

Low-temperature tunneling and rotational dynamics of the ammonium cations in $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$

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Low-temperature neutron scattering spectra of diammonium dodecahydro-*closo*-dodecaborate $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ reveal two NH_4^+ rotational tunneling peaks (e.g., 18.5 μeV and 37 μeV at 4 K), consistent with the tetrahedral symmetry and environment of the cations. The tunneling peaks persist between 4 K and 40 K. An estimate was made for the tunnel splitting of the first NH_4^+ librational state from a fit of the observed ground-state tunnel splitting as a function of temperature. At temperatures of 50 K–70 K, classical neutron quasi-elastic scattering appears to dominate the spectra and is attributed to NH_4^+ cation jump reorientation about the four C_3 axes defined by the N–H bonds. A reorientational activation energy of 8.1 ± 0.6 meV (0.79 ± 0.06 kJ/mol) is determined from the behavior of the quasi-elastic linewidths in this temperature regime. This activation energy is in accord with a change in NH_4^+ dynamical behavior above 70 K. A low-temperature inelastic neutron scattering feature at 7.8 meV is assigned to a NH_4^+ librational mode. At increased temperatures, this feature drops in intensity, having shifted entirely to higher energies by 200 K, suggesting the onset of quasi-free NH_4^+ rotation. This is consistent with neutron-diffraction-based model refinements, which derive very large thermal ellipsoids for the ammonium-ion hydrogen atoms at room temperature in the direction of reorientation. © 2011 American Institute of Physics. [doi:10.1063/1.3624495]

I. INTRODUCTION

The icosahedral $\text{B}_{12}\text{H}_{12}^{2-}$ anion has received much attention due to its formation as a stable side-product of dehydrogenation reactions of alkali and alkali-earth borohydrides,^{1–5} which are candidates for hydrogen-storage materials. With a -2 charge, the bonding orbitals of the anion are filled, and the electrons are delocalized around the boron cage.^{6,7} The icosahedron is thermally and chemically very stable.⁸ Recently, $\text{B}_{12}\text{H}_{12}^{2-}$ reorientational dynamics have been characterized within the cubic $\text{Cs}_2\text{B}_{12}\text{H}_{12}$ lattice by quasi-elastic neutron scattering (QENS).⁹ Even for this least sterically hindered of the alkali and alkaline-earth dodecahydro-*closo*-dodecaborates, $\text{B}_{12}\text{H}_{12}^{2-}$ reorientational dynamics is not readily observed until ≈ 430 K for instrumental resolutions of 1 μeV ,⁹ a dynamical “sluggishness” partially attributable to the relatively large moment of inertia of the $\text{B}_{12}\text{H}_{12}^{2-}$ icosahedron.

The $\text{B}_{12}\text{H}_{12}^{2-}$ anion possesses a hydrogen mass fraction of 8.5%. By combining this anion with a hydrogenous cation, one can form a potentially useful hydrogen-storage compound with an even higher hydrogen content. Indeed, a recent *ab initio* study¹⁰ suggests that, not only is $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ a potential hydrogen-storage candidate because of its 11.3% hydrogen mass fraction, but also because density functional

theory (DFT) calculations predict favorable thermodynamics for hydrogen release.

Diammonium dodecahydro-*closo*-dodecaborate crystallizes in the cubic $Fm\bar{3}$ space group with lattice parameter $a = 10.8781$ Å.¹¹ It is isostructural with $\text{Cs}_2\text{B}_{12}\text{H}_{12}$, $\text{Rb}_2\text{B}_{12}\text{H}_{12}$, and $\text{K}_2\text{B}_{12}\text{H}_{12}$.¹¹ The Rb^+ and NH_4^+ ionic radii are very similar (1.47 Å), as are the lattice parameters of the corresponding $\text{B}_{12}\text{H}_{12}$ salts: $\text{Rb}_2\text{B}_{12}\text{H}_{12}$ is cubic with $a = 10.8674$ Å. Because of the similar lattice parameters, the rotational dynamics of the $\text{B}_{12}\text{H}_{12}^{2-}$ icosahedron in $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ are expected to be observed on the same backscattering spectrometer at and above 475 K as for the Rb compound.¹² Yet, such dynamics are not easily studied, since $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ is known to polymerize at temperatures between 473 K and 673 K.¹³ In fact, our own differential scanning calorimetry and thermogravimetric analysis measurements of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ under flowing He indicate no significant mass change until 610 K at which point an endothermic decomposition occurs with roughly a 4.5% initial mass loss.

Since the ammonium cation is relatively lightweight and possesses a reorientational moment of inertia two orders of magnitude less than that for $\text{B}_{12}\text{H}_{12}^{2-}$, one expects NH_4^+ reorientational dynamics in this compound to be more rapid than $\text{B}_{12}\text{H}_{12}^{2-}$ dynamics and observable at much lower temperatures. In fact, low-temperature rotational tunneling peaks and quasi-elastic neutron scattering of many ammonium salts have already been studied.^{14–16} Interestingly, the

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dodecahydro-*closo*-dodecaborate anion may be the largest counter-ion for which ammonium rotational tunneling and dynamics has yet to be probed. Tunneling spectra are very sensitive to the potential energy surface: The magnitude of the splitting is related almost exponentially to the height of the rotational barrier¹⁷ and, in the case of tetrahedral species, the tunneling features are determined by the local symmetry.¹⁸

In the current paper, we report neutron scattering results of the low-temperature dynamical behavior of the NH_4^+ cations in $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, which are relatively unperturbed by the orders-of-magnitude slower $\text{B}_{12}\text{H}_{12}^{2-}$ reorientations. We find that the NH_4^+ cations, which are surrounded by large $\text{B}_{12}\text{H}_{12}^{2-}$ anions, experience an unusually low barrier to rotation and exhibit rotational tunneling between 4 K and 40 K that completely transforms into thermally activated rotational jump diffusion by 60 K.

