

## Supporting information

### **$^{11}\text{B}$ and $^{89}\text{Y}$ solid state MAS NMR spectroscopic investigations of the layered borides $\text{YTB}_4$ ( $T = \text{Mo, W, Re}$ )**

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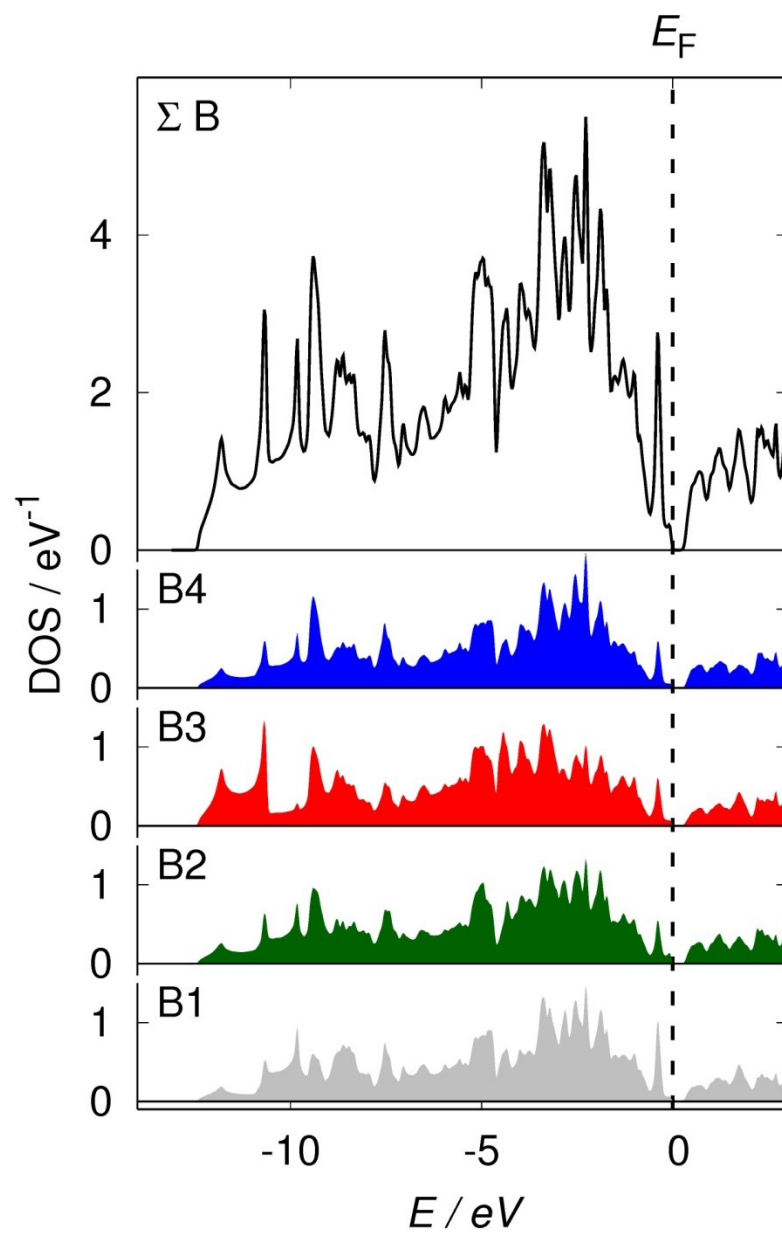
