Towards homonuclear *J* solid-state NMR correlation experiments for half-integer quadrupolar nuclei: experimental and simulated ¹¹B MAS spin-echo dephasing and calculated ² J_{BB} coupling constants for lithium diborate

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Supporting Information

S1. Additional Experimental Results



Fig. S1 (a) Powder X-ray diffraction pattern obtained for polycrystalline lithium diborate with 5% ¹¹B isotopic abundance, as recorded on a Panalytical Xpert Pro diffractometer with Cu K_{α} radiation, scanned at 0.24 degrees/min. The experimental pattern is compared with a literature pattern for Li₂B₄O₇ (diomignite).¹ (b) Raman spectra of the samples of polycrystalline lithium diborate with different degrees of ¹¹B isotopic abundance. Spectra were recorded using a JASCO NRS-3100 microRaman spectrophotometer and a Torsana Starbright 785 nm SLM diode laser. The displayed plots each correspond to a sum over three runs.

Normalised spin-echo dephasing curves for the polycrystalline lithium diborate samples with 25% and 100% ¹¹B isotopic abundance, recorded at 20 kHz MAS are shown in Fig. S2, together with best fits (see Table S1) to a mono-exponential function (eqn (S1)) and a bi-exponential function (eqn (S2))

$$S(\tau) = A e^{-\tau/T_2'} \tag{S1}$$

$$S(\tau) = A(pe^{-\tau/T'_{2a}} + (1-p)e^{-\tau/T'_{2b}})$$
(S2)

It is evident that the data is not perfectly fitted by a mono-exponential decay curve, in particular for the B4 site. By contrast, the bi-exponential function results in much improved fits to the experimental data.



Fig. S2 ¹¹B (14.1 T) MAS (20 kHz) spin-echo dephasing curves for a sample of polycrystalline lithium diborate with (a, b) 25% and (c, d) 100% ¹¹B isotopic abundance. Best fits (solid blue (B3) and green (B4) lines) to a mono-exponential function (eqn (S1)) and a bi-exponential function (eqn (S2)) are shown in (a, c) and (b, d), respectively (see Table S1). Note the five times longer maximum spin-echo duration, τ , for the (a, b) 25% case as compared to the (c, d) 100% case.

Site	abundance	Fit Type	Α	р	T'_{2a}/ms	T'_{2b} / ms	$T'_{2[a+b]}/ms$
B3	25%	bi-exp	0.98 ± 0.01	0.11 ± 0.02	7.8 ± 2.1	51.8±1.6	47.0
B3	25%	mono-exp	0.97 ± 0.01		$44.7{\pm}1.1$		
B4	25%	bi-exp	1.03 ± 0.01	0.35 ± 0.02	1.6 ± 0.1	19.0±0.7	12.9
B4	25%	mono-exp	0.93 ± 0.02		10.9 ± 0.9		
B3	100%	bi-exp	1.01 ± 0.01	0.33 ± 0.17	$3.6{\pm}1.4$	11.9±1.9	9.2
B3	100%	mono-exp	0.99 ± 0.01	-	8.5±0.3	-	
B4	100%	bi-exp	1.07 ± 0.02	0.95 ± 0.06	2.0 ± 0.2	16.4±25.8	2.7
B4	100%	mono-exp	1.06 ± 0.02	-	2.1 ± 0.1	-	

Table S1 Fit parameters of spin-echo dephasing curves for polycrystalline lithium diborate at20 kHz MAS presented in Fig. S2

It is also necessary to consider the effect of the *rf* amplitude for the spin-echo 180° pulse. For NMR of half-integer quadrupolar nuclei, different nutation frequencies are observed depending on the strength of the *rf* nutation frequency, ω_1 , as compared to the magnitude of the quadrupolar interaction. In the "soft" pulse limit where $\omega_1 \ll \omega_Q$, only the central transition is affected and nutation is I + 1/2 times faster than the other limiting case, the "hard" pulse limit where $\omega_1 \gg \omega_Q$, with a range of behaviour being observed between these two limits.² For lithium diborate, the B3 site (larger C_Q) nutates faster than the B4 site (smaller C_Q), i.e., for a fixed *rf* amplitude, a null corresponding to a 180° pulse is observed at a shorter pulse duration for the B3 as compared to the B4 site – this is illustrated in Fig. S3.



Fig. S3 Nutation behaviour for the B4 (green, $C_Q = 0.5$ MHz) and B3 (blue, $C_Q = 2.60$ MHz) sites in polycrystalline lithium diborate. Specifically, spectra are plotted as a function of the pulse length for a one-pulse experiment with a fixed *rf* amplitude, corresponding to a first zero crossing at 4.2 µs and 2.6 µs for the B4 and B3 sites, respectively.