II. EXPERIMENTAL

The sample was isolated from an aqueous solution of $(\text{NH}_4)_2^{11}\text{B}_{12}\text{H}_{12}$ prepared from $(\text{H}_3\text{O})_2^{11}\text{B}_{12}\text{H}_{12}$ and 1.0 M ammonium hydroxide. $(\text{H}_3\text{O})_2^{11}\text{B}_{12}\text{H}_{12}$ was obtained by passing a concentrated aqueous solution of $\text{Cs}_2^{11}\text{B}_{12}\text{H}_{12}$ ($> 99.8\%$ ^{11}B) (Katchem) (Ref. 19) through a strongly acidic ion-exchange column.

All neutron scattering measurements were made at the NIST Center for Neutron Research (NCNR). The tunneling and QENS measurements between 4 K and 70 K were performed on the high flux backscattering spectrometer (HFBS).²⁰ The data were collected from polycrystalline powder with an estimated 88% transmission contained in an aluminum foil packet shaped into an annular geometry inside a cylindrical aluminum can. The sample can was sealed in a He-gas-filled glove box and subsequently placed in a He closed-cycle refrigerator for neutron measurements. With an incident neutron wavelength of 6.27 Å, the HFBS covers a momentum transfer (Q) range of 0.2 Å^{-1} – 1.75 Å^{-1} . Within the $\pm 36 \mu\text{eV}$ window, the average energy resolution of the elastic line was $1.03 \mu\text{eV}$ FWHM. Within the $\pm 42.5 \mu\text{eV}$ window, at which the Doppler drive operates at an atypical 60 Hz, the energy resolution of the elastic line was $1.2 \mu\text{eV}$. Additional quasi-elastic spectra were collected on the disc chopper spectrometer (DCS) (Ref. 21) between 80 K and 200 K with 4.8 Å (3.55 meV) incident neutrons in the medium-resolution mode, yielding a $56.1 \mu\text{eV}$ elastic resolution. The quasi-elastic spectra were reduced and analyzed using the DAVE (Ref. 22) software package.

Vibrational spectra at 4 K, 40 K, 80 K, and 200 K were collected on the filter-analyzer neutron spectrometer²³ between 3 meV and 160 meV. Both PG(002) and Cu(220) monochromators were used, each with pre- and post-monochromator collimations of 20 min of arc. Spectral resolution varied from 1.13 meV at 3 meV to 4.7 meV at 160 meV. The low-energy vibrational spectrum was also collected on DCS at 4 K with 2.43 Å (13.9 meV) incident neutrons (spectral resolution: 0.2 meV–0.3 meV FWHM) and at 80 K and 200 K with 4.8 Å neutrons, collected in neutron energy gain (spectral resolution: 60 μeV –660 μeV FWHM).

Neutron powder diffraction (NPD) data were collected on the high-resolution powder neutron diffractometer (BT1) utilizing a Cu(311) monochromator to select 1.540 Å incident neutrons with 60 min of arc in-pile collimation. Diffraction patterns were collected over 2θ scattering angles of 3° – 168° , with 0.05° steps.

First-principles calculations were performed within the plane-wave implementation of DFT using the PWSCF package.²⁴ We used Vanderbilt-type ultrasoft potentials with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 544 eV was found to be enough for the total energy to converge within 0.5 meV/atom. Structure optimizations were first performed with respect to atomic positions, with the lattice parameters fixed at the experimental values. Phonon calculations were then performed on the relaxed structures using the supercell method with finite displacements.²⁵

III. RESULTS AND DISCUSSION

A. Low-temperature tunneling

From HFBS measurements, NH_4^+ ion rotational tunneling peaks are observed for $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ at 18.5 μeV and 37 μeV at 4 K as shown in Fig. 1. (A complementary 4 K DCS measurement at lower resolution confirmed the lack of any additional higher energy tunneling features; see Fig. S1 in the supplemental information (SI).²⁶) These tunneling peaks are resolved at temperatures between 4 K and 40 K (Fig. 1(c)). Both peaks shift to lower energy as the temperature increases. Around 50 K, the tunneling peaks collapse into a quasi-elastic neutron scattering spectrum, dominated by thermally activated jumps *over* (instead of tunneling through) the rotational barrier.

