## **Supporting Information for:**

## Structural and Dynamical Properties of Potassium Dodecahydro-monocarba-*closo*-dodecaborate: KCB<sub>11</sub>H<sub>12</sub>

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N.B., for all supporting figures, standard uncertainties are commensurate with the observed scatter in the data, if not explicitly designated by vertical error bars.



**Figure S1**. Experimental (circles), fitted (line), and difference (line below observed and calculated patterns) XRD profiles for KCB<sub>11</sub>H<sub>12</sub> at 122 K ( $\lambda$ =0.45236 Å). Vertical bars indicate the calculated positions of Bragg peaks of KCB<sub>11</sub>H<sub>12</sub> (S.G. *P*2<sub>1</sub>/*c*, Wt. Frac.: 98.845(3) %) and trace KCl impurity (Wt. Frac.: 1.155(16) %) (from the top). R<sub>wp</sub>=0.0243, R<sub>p</sub>=0.0187,  $\chi^2$ =1.08. Refined lattice parameters of low-*T* phase KCB<sub>11</sub>H<sub>12</sub>: *a*=9.8966(5) Å, *b*=19.4811(5) Å, *c*=9.8964(6) Å,  $\beta$ =93.545(2)°, and *V*=1904.3(1) Å<sup>3</sup>.



**Figure S2.** Experimental (circles), fitted (line), and difference (line below observed and calculated patterns) XRD profiles for KCB<sub>11</sub>H<sub>12</sub> at 298 K ( $\lambda$ =0.45236 Å). Vertical bars indicate the calculated positions of Bragg peaks of KCB<sub>11</sub>H<sub>12</sub> (S.G. *P*2<sub>1</sub>/*c*, Wt. Frac.: 98.977(2) %) and trace KCl impurity (Wt. Frac.: 1.023(1) %) (from the top). R<sub>wp</sub>=0.0219, R<sub>p</sub>=0.0166, and  $\chi^2$ =0.97. Refined lattice parameters of low-*T* phase KCB<sub>11</sub>H<sub>12</sub>: *a*=9.9792(6) Å, *b*=19.6782(6) Å, *c*=9.9841(6) Å, *β*=93.2668(20)°, and *V*=1957.41(15) Å<sup>3</sup>.



**Figure S3.** Experimental (circles), fitted (line), and difference (line below observed and calculated patterns) SXRPD profiles for KCB<sub>11</sub>H<sub>12</sub> at 450 K ( $\lambda$ =0.45236 Å). Vertical bars indicate the calculated positions of Bragg peaks of KCB<sub>11</sub>H<sub>12</sub> (S.G. *Fm*-3*m*, Wt. Frac.: 98.986(2) %) and trace KCl impurity (Wt. Frac.: 1.01(2) %) (from the top). R<sub>wp</sub>=0.0261, R<sub>p</sub>=0.0185, and  $\chi^2$ =1.14. Refined lattice parameters of high-*T* phase KCB<sub>11</sub>H<sub>12</sub>: *a*=10.1502(6) Å and *V*=1045.75(18) Å<sup>3</sup>.



**Figure S4.** Exemplary QENS spectrum for KCB<sub>11</sub>H<sub>12</sub> at 473 K ( $Q = 1.0 \text{ Å}^{-1}$ ) using 8 Å wavelength neutrons (with 30 µeV fwhm resolution). Spectra were fit with a delta function and one Lorentzian component, both convoluted with the instrumental resolution function, on top of a flat background.



**Figure S5.** Exemplary QENS spectrum for  $\text{KCB}_{11}\text{H}_{12}$  at 473 K ( $Q = 1.20 \text{ Å}^{-1}$ ) using 4.8 Å wavelength neutrons (with 56 µeV fwhm resolution). Spectra were fit with a delta function and two Lorentzian components, all convoluted with the instrumental resolution function, on top of a flat background.



**Figure S6.** *Q*-dependence of the broader "overdamped-vibration" component intensity for KCB<sub>11</sub>H<sub>12</sub> at 410 K and  $\lambda$ =4.8 Å. The data were fit according to the incoherent neutron scattering law of the harmonic oscillator in the case of the one-phonon approximation:  $I=AQ^2\exp(-\langle u^2 \rangle Q^2)$ , where *I* is the scattering intensity of the broader component, *A* is a constant, and  $\exp(-\langle u^2 \rangle Q^2)$  is the Debye-Waller factor, with  $\langle u^2 \rangle$  being the mean-squared displacement of the H atoms. From the fit (red), the root-mean-squared displacement  $\langle u^2 \rangle^{\frac{1}{2}} = 0.41(3)$  Å.



