</td>
<td>-0.36</td>
<td>0.48</td>
<td>2.48</td>
</tr>
<tr>
<td>1, 5</td>
<td>3.38</td>
<td>0.40</td>
<td>2.16</td>
<td>0.79</td>
<td>-0.28</td>
<td>0.60</td>
<td>2.47</td>
</tr>
<tr>
<td>1, 5, 2</td>
<td>-3.91</td>
<td>0.46</td>
<td>2.16</td>
<td>0.79</td>
<td>-0.25</td>
<td>0.85</td>
<td>2.47</td>
</tr>
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<td>1, 5, 2, 3</td>
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<td>0.42</td>
<td>2.82</td>
<td>0.45</td>
<td>0.29</td>
<td>0.81</td>
<td>2.45</td>
</tr>
<tr>
<td>1, 5, 4</td>
<td>-3.91</td>
<td>0.47</td>
<td>5.49</td>
<td>0.31</td>
<td>0.25</td>
<td>0.96</td>
<td>2.45</td>
</tr>
<tr>
<td>1, 2, 3, 4, 5</td>
<td>-3.79</td>
<td>0.43</td>
<td>-2.62</td>
<td>0.59</td>
<td>0.32</td>
<td>0.65</td>
<td>2.42</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Index of water molecule removed in the calculation.
[4]B(1), [3]B(2), [4]B(3), [4]B(4) and [3]B(5) sites in ulexite are 0.00485, 0.1119, 0.00078, −0.00115 and 0.0538, respectively. The large $\Delta n_p$ values correspond to the [3]B sites, and the calculated $\Delta n_p$ values can qualitatively explain the signs as well as the magnitudes of $C_Q$ for [3]B and [4]B in ulexite. Similarly, the calculated $\Delta n_p$ value of 0.0005 for [6]Na in ulexite corresponds well to its small experimental $C_Q$ value (Fig. 2b and Table 1). In comparison with [4]B sites, the large positive $C_Q$ values of the [3]B sites are due to deficiency in the negative charge in $p_z$ relative to the $\sigma$-bonding $p_x$ and $p_y$ orbitals. As the $B_p$ orbital is not full (eqn (3)) it gives rise to weak $B_p\pi$ bonding.

Theoretical calculations also provide information about the orientation of the EFG tensors at the B sites, which can assist in structural interpretations of experimental QI parameters that are not available from powder NMR spectra. The orientations of the EFG tensor elements at each B site in the pentaborate FBB are illustrated by Fig. 1. The unique EFG element $V_{zz}$ at the two BO$_3$ sites ([3]B(2) and [3]B(5)) is approximately perpendicular to the trigonal plane. Such an orientation of $V_{zz}$ and values close to 0 for $\eta$, which are common for all BO$_3$ units, are caused by $sp^3$ hybridization. Fig. 1 also shows that $V_{xx}$ and $V_{yy}$ at the [4]B sites lie between the B-O bonds in the BO$_3$ plane.

Hansen et al. noted that interpretation of the EFG tensor orientation for the BO$_3$ sites is less straightforward, because the three tensor elements are often oriented between the B-O bonds of the BO$_3$ tetrahedra due to the character of $sp^3$ hybridization at the [4]B sites (Fig. 1). The calculated $V_{zz}$ at [4]B(3) in ulexite is approximately parallel to the shortest B-O bond (1.449 Å) and has a negative sign for $C_Q$, indicating that $p_z$ with the highest electron density distribution is along this bond. Similarly, the smallest EFG component, $V_{xx}$, corresponds to the longest B-O bond (1.496 Å) at the [4]B(4). The EFG tensor components for [4]B(1), where the four B-O bond distances are similar, do not coincide with any of the B-O bonds.

The calculated total charge inside the spheres around B atoms at the [4]B sites in ulexite is $−2.88$ eV, in comparison with $2.99$ eV at the [3]B sites, and the calculated valence densities at the former are $−0.2$ eV higher than those at the latter. The larger total charges at the [3]B sites may be caused by their shorter B-O bonds, such that more charge from neighboring O enters the B atomic sphere through B-O bonding. The shorter B-O bond distances for [3]B also lead to stronger antibonding and thus more unoccupied orbitals, less interstitial charge and lower valence density around the [3]B atomic sphere.

The B atoms in each pentaborate FBB in ulexite are closely linked, resulting in stronger intraunit interactions within an FBB than interunit interactions between FBBs. In particular, the B $2p_x$ orbital is oriented toward open space without any neighboring atoms. This orientation is obviously responsible for the insensitivity of the B $2p_x$ orbital (and $C_Q$) at the [3]B sites to neighboring atoms and local structural environments in general. The same is true for the B $2p_y$ orbitals and the $C_Q$ values at the [4]B sites, which always point to atoms within the FBB.