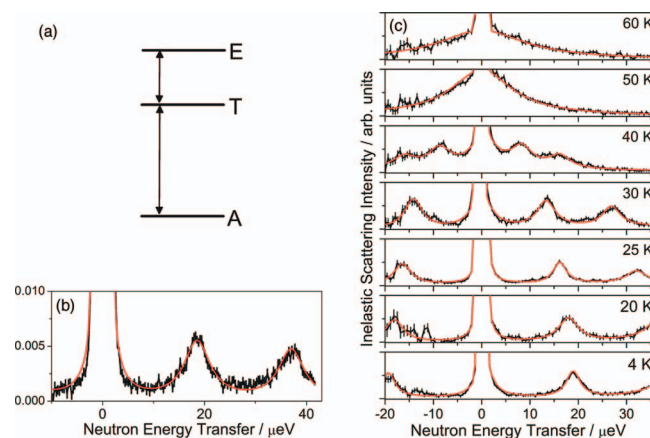


FIG. 1. (a) Two features with one tunnel splitting twice that of the other is characteristic of A-T and T-E rotational transitions in tetrahedral symmetry, resulting from overlap between rotational configurations 120° apart. (b) Backscattering spectrum showing tunnel splitting of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ at 4 K. (c) The tunneling spectra as a function of temperature. The observed spectra are shown in black in (b) and (c). The red trace is a fit in which the tunnel peaks are represented by Lorentzians. The peak energy shifts lower as temperature increases. As the temperature increases, a second tunneling peak moves into the backscattering energy window of Fig. 1(c). By 50 K, the tunneling peak is indistinguishable from a typical quasi-elastic feature. The error bars represent an uncertainty of one standard deviation.

The tunnel splitting is much larger for the ammonium cations in $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ than for those in previously observed compounds, e.g., $(\text{NH}_4)_2\text{S}_2\text{O}_8$ exhibits a tunnel splitting of $1.09 \mu\text{eV}$,¹⁴ $(\text{NH}_4)_2\text{SnCl}_6$, $1.5 \mu\text{eV}$ and $3.0 \mu\text{eV}$,¹⁶ and NH_4ClO_4 , $5.75 \mu\text{eV}$.²⁷ Since a larger tunnel splitting corresponds to a smaller rotational barrier, this indicates that the barrier to ammonium rotation in $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ is comparatively low, with strong coupling between orientations along the rotational coordinate. Because the ammonium cation generally sits in an ionic crystal lattice, ammonium rotational potential barriers are usually fairly large.¹⁷ Although $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ is also an ionic salt, the electronic stability from the delocalized electrons and the large size of the $\text{B}_{12}\text{H}_{12}$ counter-anion create a softer ammonium rotational potential in this crystal lattice.

As a tetrahedral symmetric top, the ammonium cation has three types of rotational states: A (fivefold degenerate), T (ninefold degenerate), and E (twofold degenerate).^{16,18,28} The rotational states are split by the coupling between rotational configurations or “pocket states.” That the energy of the $A \leftrightarrow T$ transition is twice that of the $T \leftrightarrow E$ transition (as manifested by the two tunneling peaks for $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ and depicted in Fig. 1(a)) arises from a small but non-negligible overlap between the wavefunctions of rotational configurations that differ by 120° and negligible overlap between wavefunctions for rotational configurations that differ by 180° .^{18,28} From the tunnel splitting, therefore, it is apparent that the NH_4^+ librational potential has minima every 120° , along the C_3 rotational coordinate. Deviations from tetrahedral symmetry would lift the degeneracy of the T states, producing a more complicated spectrum.¹⁷

The tunnel splitting as a function of temperature is presented in Fig. 2. This temperature behavior has been observed, for example, in $(\text{NH}_4)_2\text{SnCl}_6$ (Ref. 16) and can be attributed to increasing thermal population of the higher quanta librational and other low-energy modes.²⁹ A fit of the observed tunneling energy E_0^{tun} of the ground state libration E_0^{lib} with temperature yields tunnel splitting values (E_1^{tun}) for the one-

quanta librational mode, E_1^{lib} ,^{16,29}

$$E_0^{\text{tun}}(T) = \frac{\sum_{n=0}^N E_n^{\text{tun}}(T=0) \exp(-E_n^{\text{lib}}/kT)}{\sum_{n=0}^N \exp(-E_n^{\text{lib}}/kT)}. \quad (1)$$

The value used for E_1^{lib} is 7.8 meV , as observed (*vide infra*) in neutron vibrational spectra. Higher quanta librational states could not be identified, so were not included (i.e., $N = 1$). From these values, the tunneling splitting for the first-excited librational state E_1^{tun} is calculated as $109 \pm 3 \mu\text{eV}$ (with the corresponding A to T transition of $218 \mu\text{eV}$). The accuracy of this value would be slightly greater if higher level librational energies were known or if the tunnel splitting had been measured over a greater temperature range. However, this equation models a phenomenon observed at low energies, present over a limited temperature range, where the ground and first librational states are the major contributors, so exclusion of higher quanta terms does not appreciably alter the quality of the present results. This approach assumes a one-dimensional potential energy surface, which clearly is not the case for a tetrahedral cation, but it seems an adequate approximation for this and similar¹⁶ systems. The fit to the experimental data predicts that the apparent tunnel splitting is less than the instrument resolution by 55 K and equals zero at 57 K . Therefore, the spectrum observed at 50 K may still contain underlying and overlapping tunnel features, even though it appears to be dominated by quasi-elastic scattering.