The spin-echo dephasing curves presented in Figs. 3 & 4 of the main text were obtained for a central-transition selective 180° pulse of duration 25 µs as optimised on the B3 site. As shown in Fig. S4, similar behaviour was observed for the case of a central-transition selective 180° pulse of duration 25 µs, but optimised on the B4 site (i.e., with a different ω_1). In this context, it is to be noted that phase cycling selects a change of coherence order $\Delta p = \pm 2$ for the 180° pulse, i.e., transfer from p = +1 to p = -1. Thus, an imperfect 180° pulse should only affect the overall intensity and not the observed rate of coherence dephasing.



Fig. S4¹¹B (14.1 T) MAS (20 kHz) spin-echo (90° – $\tau/2 - 180° - \tau/2 - t_{acq}$) dephasing curves with best fits (see Table S2) for the B4 (circles) and B3 (squares) sites in a sample of polycrystalline lithium diborate with 100% ¹¹B isotopic abundance. Data was recorded for *rf* amplitudes corresponding to a central-transition selective 180° pulse of duration 25 µs as calibrated for the B3 site (filled symbols, as in main text Figs.) or the B4 site (open symbols).

Table S	52 Fit parameters	of spin-echo	dephasing c	curves for p	olycrystalline	lithium	diborate	at
100% 1	¹ B isotopic abund	lance and 20 l	kHz MAS p	resented in	Fig. S4.			

Site	Remarks	Α	р	T'_{2a} / ms	T'_{2b}/ms	$T'_{2[a+b]}/ms$
B3	B3 opt. ^a	1.02 ± 0.01	0.20 ± 0.05	2.2±0.7	12.1±0.7	10.1
B3	B4 opt. ^a	1.01 ± 0.01	0.33 ± 0.17	3.6±1.4	11.9±1.9	9.2
B4	B3 opt. ^a	1.07 ± 0.02	0.90 ± 0.08	1.9 ± 0.2	12.4±9.9	3.0
B4	B4 opt. ^b	1.06 ± 0.02		2.1±0.1	-	

^{*a*} Fit to the bi-exponential function in eqn (S2), with $T'_{2[a+b]}$ defined in eqn (4). ^{*b*} Fit to the monoexponential function in eqn (S1)

Fig. S5 compares spin-echo dephasing curves obtained for different *rf* amplitudes corresponding to 180° pulse durations (for the B3 site) of 4.2 μ s and 25 μ s. Faster dephasing is observed for the higher *rf* nutation frequency (corresponding to the shorter 180° pulse duration), with the effect being more pronounced for the B4 site (smaller *C*_Q).



Fig. S5 ¹¹B (14.1 T) MAS (20 kHz) spin-echo dephasing curves for the (a) B3 and (b) B4 site for a sample of polycrystalline lithium diborate with 100% ¹¹B isotopic abundance. Data was recorded for *rf* amplitudes corresponding to 180° pulse durations (as calibrated for the B3 site) of 4.2 μ s ("hard", orange and red) and 25 μ s ("soft", blue and green). Solid lines correspond to best fits to a mono or bi-exponential function (eqn (S1, S2)) – see Table S3. The data for a 25 μ s 180° pulse duration are repeated from Fig. 4d in the main text.

Table S3 Fit parameters of spin-echo dephasing curves for polycrystalline lithium diborate at100 % 11 B isotopic abundance and 20 kHz MAS presented in Fig. S5.

Site	180° pulse	A	р	T'_{2a} / ms	T'_{2b} / ms	$T'_{2[a+b]}/ms$
B3	$25 \ \mu s^a$	1.02 ± 0.01	0.20 ± 0.05	2.2±0.7	12.1±0.7	10.1
B3	4.2 μs^a	1.29 ± 0.22	0.31 ± 0.12	0.1 ± 0.0	9.5±0.3	6.6
B4	$25 \ \mu s^a$	1.07 ± 0.02	0.90 ± 0.08	1.9 ± 0.2	12.4±9.9	3.0
B4	4.2 μs^b	1.10 ± 0.22	-	1.3±0.1	-	

^{*a*} Fit to the bi-exponential function in eqn (S2), with $T'_{2[a+b]}$ defined in eqn (4). ^{*b*} Fit to the monoexponential function in eqn (S1)

Table S4 Correlation coefficients^a between pairs of extracted parameters for the fits to ¹¹BMAS NMR spin-echo dephasing curves presented in Tables 3, 4, S1, S2 & S3.