**Figure S7.** *Q*-dependence of the narrower quasielastic component linewidth  $\Gamma$  for KCB<sub>11</sub>H<sub>12</sub> at 473 K using 4.8 Å and 8 Å neutrons.



**Figure S8.** The CB<sub>11</sub>H<sub>12</sub><sup>-</sup> anion geometry, used as a guide for the EISF models. H atoms are numbered for convenience. H1 and H12 are apical H atoms. H2, H3, H4, H5, and H6 form one quintet band of equatorial H atoms. H7, H8, H9, H10 and H11 form the other quintet band of equatorial H atoms. Average H-H distances were determined from refined models based on x-ray diffraction data for the ordered room-temperature KCB<sub>11</sub>H<sub>12</sub>. The following distances were used to derive the EISF model curves in Figure 8 of the text. The apical-apical distance, *d*, between H1 and H12 is 5.51 Å. The *intra*-band nearest-neighbor equatorial H atom distance, *d*<sub>2</sub>, (e.g., between H2 and H3) is 2.94 Å. The band diameter  $r = \frac{d_2}{\sqrt{2(1-\cos(2\pi/5))}} = 2.50$  Å. The remaining distances are calculated using the band diameter, and are  $d_1 = 1.54$  Å,  $d_3 = 4.05$  Å,  $d_4 = 4.76$  Å and 2r = 5.00 Å. Upon isotropically rotating the anion, the radius of the spherical surface formed by the H atoms is  $r_e = 2.76$  Å.

## Model EISFs for Various Reorientational Mechanisms for the CB11H12 Anion

The elastic incoherent structure factors (EISFs) reflect the composite motions of all twelve H atoms of the CB<sub>11</sub>H<sub>12</sub><sup>-</sup> (rigid-body) anions. The following EISF models for CB<sub>11</sub>H<sub>12</sub><sup>-</sup> anion reorientations were included for comparison in Figure 8 of the text and are constructed below, according to the general methodology described elsewhere,<sup>S1</sup> in terms of the various possible H-H distances for the anion shown in Figure S8. (N.B.,  $j_0(x) = \frac{\sin(x)}{x}$ , the zeroth-order spherical Bessel function.)

For five-fold jumps around the  $C_5$  anion symmetry axis, the two apical H atoms remain stationary while the ten equatorial H atoms undergo five-fold jumps with jump distances of  $d_2 = 2.94$  Å and  $d_4 = 4.76$  Å. The EISF is then defined as:

$$\text{EISF}_{C_5} = \frac{2}{12} + \frac{10}{12} \times \frac{1}{5} [1 + 2j_0(Qd_2) + 2j_0(Qd_4)] = \frac{1}{6} + \frac{1}{6} [1 + 2j_0(Qd_2) + j_0(Qd_4)].$$

Rotational diffusion (small-angle jump diffusion) around the anion  $C_5$  symmetry axis below  $Q = 2.5 \text{ Å}^{-1}$  can be approximated by considering a model with ten angular jump positions instead of five, in which case the two apical H atoms still remain stationary while the ten equatorial H atoms undergo ten-fold jumps with jump distances of  $d_1 = 1.54 \text{ Å}$ ,  $d_2 = 2.94 \text{ Å}$ ,  $d_3 = 4.05 \text{ Å}$ ,  $d_4 = 4.76 \text{ Å}$  and 2r = 5.00 Å (Figure S8). The EISF is defined as:

$$\text{EISF}_{C_{10}} = \frac{2}{12} + \frac{10}{12} \times \frac{1}{10} [1 + 2j_0(Qd_1) + 2j_0(Qd_2) + 2j_0(Qd_3) + 2j_0(Qd_4) + j_0(Q2r)].$$

The isotropic rotational diffusion of H over a spherical surface of radius  $r_e = 2.76$  Å, is defined as:

 $\mathrm{EISF}_{iso} = j_0^2 (Qr_e).^{\$2}$ 

The EISF models of five-fold uniaxial reorientations around the  $C_5$  symmetry axis involving the addition of changes in the direction of this axis toward neighboring ( $\pm 1 \pm 1 \pm 1$ ) directions was calculated numerically, by taking into account all the possible positions that the H atoms can visit.



**Figure S9** Nyquist plots for  $KCB_{11}H_{12}$  at various temperatures above the order-disorder phase transition.

## References

- S1 Yildirim, T.; Gehring, P. M.; Neumann, D. A.; Eaton, P. E.; Emrick, T. Phys. Rev. B 1999, 60, 314–321.
- S2 Bée, M. Quasielastic Neutron Scattering, Principles and Applications in Solid State Chemistry, Biology and Materials Science. Adam Hilger: Bristol, **1988**.