B. Ammonium dynamics

As expected from the suggested collapse in tunnel splitting above 50 K as illustrated in Fig. 2, the 60 K spectrum displays a classical quasi-elastic scattering behavior. A neutron quasi-elastic scattering spectrum consists of an elastic line of instrument-limited width and a temperature-sensitive quasi-elastic feature centered about the elastic line. The quasi-elastic feature has its origins in energy transfer between the neutron and a scatterer, usually a hydrogen atom, undergoing Doppler motion: in this case an occasional jump to a different orientation. The ratio of the elastic line to the total scattering is the elastic incoherent structure factor (EISF), which has a Q-dependence determined by the geometry of the reorienting hydrogen atoms and an intensity determined by the number of hydrogen atoms participating.

An established model for the EISF in which hydrogen atoms jump about all four threefold axes of the ammonium tetrahedron with an equivalent time constant is³⁰

$$\text{EISF}_{4C_3} = \frac{1}{4}(1 + 3j_0(Qd)). \quad (2)$$

In which d is the hydrogen jump distance and $j_0(Qd)$ is the zeroth-order Bessel function, which results from orientational averaging of a polycrystalline sample. In this proposed scenario, the hydrogen atoms jump only to positions occupied previously by other hydrogen atoms, thus preserving crystallographic order. For every eight ammonium H atoms that participate in the reorientations that contribute to the quasi-elastic

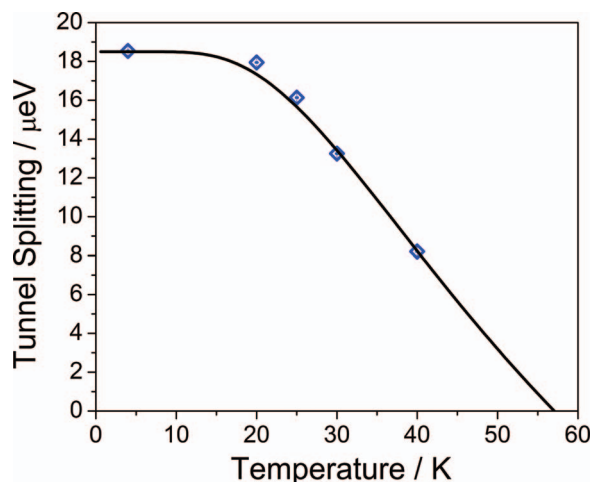


FIG. 2. The E-T rotational tunnel splitting (blue diamonds) as a function of temperature. As higher librational states become populated, the observed splitting energy decreases. The solid line is a fit to Eq. (1). The error bars in the tunnel splitting are slightly smaller than the symbol.

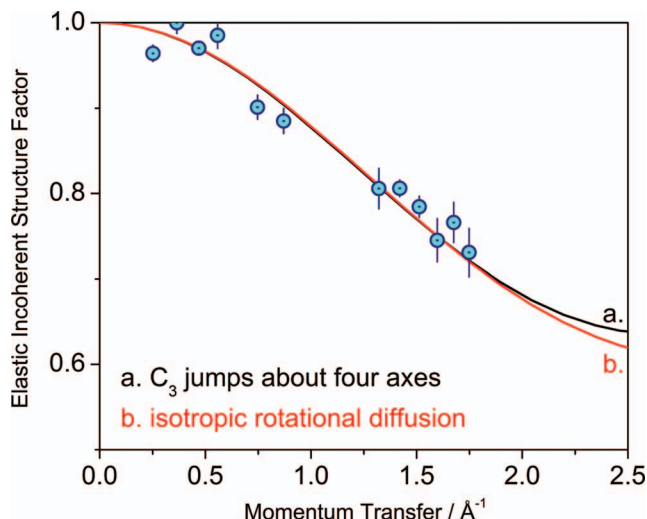


FIG. 3. The experimental EISF for NH_4^+ hydrogen dynamics at 60 K is shown as cyan circles. Three detectors have been masked due to the presence of Bragg scattering. The data are compared with a model for jump reorientation about all four threefold axes (a, blue), and for isotropic rotational diffusion (b, red). The model functions take into account the 12 $\text{B}_{12}\text{H}_{12}^{2-}$ (elastically-scattering) hydrogen atoms per eight NH_4^+ hydrogen atoms.

scattering, there are 12 H atoms on the much more slowly reorienting $\text{B}_{12}\text{H}_{12}^{2-}$ anion that contribute only to the elastic scattering at the low temperatures of this study. Taking into account the H atoms from the $\text{B}_{12}\text{H}_{12}^{2-}$ anion, the appropriately weighted EISF becomes

$$\text{EISF}_{4\text{C}_3} = \left(\frac{12}{20}\right) + \left(\frac{8}{20}\right) \frac{1}{4} (1 + 3j_0(Qd)). \quad (3)$$

This model is in good agreement with the data observed at 60 K and presented in Fig. 3. Since the observed data are expected to contain coherent elastic intensity contributions from two strong Bragg peaks at momentum transfers $\approx 1.00 \text{ \AA}^{-1}$ and $1.15 \text{ \AA}^{-1}$, we have masked those detector regions.

Another possible model for tetrahedron dynamics is shown in Fig. 3. This is the model for isotropic rotational diffusion, in which a hydrogen atom can be found anywhere on the surface of a sphere with a radius r equal to the NH bond distance.³¹ Such reorientation would destroy the ordering of the ammonium hydrogen atoms that is observed with neutron diffraction,

$$\text{EISF}_{\text{iso}} = j_0^2(Qr). \quad (4)$$

Modified for this system, the EISF becomes

$$\text{EISF}_{\text{iso}} = \frac{3}{5} + \frac{2}{5} j_0^2(Qr). \quad (5)$$

The EISF for isotropic rotational diffusion is distinguishable from the EISF for the 120° jump diffusion about all axes only at momentum transfers higher than accessible with this instrument. Under these experimental restrictions, determining the thermal parameters of hydrogen (or deuterium) from neutron diffraction measurements is the best method to distinguish between the two models. Such measurements have been performed at 8 K, 50 K, and 300 K, and the results are discussed below.