Table	Site	¹¹ B	MAS /kHz	Remarks	А, р	A, T'_{2a}	A, T'_{2b}	p, T'_{2a}	p, T'_{2b}	T^\prime_{2a} , T^\prime_{2b}
3	B3	5%	20		-0.70	-0.15	-0.74	-0.37	0.23	0.37
3	B3	25%	20		0.18	-0.22	-0.49	-0.92	-0.87	0.76
3	B3	100%	20		0.27	-0.29	-0.59	-0.93	-0.89	0.79
3	B4	5%	20		-0.05	-0.18	-0.56	-0.79	-0.64	0.58
3	B4	25%	20		0.08	-0.24	-0.65	-0.85	-0.70	0.65
3	B4	100%	20		0.35	-0.28	-0.60	-0.92	-0.90	0.76
4	В3	100%	5		-0.56	-0.72	-0.49	0.97	0.97	0.91
4	B3	100%	10		-0.42	-0.55	-0.37	0.97	0.98	0.92
4	B3	100%	16		0.39	-0.34	-0.53	-0.98	-0.97	0.91
4	B3	100%	20		0.27	-0.29	-0.59	-0.93	-0.89	0.79
4	B4	100%	5		-0.50	-0.77	-0.40	0.90	0.94	0.78
4	B4	100%	10		-0.41	-0.63	-0.33	0.92	0.94	0.80
4	B4	100%	16		-0.34	-0.60	-0.26	0.89	0.92	0.76
4	B4	100%	20		0.35	-0.28	-0.60	-0.92	-0.90	0.76
S1	В3	25%	20	(mono)	-	-0.46	-	-	-	-
S1	B4	25%	20	(mono)	-	-0.53	-	-	-	-
S1	B3	100%	20	(mono)	-	-0.55	-	-	-	-
S1	B4	100%	20	(mono)	-	-0.66	-	-	-	-
S2	В3	100%	20	B4 opt.	-0.36	-0.53	-0.32	0.96	0.97	0.87
S2	B4	100%	20	B4 opt.		-0.65	-		-	-
S 3	B3	100%	20	4.2 μs	0.99	-0.96	-0.21	-0.95	-0.17	0.29
S 3	B4	100%	20	4.2 μs, mono	-	-0.70	-	-	-	-
^a See Re	f. ³ for a	a discussio	on of the use of	correlation coeff	ficients in s	pin-echo fits.				

S2. Additional Simulation Details and Results

Evolution under free precession Hamiltonians does not mix coherence orders and the associated propagator matrix representations are block-diagonal. Hence experiments involving only free precession can be numerically simulated efficiently by taking advantage of this block structure. In general, however, *rf* pulses mix coherence orders and the associated propagator matrices are not block-diagonal (with respect to the irradiated spins). This makes simulations involving RF much slower than those involving only free precession. An important exception to this "breaking" of the block structure occurs for ideal π pulses. Such pulses only exchange coherences between corresponding elements of blocks of coherence order *n* and *-n* in the density matrix. Hence a simple spin-echo sequence can be simulated without "breaking" the free precession block structure, provided that the effect of the inversion pulse can be implemented by the exchange of the related coherences, and application of phase factors which depend on the phase of the pulse.

Such an exchange operator has been implemented in the general simulation program, pNMRsim. The propagator matrix for an ideal π inversion with *x* phase is stored in a sparse representation (one non-zero element per row of the matrix). The phase of these elements is adjusted for the required phase by an appropriate rotation about *z*.⁴⁻⁵ The density matrix after the inversion is then evaluated by scanning over the elements of the initial density matrix and determining which element of the new density matrix it is transformed into and with what phase factor. The full source code is available from the pNMRsim web pages (file InversionGenerator.cc in the libcmatrix library).⁶



Fig. S6 Simulated (14.1 T, 20 kHz MAS) spin-echo dephasing curves for a pair of dipolarcoupled ¹¹B nuclei with the same isotropic chemical shift, where C_Q equals 0.5 MHz (B4 site, top) or 2.6 MHz (B3 site, bottom). Simulations were performed for $d_{jk} = -500$ Hz (red), -1kHz (green), or -2 kHz (blue) for evolution under second-order quadrupolar interactions (η_Q = 0), where the quadrupolar tensors for the two spins were co-linear and perpendicular to the dipolar tensor (i.e., the internuclear vector).



