

Hydrogen dynamics of the dodecahydro-*closo*-dodecaborate crystals

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Introduction

Dicesium dodecahydro-*closo*-dodecaborate, Cs₂B₁₂H₁₂, is the heavy cousin of the lighter alkali-metal dodecahydro-*closo*-dodecaborates (e.g., Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂), which have particular importance in current hydrogen-storage research, as they are known to be intermediates in the dehydrogenation of the corresponding alkali-metal tetraborohydrides.¹ These compounds are ionically bonded salts comprised of alkali-metal cations and dodecahydro-*closo*-dodecaborate (i.e., B₁₂H₁₂²⁻) icosahedral anions. Fundamental information concerning B₁₂H₁₂²⁻ bonding potentials and dynamics, which are largely unknown, may provide valuable insights for understanding their stability and reactivity.

Recent ¹H and ¹¹B NMR spectroscopy results² suggest that the B₁₂H₁₂²⁻ anions in the alkali-metal salts undergo rapid reorientational motions, with the motional frequency at a given temperature increasing as the cation radius and unit-cell dimensions increase. In order to explore the details of the anion motions, we have investigated the dynamics of B₁₂H₁₂²⁻ anions by neutron scattering techniques. To observe anion dynamics at reasonably low temperatures, we chose Cs₂B₁₂H₁₂, the salt with the largest alkali-metal cation (and hence the largest lattice constant). We have probed both the B₁₂H₁₂²⁻ reorientational dynamics by quasielastic neutron scattering (QENS) and the torsional and translational vibrational modes by neutron vibrational spectroscopy (NVS). In isolation, the B₁₂H₁₂²⁻ anion is a regular icosahedron but is susceptible to symmetry breaking by its environment.^{3,4} Cs₂B₁₂H₁₂ crystallizes in the cubic space group Fm-3.⁵ No phase transition was observed with DSC measurements² over the temperature range of 123 K to 673 K.

Experimental

All measurements were performed at the NIST Center for Neutron Research. The QENS measurements were performed on the High Flux Backscattering Spectrometer (HFBS)⁶ with an incident neutron wavelength of 6.27 Å, momentum transfer (*Q*) over a range of 0.2 Å⁻¹ to 1.75 Å⁻¹, and a resolution of 0.83 μeV in most detectors. The quasielastic spectra were reduced and analyzed using the DAVE⁷ software package. The vibrational density of states (VDOS) at 4 K was collected in neutron energy loss on the Filter Analyzer Spectrometer (FANS)⁸ and the VDOS at 100 K and higher were collected on the Disc Chopper Spectrometer (DCS).⁹

Results

QENS spectra are composed of a strong elastic peak (a delta function convolved with a Gaussian-like instrument resolution function), and a broad quasielastic feature (usually fitted with a Lorentzian) that is a result of energy transfer (both loss and gain) between the neutron and the molecular system due to hydrogen motion. The ratio of the intensity of the elastic and quasielastic scattering spectral features as a function of neutron momentum transfer (*Q*) can provide insight into the geometric mechanism of the rotational or translational motion. The *Q*-dependent, elastic incoherent structure factor (*EISF*) is the ratio of the elastic peak area to the sum of elastic and quasielastic peak areas

The experimental *EISF* data between 430 K and 480 K are shown in Fig. 1. Figure 1 also depicts the calculated *EISFs* corresponding to likely reorientation models for the B₁₂H₁₂²⁻ icosahedral anion. If we ignore the crystal symmetry and focus on the local icosahedral symmetry of the B₁₂H₁₂²⁻ anion, there are three types of symmetry axes to consider, C₂, C₃, and C₅, around which rotational jumps (of 180°, 120°, and 72°, respectively) leave the apparent orientation of the anion unchanged. Possible reorientational mechanisms under consideration are: (a) discrete reorientational jumps about one of the C₂ symmetry axes of the anion; (b) discrete reorientational jumps about one of the C₃ symmetry axes of the anion; (c) discrete reorientational jumps about one of the C₅ symmetry axes of the anion; (d) independent reorientational jumps around two axes, either C₃ or C₅, on the same time scale; (e) discrete jumps about multiple axes to any of the other hydrogen positions of the icosahedron and (f) isotropic rotational diffusion.

For reasons discussed in detail elsewhere,¹⁰ many of the possible reorientation mechanisms could be eliminated. The data at 430 K fit best with the single-axis jump reorientation model about either a C₃ or C₅ axis. At 457 K the molecule seems to progress through an intermediate dynamic. And at 480 K the data fit best to a two-axis reorientation model that could be about two C₃ axes, two C₅ axes, or one C₃ axis and one C₅ axis.

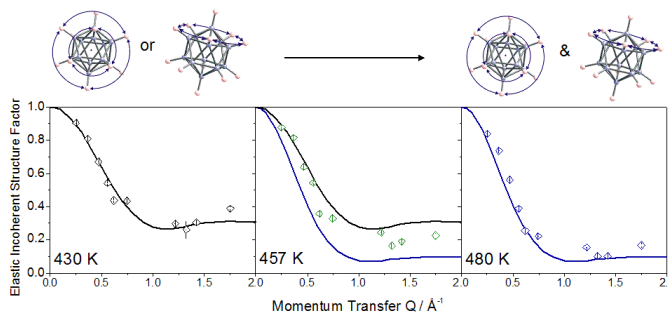


Figure 1. The experimental *EISF* for data observed (left to right) at 430 K, 457 K, and 480 K. These are compared with a model for single-axis C₃ or C₅ reorientation (black) and a model for two-axis C₃ and/or C₅ reorientation (blue).