Another model for tetrahedron reorientation is of discrete jumps around only one threefold axis defined by one preferred ammonium NH bond.³² This model was previously used to represent the ammonium dynamics of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in which the ammonium reorients about a strong hydrogen bond.¹⁴ This interaction breaks the tetrahedral symmetry such that only one tunnel splitting is observed, and, therefore, is clearly an inappropriate model for the current system.

The observed EISF data at 60 K agree with both the 120° jump rotation model about all four C_3 axes and the isotropic rotational diffusion model. The quasi-elastic scattering above 50 K is an evolution of the lower temperature tunneling features. That the tunnel splitting occurs on the threefold potential surface of the librational mode makes it likely that the dynamic observed is the C_3 jump, at temperatures just above that observed for the tunneling regime. However, it is expected that as the temperature increases and kT becomes much greater than the activation energy for C_3 reorientation (see the next subsection), the NH_4^+ dynamics will be better described as isotropic rotational diffusion or quasi-free rotation.

C. Activation energy

The linewidths Γ of the quasi-elastic features (summed over all Q) as a function of temperature, fit to an Arrhenius function ($\Gamma = \Gamma_0 \exp(-E_a/kT)$), yields an activation energy E_a for NH_4^+ reorientation. These data and corresponding fit are presented in Fig. 4. From quasi-elastic spectra collected in the limited range between 50 K and 70 K, the activation energy and time constant ($\tau_0 = h/\Gamma_0$) were derived as $8.1 \pm 0.6 \text{ meV}$ ($0.79 \pm 0.06 \text{ kJ/mol}$) and $(8 \pm 1) \times 10^{-11} \text{ s}$, respectively. If it is assumed that the ratio of populations n_i of first-excited-state to ground-state librational levels follows a Boltzmann distribution ($n_1/n_0 = \exp(-E^{lib}/kT)$), then over this temperature range, the first-excited-state population

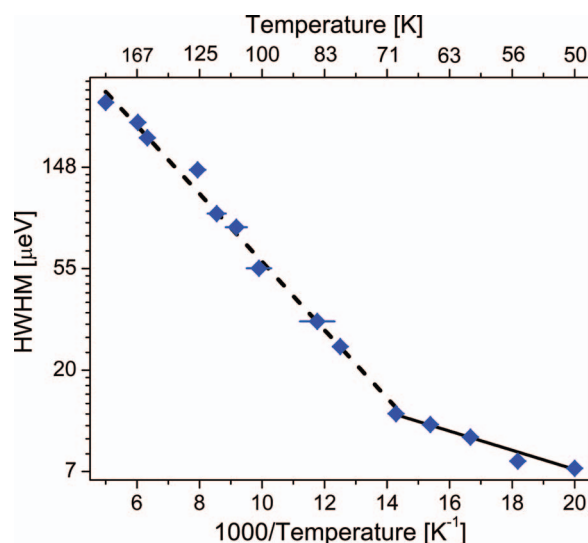


FIG. 4. A plot of quasi-elastic linewidth as a function of temperature. Error bars represent one standard deviation in fitted linewidth, and for some points, temperature. Fit to an Arrhenius function, the slope between 50 K and 70 K yields an effective activation energy of $8.1 \pm 0.6 \text{ meV}$. Above 70 K the ammonium changes dynamics, approaching quasi-free rotation.

varies from 16% to 27% that of the ground state. Hence, this nontrivial excited-state population means that the derived value most likely stems from the excited librational state. Using the NH_4^+ moment of inertia I around each N–H axis ($4.7 \times 10^{-47} \text{ kg m}^2$) and a librational energy of 7.8 meV ($E^{\text{lib}} = 1.2 \times 10^{-21} \text{ J}$), the barrier to reorientation V_0 can be calculated³³ from

$$V_0 = \frac{1}{9} \frac{(E^{\text{lib}} + (5\hbar^2/2I))^2}{\hbar^2/2I}, \quad (6)$$

as 1.92 kJ/mol or 19.9 meV. This equation is valid for rotation about a threefold cubic axis, defined by one N–H bond. These results for activation energy E_a and barrier height V_0 can be compared using a simplified and essentially lower limit value of the zero-point energy that includes only the librational mode, such that $V_0 = (1/2)E^{\text{lib}} + E_a$, yielding a potential barrier of 12 meV, roughly 8 meV less than that calculated with Eq. (6). This is not surprising given the simplified V_0 calculation and the probable underestimation of the E_a mentioned above. However, if the derived E_a is reflective of reorientational jumps from the first-excited librational level, then $V_0 = (3/2)E^{\text{lib}} + E_a = 19.8 \text{ meV}$, in excellent agreement with the result from Eq. (6) above. The change in dynamics observed between 70 K and 80 K is presumably due to NH_4^+ cations breaching the barrier to reorientation, similar to what has been observed³⁴ for ZIF-8 methyl groups. Additionally, this indicates that there is not likely a bound second librational level.