Fig. S7 Simulated (14.1 T, 20 kHz MAS) spin-echo (90° – $\tau/2 - 180° - \tau/2 - t_{acq}$) dephasing curves for a pair of dipolar-coupled ($|d_{jk}| = 500$ Hz) ¹¹B nuclei with the same isotropic chemical shift and C_Q equal to 2.6 MHz and η_Q equal to 0, as in the case of the B3 site in lithium diborate. Simulations are presented for: first-order quadrupolar interaction including the 180° pulse (yellow); first-order quadrupolar interaction omitting the 180° pulse (blue); second-order quadrupolar interaction including the 180° pulse (red); second-order quadrupolar interaction omitting the 180° pulse (green). The principal axes systems of the two quadrupolar tensors and the dipolar interaction are perpendicular to each other. Other simulation details are as given in the caption for Fig. 5 in the main text.



Fig. S8 The dependence of NMR spin-echo dephasing on the MAS frequency, as simulated for a pair of dipolar-coupled $(|d_{jk}| = 500 \text{ Hz})^{11}\text{B}$ nuclei with the same isotropic chemical shift at 14.1 T. Four different values of quadrupolar coupling strength, $\omega_Q/2\pi = 3C_Q/[4I (2I - 1)]$ (equal to $C_Q/4$ for I = 3/2) are considered ($\eta_Q = 0$). The degree of spin-echo dephasing is determined as the simulated spin-echo intensity at $\tau \sim 0.5$ ms. The plots correspond to (a) first-order quadrupolar interaction, parallel quadrupolar tensors; (b) second-order quadrupolar interaction, parallel quadrupolar tensors; (c) first-order quadrupolar interaction, perpendicular quadrupolar tensors; (d) second-order quadrupolar interaction, perpendicular tensors. Other simulation details are as given in the caption for Fig. 5.

S3. Representative pNMRsim Input File

```
spinsys {
           nuclei 11B 11B
           proton_frequency 600e6
           shift 1 $1
           shift 2 $1
           quadrupole 1 1 $2 0 0 0 0
           quadrupole 2 1 $2 0 0 90 90
           dipole 1 2 -$3 0 90 0
}
par {
                             $4
           spin_rate
           start_operator
                             Inx
           detect_operator
                            Inc
                             $4
           sw
           crystal_file
                            3zcw30
           maxdt
                             1
                             1
           np
           variable rotor_period 1e6/$4
           variable twentymillisecondofrotorperiods $4/50
           variable rotor_count {0:$twentymillisecondofrotorperiods}
           delay $rotor_period
           store delay
}
pulseq {
           prop delay $rotor_count
           pulse180 x
           prop delay $rotor_count
           acq
}
proc {
           save $(name)_cs-$1_cq-$2_d-$3_m-$4.fid -simpson
}
```

Note that the simulations did not include the second-order effects due to cross-terms between the quadrupole coupling and the dipolar/J couplings (command line flag: -enable:classicQ). These terms are not expected to have a significant impact (see section S4) and their inclusion slows down the simulation significantly.

S4 Second-Order Cross Terms

This section estimates the size of second-order cross terms – the analysis is based on Ref.⁷.

Quadrupolar/Dipolar Cross Terms

The effect of this cross term on a spin I from a remote spin S at distance *r* is proportional to $(\gamma_I \omega_Q^{PAS}(S)/r^{-3} B_0)$. By comparison with examples in Ref. ⁷ (e.g., ²³Na NMR of NaBrO₃ at 9.4 T in Figure 17), the cross terms can be estimated to be of magnitude (assuming a B-B distance of 2.5 Å)

Site of nucleus	remote nucleus	cross term splitting
B4	B3 ¹¹ B	~10.6 Hz
B4	B3 ¹⁰ B	~11.0 Hz
B3	B4 ¹¹ B	~2.1 Hz
B3	B4 ¹¹ B	~2.2 Hz

Note that the higher quadrupole moment of ${}^{10}B$ is countered by the effect of spin quantum number in ω_0^{PAS} .

For cross terms to ${}^{6}\text{Li}/{}^{7}\text{Li}$, typical C_Q values are 0.02 and 0.6 MHz, respectively, and nearest B-Li distances are 2.7 Å, giving cross terms no bigger than 3-4 Hz at most.

Quadrupolar/CSA Cross Terms

The cross term between the quadrupolar and CSA interactions on the same spin is proportional to $\omega_Q^{PAS} \delta_{CS}$. By comparison with the case of Co(acac)₃ (see Fig. 25 of Ref. ⁷), and given GIPAW (CASTEP) calculated δ_{CSA} values of ~8 ppm for both B3 and B4 (see below), maximum cross term splittings would be ~8 Hz (B3) and ~1.5 Hz (B4).