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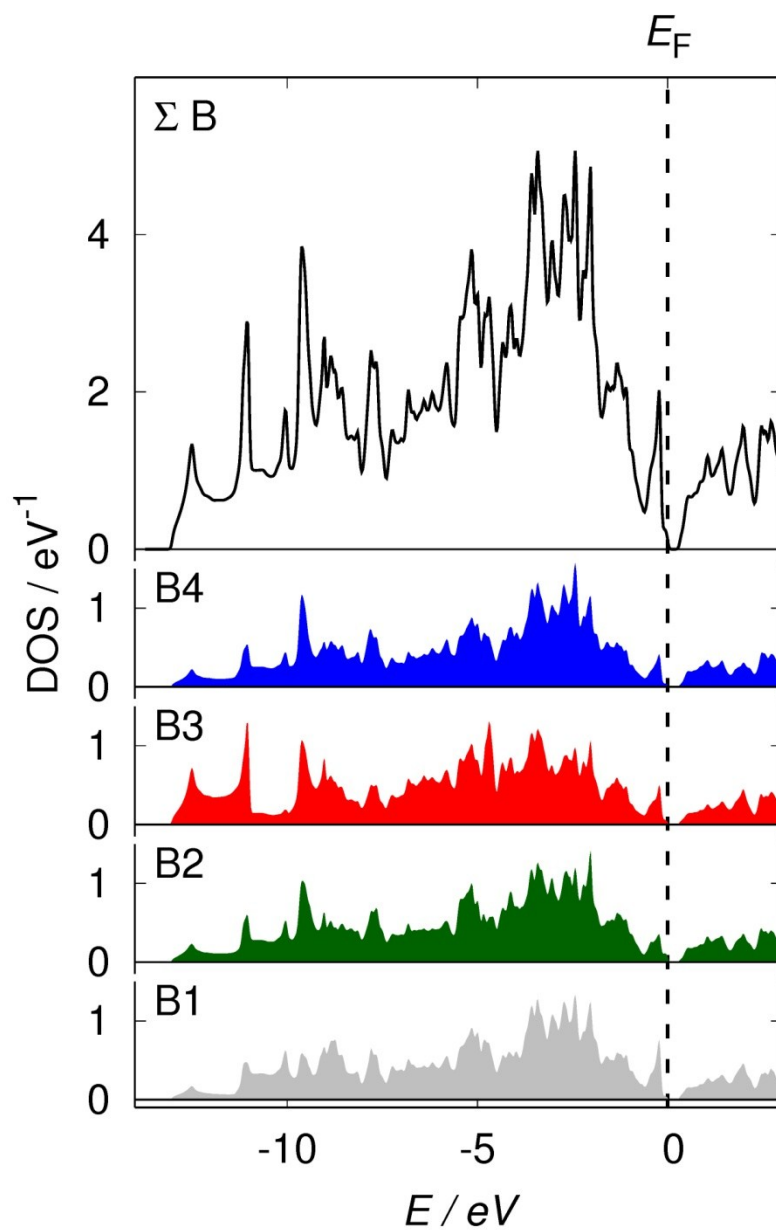
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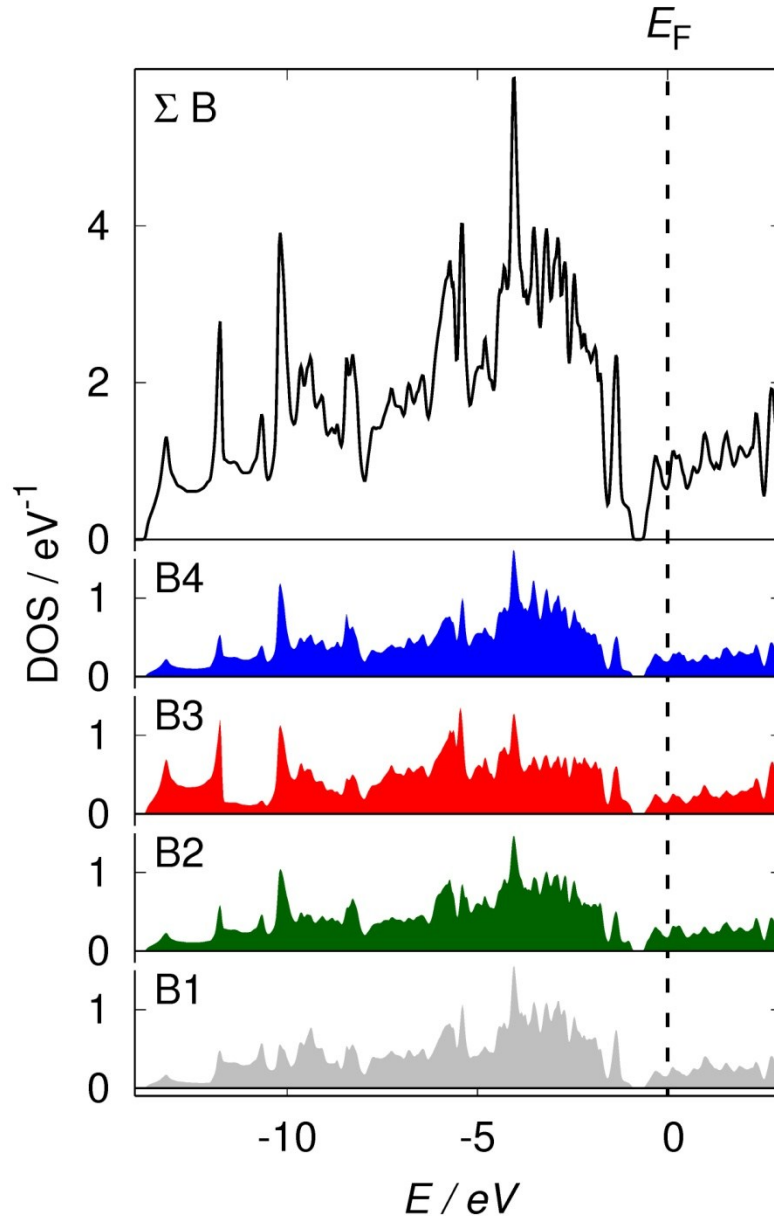
## Density of States Calculations.