D. Vibrational density of states

The vibrational density of states (VDOS) of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ (and isostructural $\text{Rb}_2\text{B}_{12}\text{H}_{12}$), at 4 K shown in Fig. 5 is similar to that for other dodecahydro-closo-dodecaborate salts.³⁵ It should be noted that the spectra

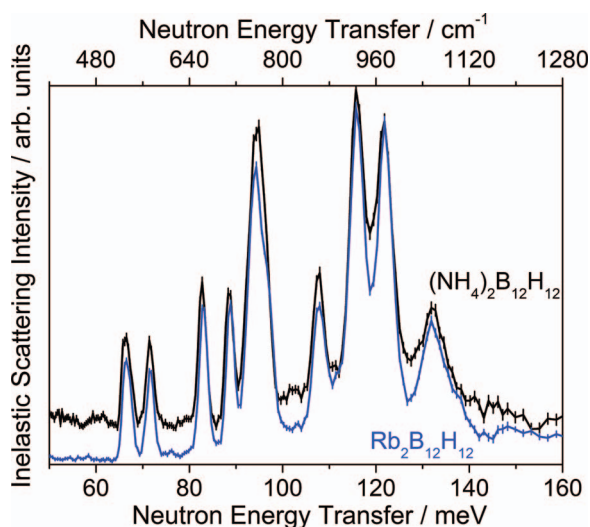


FIG. 5. The neutron vibrational spectrum above 50 meV for $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ (black) compared with the vibrational spectrum for $\text{Rb}_2\text{B}_{12}\text{H}_{12}$ (blue) (Ref. 35). Other than the increased background levels, the $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ spectrum is very similar to the $\text{Rb}_2\text{B}_{12}\text{H}_{12}$ vibrational spectrum, with the $\text{B}_{12}\text{H}_{12}^{2-}$ molecular vibrations isolated from the NH_4^+ modes. Error bars represent uncertainties of one standard deviation.

measured by neutrons provide a VDOS, which largely reflects the frequency spectrum weighted by the amplitude of the hydrogen atoms in the various normal modes of the system (because of the very large hydrogen cross section). The features observed between 40 meV and 160 meV can be attributed to the icosahedron cage of the $\text{B}_{12}\text{H}_{12}^{2-}$ anion. Cage deformations are observed between 65 meV and 100 meV as well as 120 meV and 135 meV. Hydrogen wags are observed throughout the 100 meV–135 meV range. The energies of the B–H stretching modes are too high to be observed in the spectra presented here. The ammonium vibrational modes are also expected to be largely outside this spectral range. A higher background is the biggest difference between the $\text{Rb}_2\text{B}_{12}\text{H}_{12}$ and $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ VDOS, which presumably originates from combination bands and overtones of the additional NH_4^+ hydrogen-atom scattering in the low-energy regime.

The low-energy VDOS at 4 K, shown in Fig. 6, is a broad band with peaks at 7.8 meV, 9.2 meV, and 10.6 meV. The larger energy range of Fig. 6(b) shows an additional feature at 13.8 meV. Minor spurious contaminant peaks stemming from a small fraction of higher-order diffraction events from the monochromator (leading in turn to a small fraction of incident neutrons with one-half of the expected wavelength) contribute intensity at $\approx 15.7 \text{ meV}$ and are designated with asterisks. Based on observations and calculations of the alkali and alkaline-earth dodecahydro-closo-dodecaborates,³⁵ it is expected that the $\text{B}_{12}\text{H}_{12}^{2-}$ translation and libration modes contribute intensity near 11 meV and 14 meV, respectively, although they are likely not as isolated from the counter-ion in the present system. These modes soften as the temperature increases, e.g., the $\text{Cs}_2\text{B}_{12}\text{H}_{12}$ translation and libration modes shift downward by 0.5 meV and 1 meV, respectively, as the temperature warms from 4 K to 300 K.⁹

Generally speaking, the energy of the ammonium libration decreases with activation energy and potential energy barrier (see Eq. (6)). This trend has been tabulated in a previous publication on ammonium ion tunneling.¹⁶ Ammonium reorientation activation energies for $(\text{NH}_4)_2\text{SnCl}_6$ and NH_4ClO_4 are 5 kJ/mol and 2 kJ/mol, just higher than that presented here for $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ and are assigned librations at 13.4 meV and 6 meV, respectively.¹⁶ Although a system with an activation energy of less than 1 kJ/mol following this trend would exhibit a libration below 6 meV, there are no such modes visible in the $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ spectra. There is, however, a mode at 7.8 meV that we assign to the ammonium librations. The temperature dependence of this feature (Fig. 6(b)) is consistent with an ammonium libration: as temperature increases, the intensity of the 7.8 meV peak drops and shifts to increasingly higher energies, approaching a distribution of rotational transitions characteristic of quasi-free rotation.³⁶

However, the librational modes are not expected to be isolated motions of either the NH_4^+ or the $\text{B}_{12}\text{H}_{12}^{2-}$ ion, as evidenced by the softened potential of this NH_4^+ cation relative to those ammonium compounds with smaller counter-anions. The barrier to ammonium rotation may be lowered by a cooperative gearing libration of the $\text{B}_{12}\text{H}_{12}^{2-}$ anion. It is possible that librational modes contribute more intensity