S5 J Coupling Calculations

Geometry optimisations used ultrasoft-pseudopotentials generated on-the-fly by the CASTEP code. The construction parameters are:

Atom	Core-	Local	$r_{\rm loc}$	<i>r</i> _{nonloc}	r _{aug}	pseudopotential	PAW projectors
	states	channel	(a.u.)	(a.u.)	(a.u.)	projectors	
Li		р	1.2	1.2	0.84	1×1s, 2×2s	1×1s, 2×2s
В	1s	d	1.4	1.4	1.0	2×2s, 2×2p	2×2s, 2×2p
0	1s	d	1.0	1.3	0.7	2×2s, 2×2p	2×2s, 2×2p

Definitions:

 $r_{\rm loc}$ is the pseudisation radius for the local component of the pseudopotential

 r_{nonloc} is the pseudisation radius for the non-local components of the pseudopotential

 r_{aug} is the pseudisation radius for the charge augmentation functions.

The corresponding CASTEP on-the-fly strings used to generate these potentials are

```
Li 1|1.2|12|14|16|10U:20UU(qc=5.5)
```

- B 2|1.4|1.4|1.0|3|6|8|20:21
- 0 2 1.0 1.3 0.7 13 16 18 20:21 (qc=7)

The calculation of NMR parameters used norm-conserving potentials constructed using the following parameters.

Atom	Core-	Local	r _{nonloc}	pseudopotential	PAW projectors
	states	channel	(a.u.)	projectors	
Li	1s	S	2.0	1×2p	N/A
В	1s	р	1.85	1×2s	1×2s, 1×2p, 1×3s,
					1×3p
0	1s	р	1.3	1×2s	1×2s, 1×2p, 1×3s,
					1×3p

Ultrasoft potentials are considered state-of-the-art – due to their computational efficiency, but also because they provide an easy route to include semi-core states into the

calculation. At the present time, it is possible to compute chemical shifts and electric field gradients with ultrasoft potentials – but calculations of *J* couplings are limited to only norm-conserving potentials. To check the effect of the Li 1s states on the computed B NMR parameters, we also computed the B electric-field gradient and chemical shifts using the ultrasoft potentials given above. The results were not affected and we therefore make the assumption that the Li 1s states will not play a role in the ²*J*_{BB} couplings.

Conventions

The calculations provide the full *J* tensor. The principal components can be obtained from the symmetric part of the *J* tensor, labelled according to the Haeberlen convention: $|j_3 - j_{iso}| \ge |j_1 - j_{iso}| \ge |j_2 - j_{iso}|$

The isotropic *J* coupling is given by:

$$j_{\rm iso} = (1/3) (j_1 + j_2 + j_3)$$
 (S3)

The *J* anisotropy is defined as:

$$\Delta_j = j_3 - [(j_1 + j_2) / 2] \tag{S4}$$

In the following Tables, it is the *J* anisotropy as defined in eqn (S4) that is specified. Note the difference compared to the reduced anisotropy, δj , that is defined in analogy to that commonly used to specify the chemical shift anisotropy:

$$\delta_j = j_3 - j_{iso} = (2/3) j_3 - (1/3) (j_1 + j_2) = (2/3) \Delta_j$$
(S5)

The *J* asymmetry is defined as:

$$\eta_j = (j_2 - j_1) / (j_3 - j_{iso})$$
(S6)

The symmetric part of the J tensor can be decomposed into isotropic and anisotropic terms:

$$\boldsymbol{J} = \boldsymbol{J}_{\rm iso} + \boldsymbol{J}_{\rm aniso} \tag{S7}$$

In the principal axes system,

$$\boldsymbol{J}_{\text{aniso}} = \begin{pmatrix} j_1 - j_{iso} & 0 & 0\\ 0 & j_2 - j_{iso} & 0\\ 0 & 0 & j_3 - j_{iso} \end{pmatrix}$$
(S8)

Similarly the dipolar coupling can be written in its principal axis system as:

$$\boldsymbol{D} = \begin{pmatrix} -d_{jk}/2 & 0 & 0\\ 0 & -d_{jk}/2 & 0\\ 0 & 0 & +d_{jk} \end{pmatrix}$$
(S9)

where d_{jk} is the dipolar coupling constant (in Hz, as defined in eqn (1) of the main text):

$$d_{jk} = -\frac{\mu_0 \gamma_j \gamma_k \hbar}{4\pi r_{jk}^3} / 2\pi$$
(S10)

NB: The dipolar coupling is a traceless tensor, i.e., it only has an anisotropic part. The asymmetry equals zero, i.e., there is axial symmetry around the internuclear vector that hence defines the principal axes system.