**Fig. S1** Site resolved electronic density of states (DOS) of YMoB<sub>4</sub> calculated by WIEN2k. The the sum of the B-sites is shown by a black line. The B1, B2, B3, and B4 sites are represented by grey, green, red, and blue areas, respectively.



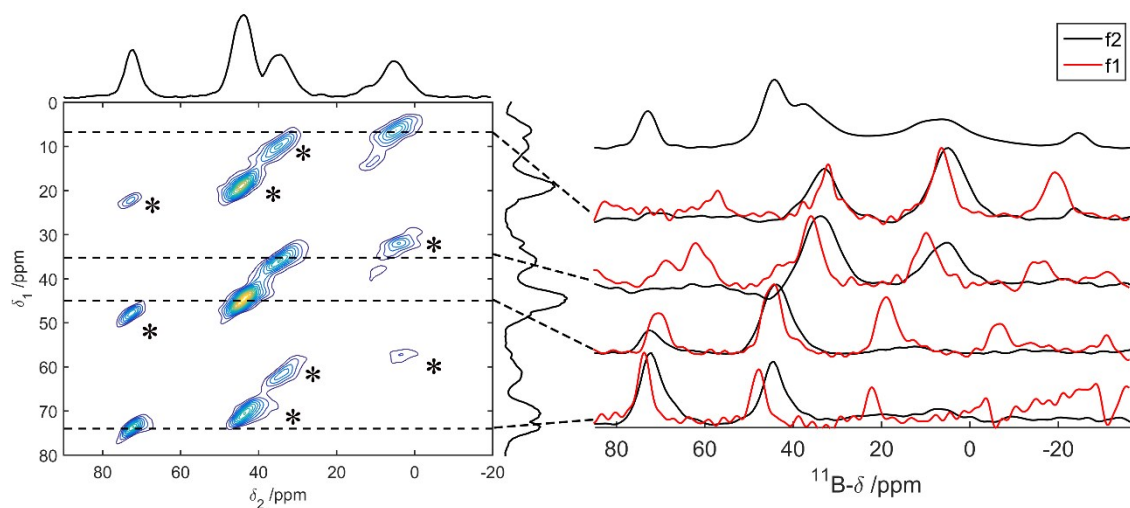
**Fig. S2** Site resolved electronic density of states (DOS) of  $\text{YWB}_4$  calculated by WIEN2k. The the sum of the B-sites is shown by a black line. The B1, B2, B3, and B4 sites are represented by grey, green, red, and blue areas, respectively.



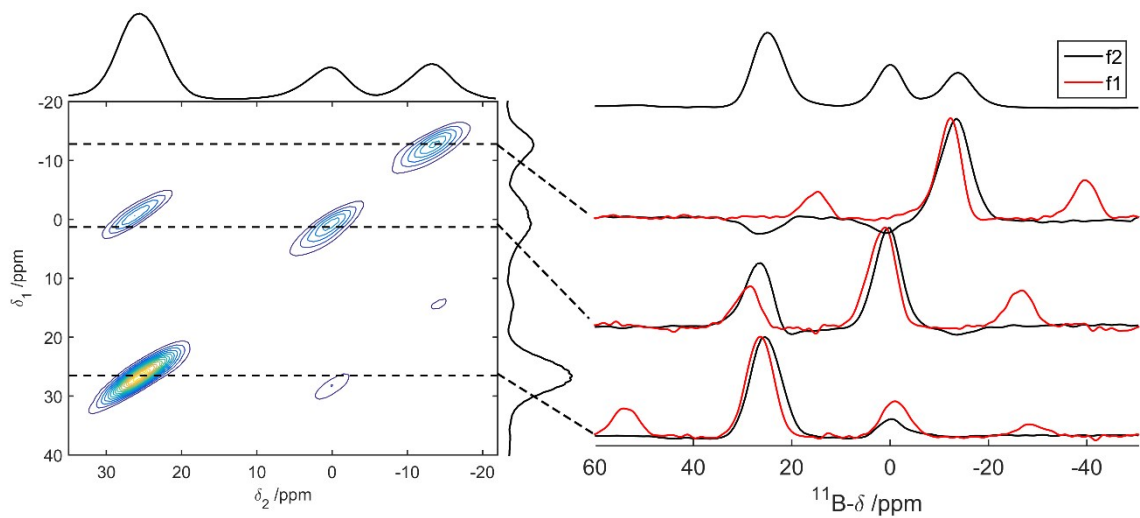
**Fig. S3** Site resolved electronic density of states (DOS) of  $\text{YReB}_4$  calculated by WIEN2k. The the sum of the B-sites is shown by a black line. The B1, B2, B3, and B4 sites are represented by grey, green, red, and blue areas, respectively.