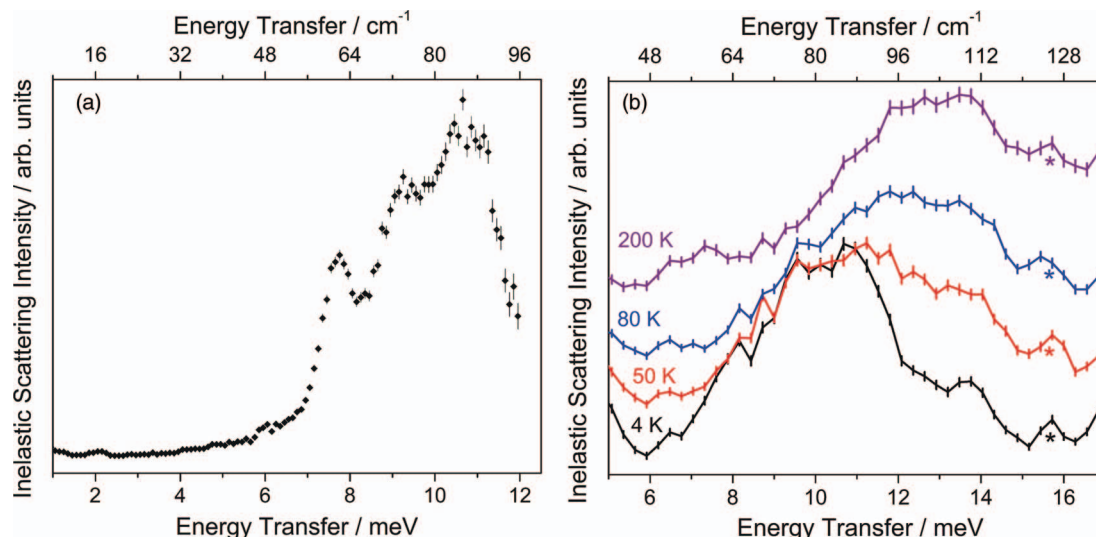


FIG. 6. The low-energy neutron vibrational spectra collected at 4 K (black, (a) and (b)), 50 K (red (b)), 80 K (blue (b)), and 200 K (purple (b)). The peak at 7.8 meV (63 cm^{-1}) is assigned to the $0-1\text{ NH}_4^+$ librational transition. The remaining vibrational intensity can be at least partly attributed to translations and librations of $\text{B}_{12}\text{H}_{12}^{2-}$. Error bars represent uncertainties of one standard deviation. The asterisks represent contaminant intensity in the spectra in (b), which were collected on a different spectrometer, with different energy resolution than the spectrum in (a).

between 6 meV and 16 meV than just the mode at 7.8 meV. These are bound librations at low temperatures, gaining in rotational freedom with temperature. Given the large barrier to $\text{B}_{12}\text{H}_{12}^{2-}$ reorientation,⁹ the icosahedron will not attain observable reorientational rates at the temperatures used here.

E. Neutron powder diffraction

The $Fm\bar{3}$ structure determined from neutron powder diffraction is consistent with that previously observed¹¹ by single-crystal x-ray diffraction at room temperature. The diffraction patterns with refinements are shown in the supplemental information (SI),²⁶ in Figs. S2, S3, and S4. At 298 K, the lattice parameter is found to be $10.8764(4)\text{ \AA}$. At 8 K, the lattice has contracted to $10.8348(2)\text{ \AA}$ but remains in the cubic phase. Derived thermal ellipsoids (in Table S1 of Ref. 26 and Fig. 7) indicate that the ammonium hydrogen atoms are localized in an ordered tetrahedral configuration at 8 K and 50 K. This supports the dynamic model of discrete jumps about the C_3 axes that was deduced from observations of quasi-elastic neutron scattering at 60 K. The ammonium hydrogen nuclei become quite delocalized at room temperature, corroborating

the model of pseudo-free rotation of the ammonium ions as temperature increases.

F. Relevance to hydrogen storage

$(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ is a lightweight material containing, a mass fraction of 11.3% hydrogen. A recent *ab initio* study¹⁰ reports that release of hydrogen from this material is energetically favorable. The scope of the study does not include the energetics of the reverse reaction, nor does it present the energetics of the dehydrogenation reaction compared with a known polymerization reaction¹³ of the same material. The possibility of polymerization during hydrogen desorption, the stability of the polymerization product, and the reversibility of the desorption reaction must be investigated before storage viability is properly assessed.

The DFT calculations reproduce the crystal structure, but it is unclear whether the frequencies of the normal modes, especially the NH_4^+ librations, were accurately reproduced. Our own DFT calculations, while in good agreement with the internal molecular vibrations (see Fig. S5 in the SI (Ref. 26)), poorly reproduce the low-frequency region (see Fig. 8) and include imaginary frequencies. This is likely due to the importance of the weak $\text{N-H}\cdots\text{H-B}$ dihydrogen-bonding interactions and the weak van der Waals interactions in intermolecular vibrations, which are known to be poorly modeled in conventional DFT. In light of the potential sensitivity of thermodynamic parameters to vibrational frequencies³⁷ and the limitations of reaction pathway calculations, thermodynamic parameters calculated for $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ based on DFT-derived vibrational spectra should be viewed with some caution. However, our results demonstrate that, at room temperature and certainly at the high temperatures relevant to hydrogen storage materials, the ammonium ion will have enough thermal motion to overcome weak interactions with the $\text{B}_{12}\text{H}_{12}^{2-}$ cage.