The Hamiltonian for a pair of dipolar and J coupled nuclei is:

$$\underline{\mathbf{H}} = \underline{\mathbf{I}}_{\mathrm{M}} \cdot \boldsymbol{J}_{\mathrm{iso}} \cdot \underline{\mathbf{I}}_{\mathrm{N}} + 2 \, \underline{\mathbf{I}}_{\mathrm{M}} \cdot (\mathbf{D} + \boldsymbol{J}_{\mathrm{aniso}}/2) \cdot \underline{\mathbf{I}}_{\mathrm{N}}$$
(S11)

Consider the case where *J* is axially symmetric ($\eta = 0$) and the *J* and *D* tensors share the same principal axes system:

$$\mathbf{D} + \mathbf{J}_{\text{aniso}}/2 = \begin{pmatrix} (-d_{jk} + j_1 - j_{iso})/2 & 0 & 0\\ 0 & (-d_{jk} + j_2 - j_{iso})/2 & 0\\ 0 & 0 & + d_{jk} + (j_3 - j_{iso})/2 \end{pmatrix}$$
(S12)

i.e.,

$$\mathbf{D} + \mathbf{J}_{\text{aniso}}/2 = \begin{pmatrix} (-d_{jk} - (\Delta j/3))/2 & 0 & 0\\ 0 & (-d_{jk} - (\Delta j/3))/2 & 0\\ 0 & 0 & + d_{jk} + (\Delta j/3) \end{pmatrix}$$
(S13)

Since, for $j_1 = j_2$, $j_1 - j_{iso} = j_2 - j_{iso} = j_1 - (1/3)(j_1 + j_2 + j_3) = j_1 - (1/3)(j_1 + j_1 + j_3) = (1/3)(j_1 - j_3) = -(1/3) \Delta_j$, while $j_3 - j_{iso} = j_3 - (1/3)(j_1 + j_1 + j_3) = (2/3)(j_3 - j_1) = (2/3) \Delta_j$. For this case, **the effective coupling equals** $d_{jk} + \Delta_j/3$. (Note that if d_{jk} is defined as a positive quantity, e.g., as in Refs.⁸⁻¹⁰, the effective coupling is $d_{jk} - \Delta_j/3$.)

For the general case, where the *J* and *D* tensors do not share the same principal axes system, we also define the angle α , as that between the internuclear vector connecting atoms A and B, and the principal direction corresponding to j_3 , where $90^\circ \ge \alpha \ge 0^\circ$.

The four Ramsey contributions to the isotropic *J* are labelled FC (Fermi contact); SD (spin dipolar); PARA (paramagnetic orbital); DIA (diamagnetic orbital).

The coupling between atoms A and B can be computed in two independent ways, considering either A or B as the perturbation. We present both as a measure of the numerical fidelity of the calculations.

NB: The stated *J* couplings are determined from the calculated reduced *J* coupling *K* (with units kg m⁻² s⁻² A⁻²) through the relation $J_{jk} = K_{jk} \gamma_j \gamma_k \hbar/2\pi$, where γ_j and γ_k are the respective gyromagnetic ratios of the coupled nuclei.

Lithium diborate (Li₂O.2B₂O₃, i.e., Li₂B₄O₇)

B3:	$C_{Q} = 3.20 \text{ MHz}$	$\eta_Q = 0.19$
B4:	$C_Q = -0.67 \text{ MHz}$	$\eta_Q = 0.52$

The calculations provide the full shielding tensor. The principal components can be obtained from the symmetric part of the shielding tensor, labelled according to the Haeberlen convention: $|\sigma_{zz} - \sigma_{iso}| \ge |\sigma_{xx} - \sigma_{iso}| \ge |\sigma_{yy} - \sigma_{iso}|$. Δ_{CSA} , δ_{CSA} and η_{CSA} are then defined as for the corresponding *J* tensor in eqn (S4) to (S6) above.

	σ_{xx}	σ_{yy}	σ _{zz}	$\Delta_{\rm CSA}$	δ_{CSA}	η_{CSA}
B3	-88.50	-90.90	-101.01	-11.31	-7.54	0.32
B4	-82.17	-78.84	-68.57	11.94	7.96	0.42

 $\delta_{iso}(B3) - \delta_{iso}(B4) = 16.9 \text{ ppm}$

2.	<i>r</i> (B-B)	∠B-O-B	Isotropic J / Hz					
<i>⁻J</i> _{11В-О-11В}	/ Å	/ °	FC	SD	PARA	DIA	TOTAL	tropy (Hz)
B4-O4-B4	2.36	109	0.00	-0.02	-0.27	0.22	-0.07	-1.83
B4-O2-B3	2.44	116	1.07	-0.04	-0.25	0.17	0.95	1.42
B4-O3-B3	2.49	119	1.30	-0.03	-0.21	0.15	1.20	1.09
B4-O1-B3	2.50	126	2.72	-0.03	-0.16	0.12	2.65	1.09
B3-O2-B4	2.44	116	1.05	-0.04	-0.25	0.17	0.94	1.44
B3-O3-B4	2.49	119	1.29	-0.03	-0.21	0.15	1.20	1.09
B3-O1-B4	2.50	126	2.70	-0.03	-0.16	0.13	2.63	1.07