In an effort to shed further light on the nature of the reorientation mechanism, we have measured the low-energy vibrational density of states of Cs₂B₁₂H₁₂ from 8 meV to 20 meV (64 cm⁻¹ to 160 cm⁻¹). Figure 2 shows the VDOS measured at 4 K, 100 K, 300 K, and 550 K. The 11.8 meV and 15.4 meV features at 4 K have been assigned to the translational and torsional modes, respectively, in good agreement with the results of previous DFT calculations.⁴ By 550 K, the translational and torsional modes have shifted roughly 1.6 meV and 2.4 meV lower in energy, respectively, both features broadening with temperature. At 4 K, the anion is primarily in its ground state, so the observed vibrational features reflect transitions from the ground-state to first-excited-state energy levels. As the temperature is increased to 550 K, several higher translational and torsional energy levels become increasingly populated, and the spectra reflect contributions from a variety of transitions (i.e., 0→1, 1→2, 2→3, etc.), whose transition energies probably differ somewhat despite being identical in the harmonic case. Hence, these multiple transitions are at least partially responsible for the apparent softening and broadening at higher temperatures.

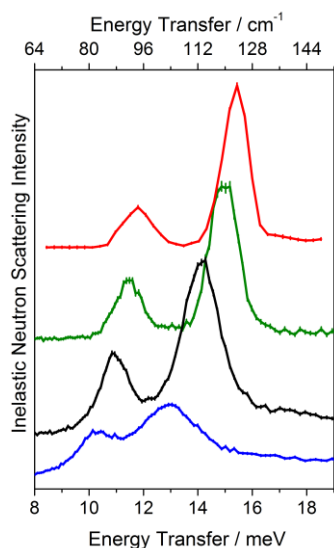


Figure 2. The low-energy VDOS of $\text{Cs}_2\text{B}_{12}\text{H}_{12}$ measured by neutron vibrational spectroscopy as a function of temperature. The spectra shown were collected (from bottom to top) at 550 K (blue), 300 K (black), 100 K (green) and 4 K (red). The feature at 11.8 meV (94 cm^{-1}) at 4 K is assigned as a translational mode, and the peak at 15.4 meV (123 cm^{-1}) as a torsional mode. As the temperature increases, both peaks decrease in energy and broaden. The error bars representing $\pm 1\sigma$ are small and are obscured by the plot traces. The spectra are vertically offset for ease of viewing.

Conclusions

Over the temperature range investigated (430 K to 530 K), the QENS and spectroscopic results suggest that the reorientation mechanism of the $\text{B}_{12}\text{H}_{12}^{2-}$ anions evolves from discrete jumps around one type of high-symmetry rotational axis (either C_3 or C_5) at the lowest temperature of 430 K to a combined mechanism involving, on average, independent (C_3 and/or C_5) two-axis discrete jumps between 480 K and 530 K.

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References

- [1] Hwang, S.-J.; Bowman, R. C.; Reiter, J. W.; Rijssenbeek, J.; Soloveichik, G. L.; Zhao, J.-C.; Kabbour, H.; Ahn, C. C., *J Phys Chem C* **2008**, 112, 3164-3169.
- [2] Tiritiris, I.; Schleid, T.; Muller, K., *Appl. Magn. Reson.* **2007**, 32, 459-481.
- [3] Allis, D. G.; Hudson, B. S., *J Phys Chem A* **2006**, 110, 3744-3749.
- [4] Verdal, N.; Zhou, W.; Stavila, V.; Her, J.-H.; Yousufuddin, M.; Yildirim, T.; Udovic, T. J., *J Alloy Compds* **2010**, In Press, doi:10.1016/j.jallcom.2010.08.024
- [5] Tiritiris, I.; Schleid, T., *Z. Anorg. Allg. Chemie* **2003**, 629, (7-8), 1390-1402.
- [6] Meyer, A.; Dimeo, R. M.; Gehring, P. M.; Neumann, D. A., *Rev. Sci. Instrum.* **2003**, 74, 2759.
- [7] Azuah, R.; Kneller, L.; Qiu, Y.; Tregenna-Piggott, P. L. W.; Brown, C.; Copley, J.; Dimeo, R., *J Res NIST* **2009**, 114, (6), 341-358.

- [8] Udovic, T. J.; Brown, C. M.; Leão, J. B.; Brand, P. C.; Jiggetts, R. D.; Zeitoun, R.; Pierce, T. A.; Peral, I.; Copley, J. R. D.; Huang, Q.; Neumann, D. A.; Fields, R. J., *Nucl. Instr. and Meth. A* **2008**, 588, 406-413.
- [9] Copley, J. R. D.; Cook, J. C., *Chem. Phys.* **2003**, 292, 477.
- [10] Verdal, N.; Udovic, T. J.; Rush, J. J.; Cappelletti, R. L.; Zhou, W., *J Phys Chem A* **2011**, 115, 2933-2938.