## $^{11}\text{B}$ TQMAS Results.

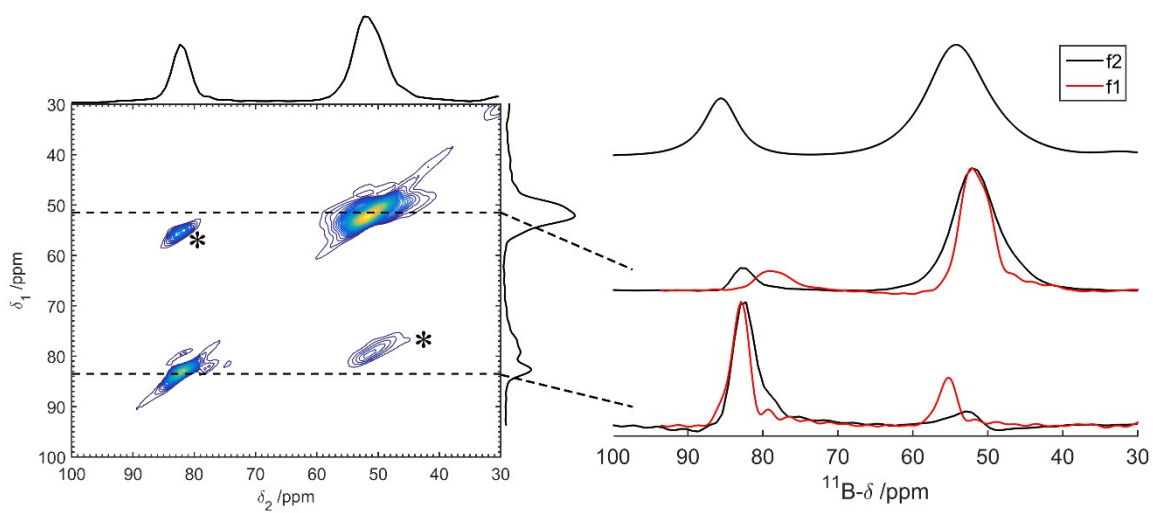
**Experimental Details.** Triple-quantum MAS NMR (MQMAS) spectra were measured at 14.1 T using the three-pulse z-filtering sequence,<sup>1</sup> using hard excitation and reconversion pulses of 4.8  $\mu\text{s}$  and 1.9  $\mu\text{s}$  length and soft detection pulses of 11  $\mu\text{s}$  length. Typical recycle delay for  $^{11}\text{B}$  was 3 s.  $^{11}\text{B}$  chemical shifts were externally referenced relative to the  $\text{BPO}_4$  secondary standard (-3.5 ppm).



**Figure S4**  $^{11}\text{B}$  MQMAS spectrum for  $\text{YWB}_4$  (left) and traces in the f1 and f2 domains (right). A  $^{11}\text{B}$  MAS spectrum is shown at the top trace on the right for the sake of comparison. Asterisks indicate spinning sidebands from the indirect dimension.



**Figure S5**  $^{11}\text{B}$  MQMAS spectrum for  $\text{YReB}_4$  (left) and traces in the f1 and f2 domains (right). A  $^{11}\text{B}$  MAS spectrum is shown at the top trace on the right for the sake of comparison.



**Figure S6**  $^{11}\text{B}$  MQMAS spectrum for  $\text{YMoB}_4$  (left) and traces in the f1 and f2 domains (right). A  $^{11}\text{B}$  MAS spectrum is shown at the top trace on the right for the sake of comparison. Asterisks indicate spinning sidebands from the indirect dimension.

**Table S1** Isotropic chemical shift ( $\delta_{\text{iso}}^{\text{MQ}}$ ) and second order quadrupolar effect parameter ( $\text{SOQE}^{\text{MQ}}$ ) obtained from the MQMAS analysis.

| Sample            | Line | $\Delta_{\text{iso}}^{\text{MQ}}$ ( $\pm 1$ ppm) | $\text{SOQE}^{\text{MQ}}$ ( $\pm 50$ kHz) |
|-------------------|------|--|---|
| YMoB <sub>4</sub> | a    | 87   | 310                                       |
|                   | b-d  | 56   | 560 <sup>a</sup>                          |
| YWB <sub>4</sub>  | a    | 73   | 1500                                      |
|                   | b    | 44   | 1200                                      |
|                   | c    | 35   | 1400                                      |
|                   | d    | 8.3  | 1900                                      |
| YReB <sub>4</sub> | a-b  | 26 <sup>a</sup>                                  | 1140 <sup>a</sup>                         |
|                   | b    | 1  | 1240                                      |
|                   | d    | -12  | 1130                                      |

## References

- (1) A. Medek, J. S. Harwood and L. Frydman, *J. Am. Chem. Soc.*, 1995, **117**, 12779–12787.