2	r (B-B)	∠В-О-В	Princi	pal Valu		Anisotropy /		
J 11B-O-11B	/ Å	/ °	j 1	j 2	j 3	$\alpha / ^{\circ}$	η_i	Hz
B4-O4-B4	2.36	109	1.04	0.04	-1.29	2.0	0.82	-1.83
B4-O2-B3	2.44	116	0.20	0.76	1.90	89.6	0.59	1.42
B4-O3-B3	2.49	119	0.65	1.04	1.93	88.8	0.53	1.09
B4-O1-B3	2.50	126	2.13	2.44	3.37	88.6	0.43	1.09
B3-O2-B4	2.44	116	0.17	0.76	1.90	88.4	0.61	1.44
B3-O3-B4	2.49	119	0.67	1.01	1.93	88.8	0.46	1.09
B3-O1-B4	2.50	126	2.12	2.43	3.35	86.9	0.44	1.07

¹ <i>J</i> _{11В-170}	r (B-O)		Isotropic <i>J</i> / Hz							
	/ Å	FC	SD	PARA	DIA	TOTAL	Hz			
B3-O1	1.36	-32.39	-0.09	4.51	-0.25	-28.22	-34.60			
B3-O2	1.37	-23.69	-0.09	4.64	-0.25	-19.39	-34.84			
B3-O3	1.37	-20.50	-0.28	4.34	-0.26	-16.69	-32.82			
B4-O1	1.45	-21.39	-0.15	2.18	-0.26	-19.61	-25.87			
B4-O4	1.45	-11.13	-0.15	2.83	-0.26	-8.71	-28.12			
B4-O3	1.50	-11.23	-0.30	1.65	-0.25	-10.14	-20.72			
B4-02	1.51	-10.42	-0.30	1.78	-0.25	-9.19	-22.07			

¹ /	r (B-O) /	Princi	ipal Values		Anisotropy /		
J 11B-17O	Å	j 1	j ₂	j ₃	$\alpha / ^{\circ}$	η_j	Hz
B3-O1	1.36	-11.05	-22.33	-51.29	3.59	0.49	-34.60
B3-O2	1.37	-2.11	-13.45	-42.62	3.29	0.49	-34.84
B3-O3	1.37	-0.62	-10.89	-38.58	3.16	0.47	-32.82
B4-O1	1.45	-10.52	-11.54	-36.86	5.64	0.05	-25.87
B4-O4	1.45	1.41	-0.08	-27.45	2.29	0.08	-28.12
B4-O3	1.50	-2.61	-3.85	-23.95	5.19	0.09	-20.72
B4-02	1.51	-1.29	-2.38	-23.90	3.27	0.07	-22.07

Lithium Metaborate (LiBO₂)

Lithium metaborate consists of $(BO_2^{-})_n$ chains of three-fold coordinated boron atoms. All B are crystallographically identical and there is a single B-O-B coupling. O1 is bridging, O2 is non-bridging. The structure used was ICSD refcode 37060, and a 2×2×1 supercell was used to compute the *J* couplings.

2.	r (B-B)	∠B-O-B		Anisotropy /				
- J _{11B-O-11B}	/ Å	/ °	FC	SD	PARA	DIA	TOTAL	Hz
B3-O1-B3	2.56	133	3.22	0.00	0.00	0.01	3.23	0.76
² J _{11B-O-11B} B3-O1-B3	r (B-B) / Å 2.56	∠B-O-B / ° 133	Princ <i>j</i> 1 3.75	tipal Valu j₂ 3.57	ıes / Hz <i>j</i> ₃ 2.41	α /° 89.46	η _j 0.23	Anisotropy / Hz –1.23
¹ J _{11B-170}	r (B-O) / Å	FC	lsot SD	ropic J / PARA	Hz DIA	TOTAL	Anisotrop Hz	ру /
B3-O2	1.32	-26.10	-0.36	5.32	-0.19	-21.32	-43	3.24
B3-O1	1.39	-26.46	-0.11	3.26	-0.21	-23.17	-30).54
B3-O1	1.41	-24.04	-0.22	3.26	-0.21	-21.21	-29	9.52

¹ /	r (B-O) /	Princi	Principal Values / Hz							
J 11B-17O	Å	j 1	j 2	jз	$\alpha / ^{\circ}$	η_j	Hz			
B3-O2	1.32	-0.23	-13.59	-50.15	0.42	0.46	-43.24			
B3-O1	1.39	-8.72	-17.26	-43.53	4.72	0.42	-30.54			
B3-O1	1.41	-7.63	-15.11	-40.89	6.58	0.38	-29.52			

Lithium Triborate (LiB₃O₅)

Lithium triborate consists of $B_3O_5^-$ rings with one four-fold coordinated B and two three-fold coordinated B. The structure was taken from ICSD 84617, and a 1×1×2 supercell was used for the calculation of the *J* couplings.