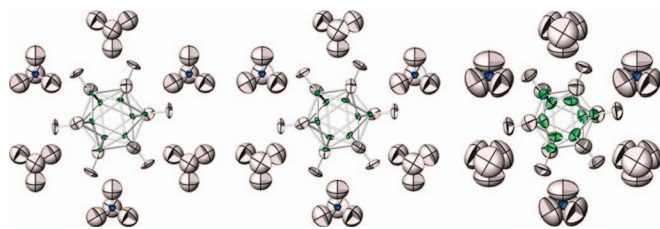


FIG. 7. $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ structural views down the $[111]$ axis showing changes in thermal ellipsoids with temperature as determined from NPD refinement at 8 K (left), 50 K (center), and 298 K (right). Boron, nitrogen, and hydrogen are in green, blue, and white, respectively.

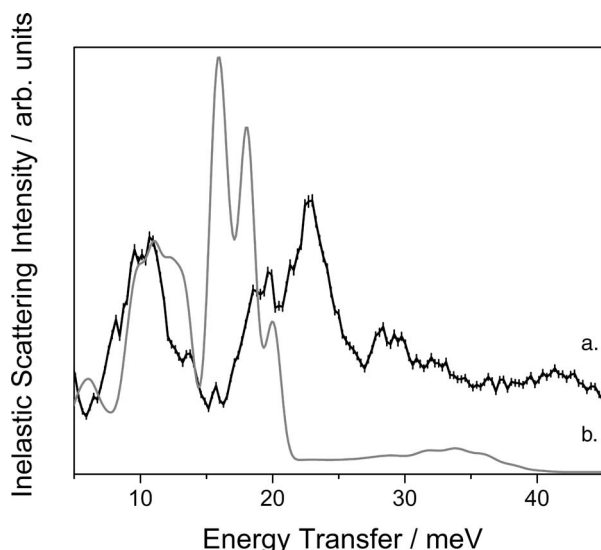


FIG. 8. (a) The low-energy neutron vibrational spectrum collected at 4 K compared with (b) the spectrum simulated from the DFT calculation.

It is as yet unknown how viable $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ might be for reversible hydrogen storage. It has been generally observed^{2–4,38–40} that if $\text{B}_{12}\text{H}_{12}^{2-}$ forms during a dehydrogenation reaction, the reversibility of the reaction suffers. However, boron-containing materials remain attractive storage materials, for their lightweight properties and for their intermediate bond strengths.⁴¹ Even if cycling conditions are optimized to minimize B_2H_6 formation and, therefore, $\text{B}_{12}\text{H}_{12}^{2-}$ production,¹ it is possible that stable boron polyhedrons (such as $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$) will accumulate over the (ideally lengthy) lifetime of a storage medium. Destabilization of these polyhedra would increase the viability of the boron-based hydrogen-storage materials considerably. For example, the addition of CaH_2 to $\text{CaB}_{12}\text{H}_{12}$ has been shown³⁹ to destabilize $\text{CaB}_{12}\text{H}_{12}$, improving hydrogen release.

IV. CONCLUSIONS

The observed tunneling splitting of $18.5 \mu\text{eV}$ is much larger than that observed previously in other ammonium systems (e.g., from $(\text{NH}_4)_2\text{S}_2\text{O}_8$ with tunneling splitting of $1.09 \mu\text{eV}$ (Ref. 14) to NH_4ClO_4 with the A-T splitting as large as $5.75 \mu\text{eV}$ (Ref. 27)), in which there is stronger ionic and possibly directional bonding between ions. The implication is that in the case of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, there is clearly coupling between ammonium ion rotational configurations, with a small barrier to rotation. The tunneling spectrum proves the tetrahedral symmetry of the ammonium ion in this crystal environment. These observations are all consistent with the dominance of weak non-directional interactions between the two ions.

Tunneling and quasi-elastic spectra in conjunction with inelastic neutron vibrational spectra, solid state DFT calculations, and diffraction results provide a thorough description of the thermal behavior and potential energy surface encountered by the ammonium ion of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$. Weak, non-isotropic

forces (such as van der Waals and dihydrogen) seem to dominate $\text{NH}_4\text{--B}_{12}\text{H}_{12}$ interactions at low temperatures, stabilizing the tetrahedral symmetry of the NH_4^+ ion and preventing its unrestricted rotation, as seen in the diffraction results at 8 K and 50 K. Ammonium reorientation observed by quasi-elastic neutron scattering between 50 K and 70 K involves discrete jumps that retain crystallographic order. Under the influence of these interactions, the ammonium ion rotates with equal probability about all four C_3 axes. These weak interactions are often poorly modeled in the DFT calculations. Such shortcomings are the suspected cause of disparities between those calculations and the observed low-energy vibrational density of states. These weak forces are overcome even at moderately low temperatures. By 70 K, the Arrhenius plot shows a change in slope, implying a change in dynamics, consistent with a breach of the rotational barrier (with its $8.1 \pm 0.6 \text{ meV}$ activation energy) encountered at the lowest temperatures. By 200 K, the low-energy density of states observed with inelastic neutron scattering displays the characteristic intensity distribution of ammonium pseudo-free rotation.

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