### 3.4. DOS calculations of EFG contributions

To further examine the insensitivity of EFG at the B sites as well as the reasons for the large differences between QI parameters for [3]B and [4]B in ulexite, the sources contributing to EFG have been investigated through theoretical analysis of DOS and the electronic charge distribution. Our DOS calculations show the energy windows that may contribute to EFG: $−\infty$ up to −3.6 (core), −3.6 to −3.5 (Na-2s), −2.8 to −2.6 (Ca-3s), −1.5 to −1.45 (Na-2p), −1.45 to −1.1 (Ca-3p and O-2s), −0.7 to −0.45 (roughly B-2s), −0.45 to Fermi energy ($E_F$) (B-2p, interacting with Na-3s, Ca-4s, O-2p and H-1s). The calculated peaks of Na-2s and Na-2p, Ca-3s are narrow, but the Ca-3p peak is much broader owing to strong hybridization between Ca-3p and O-2s. O-2s does not interact significantly with Na-2s, Na-2p or Ca-3s.

After projecting the EFG at all different energy windows into the same principal axis system, the EFG contributions from different energy windows are obtained and are summarized in Table 6. These data clearly show that there are no EFG contributions to the B sites from the three deepest states (Na-2s, Na-2p and Ca-3s). Therefore, contributions from the energy window below $−1.46$ Ry can be ignored. The interesting region starts only from $−1.46$ to $−1.1$ Ry (i.e., Ca-3p/O-2s), and the most important energy window contributing to EFG at the B sites ranges from $−1.1$ Ry to the $E_F$ of 0.033 Ry, which is a strongly broadened band containing all valence electrons such as B-2s, B-2p, Na-3s, Ca-3p, Ca-4s, O-2p and H-1s (Fig. 4a-d).

Table 6 also shows that the magnitude of the EFG contributions from the energy windows mentioned above to the [3]B sites is several times larger than that to [4]B. The contributions to EFG at [4]B from different states have opposite signs which results in a small total EFG. This is different...
from $[3]B$ where the signs of the individual contributions are the same, resulting in a large total EFG (Table 6). Another notable difference between $[4]B$ and $[3]B$ is that the Ca-3p/O-2s region contributes little to the EFG at $[4]B$ but makes an important contribution at $[3]B$ (Table 6). This non-zero contribution from Ca-3p/O-2s is surprising because there is no B orbital involved in this band. This contribution may arise from the indirect interaction between the Ca–O bond and B ‘in the way’: one or more of such bond configurations lead to non-spherical electron distributions and thus a significant EFG contribution to $[3]B$. Clearly, the small EFG at the $[4]B$ sites (B(1), B(3), B(4)) relative to those at the $[3]B$ sites (B(2) and B(5)) in ulexite are caused by multiple factors.

It is also interesting to note that there are differences between the total EFG calculated and the EFG inside the Muffin-Tin sphere at the B sites (Tables 1 and 6). These differences may be caused by the ‘lattice’ contribution (i.e., from outside the Muffin-Tin spheres). It is not surprising that the ‘lattice’ contribution to EFG is large for B, because the lighter the element, the larger the lattice EFG contribution. Table 6 also suggests that interaction between B-2s and O-2p (Fig. 4a and d) distorts B-2s (−0.6 to −0.5 Ry) from spherical symmetry, thus resulting in further anisotropic local electronic distribution and another source of contribution to EFG, i.e., both p-p and s-s contributions.

4. Conclusions

High resolution solid-state NMR experiments at 14 and 21 T provide accurate $^{11}B$ and $^{23}Na$ NMR parameters for the pentaborate mineral ulexite. The ulexite structure has been optimized using DFT calculations, resulting in better agreement with experimental $^{11}B$ QI parameters. More reasonable H–O bond distances indicate stronger hydrogen bonds than suggested by a previous XRD study. DFT calculations are used to determine the orientations of the EFG tensors at the B sites in ulexite.

The EFG is shown to arise from the anisotropic electron distribution and the variation in charge density inside the B atomic spheres at $[3]B$ and $[4]B$ are related to the differing B–O bond distances. The strong intraunit interactions within each FBB compared with interunit interactions between FBBs is a major reason for the small variation in EFG at different B sites in borates, i.e., the insensitivity of $C_Q$ and $\eta$ at the B sites in borates to local structural environments. DOS calculations show that the EFGs at the B sites in ulexite arise mainly from the valence states (B 2s and 2p, Ca 4s, Na 3s, O 2p) and that the lattice EFG contribution is also significant, however, the EFG contributions at $[3]B$ and $[4]B$ sites are different. Combining high-resolution NMR experiments with theoretical modeling is a powerful tool for probing the subtle geometric and electronic structural characters for borates.

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