2.	r	(B-B)	∠B-C)-В			Anisotrony				
J 11B-O-11B		/ Å	/ °	,	FC	SE) F	PARA	DIA	TOTAL	/ Hz
B3(a)-O2-B3(I	c)	2.40	1	18	1.35	-0	.04 -	-0.21	0.11	1.21	1.54
B3(a)-O1-B4		2.45	1	119	1.59	-0	.04 -	-0.18	0.13	1.50	1.30
B3(a)-O3-B4		2.47	1	123	2.00	-0	.04 -	-0.14	0.10	1.93	1.25
2		<i>r</i> (В-В) ∠B	-О-В	Prir	ncipal	Value	s / Hz			Anisotropy
J 11B-O-11E	3	/ Ă		/ °	<i>j</i> 1	j	2	j ₃	α/°	n,	/ Hz
B3(a)-O2-B3	3(b)	2.4	0	118	0.5	0 C	.89	2.24	88.8	8 0.38	1.54
B3(a)-O1-B4	4	2.4	6	119	0.8	B 1	25	2.37	86.9	0.43	1.30
B3(a)-O3-B4	4	2.4	.7	123	1.40	5 1	.57	2.76	89.4	0.13	1.25
	r (P C				leatror		⊔,				
¹ Lup 170	/ (Б-С)			isoliop		12		1	Anisotropy	· /
0 11B-17O	/ Å		FC	SE) P	ARA	DIA	TO	ΓAL	Hz	
B3(a)-O3	1.3	35 –	27.26	-0.	15	5.04	-0.2	5 –22	2.62	-36.0	05
B3(a)-O1	1.3	36 –	29.32	-0.	03	4.52	-0.24	4 –25	5.07	-36.7	12
B3(a)-O2	1.4	40 –	23.35	-0.	08	3.62	-0.2	4 –20	0.05	-29.9	93
$^{1}J_{11P}$ 170	r (В-С	ו (כ	Pri	ncipal	Values	s / Hz		10		Anisot	ropy /
- 11B-170	A		İ1		b	İ3		α / \circ	n,	H	Z

- 110-170	A	Ĵ1	Ĵ2	Ĵ3	α / \circ	η_j	Hz
B3(a)-O3	1.35	-4.18	-17.03	-46.65	3.8	0.53	-36.05
B3(a)-O1	1.36	-7.64	-18.41	-49.15	2.7	0.45	-36.12
B3(a)-O2	1.40	-6.17	-13.97	-40.00	3.2	0.39	-29.93

S4 References

- 1. V. T. Adamiv, Y. V. Burak and I. M. Teslyuk, J. Alloys Compd., 2009, 475, 869.
- 2. A. Samoson and E. Lippmaa, *Phys. Rev. B*, 1983, **28**, 6567.
- 3. T. N. Pham, J. M. Griffin, S. Masiero, S. Lena, G. Gottarelli, P. Hodgkinson, C. Fillip and S. P. Brown, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3416.
- 4. R. R. Ernst, G. Bodenhausen and A. Wokaun, "*Principles of Nuclear Magnetic Resonance in One and Two Dimensions*", Clarendon Press, Oxford, 1997.
- 5. P. Hodgkinson and L. Emsley, Prog. Nucl. Magn. Reson. Spectrosc., 2000, 36, 201.
- 6. P. Hodgkinson, "pNMRsim: a general simulation program for large problems in solidstate NMR" URL: <u>http://www.dur.ac.uk/paul.hodgkinson/pNMRsim/</u>.
- 7. S. E. Ashbrook, J. McManus, M. J. Thrippleton and S. Wimperis, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2009, **55**, 160.
- 8. R. K. Harris, K. J. Packer and A. M. Thayer, J. Magn. Reson., 1985, 62, 284.
- 9. S. Kroeker, R. E. Wasylishen and J. V. Hanna, J. Am. Chem. Soc., 1999, 121, 1582.
- 10. J. Vaara, J. Jokisaari, R. E. Wasylishen and D. L. Bryce, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2002, **41**, 233.