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Investigation of an unusual low-temperature phase transformation in $RbBH_4$ by neutron diffraction

Brian B. Kitchen[a], Nina Verdal[b,c,*], Terrence J. Udovic[b], John J. Rush[b,c], Michael R. Hartman[a], Daniel J. DeVries[d]

[a] Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI 48109, USA
[b] NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102, USA
[c] Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115, USA
[d] Radiation and Isotopes for Health, Delft University of Technology, Mekelweg 15, 2629 JB Delft, Netherlands

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ABSTRACT

To investigate the previously reported low-temperature phase transition in rubidium borohydride ($RbBH_4$) near 48.5 K, we carried out neutron powder diffraction and vibrational spectroscopy measurements both above and below this temperature on an isotopically-enriched sample of $Rb^{11}BD_4$. Our diffraction data reflected an average cubic $Fm\overline{3}m$ structure with BD_4^- anion orientational disorder at all temperatures, with no hint of extra Bragg peaks due to long-range orientational order below the transition temperature as reported by others. These structural results and careful analysis of torsional vibrations in $RbBD_4$ corroborate the results of prior neutron vibrational spectroscopy measurements suggesting that the low-temperature $RbBH_4$ structure indeed possesses some orientational ordering of the BH_4^- anions, but of a shorter-ranged nature insensitive to powder diffraction methods.

1. Introduction

The borohydrides are of interest as hydrogen-storage materials. In particular, the alkali-metal borohydrides have recently been the subject of intense experimental and theoretical investigation to understand their structural and dynamical properties. A number of previous studies [1,2] have established that the alkali borohydrides, aside from $LiBH_4$, all have a cubic structure at high temperatures. In $NaBH_4$ and KBH_4, there is a low-temperature phase transition to a tetragonal structure ($P4_2/nmc$) with ordering of the BH_4^- ions. However, the heavier Rb and Cs borohydrides, while exhibiting evidence of a low-temperature transition by heat capacity [3–5] and, very recently, neutron vibrational spectroscopy (NVS) [6] studies, have thus far shown no clear evidence for a structural change at their transitions, which is highly unusual.

Renaudin et al. [2] investigated this transition for both the Rb and Cs compounds via X-ray diffraction (XRD) and neutron powder diffraction (NPD) measurements. No structural transitions were explicitly determined by XRD between 10 K and 295 K (over a momentum transfer (Q)-range of $0.71\ \text{Å}^{-1} \leq |\vec{Q}| \leq 6.2\ \text{Å}^{-1}$). Further investigations using NPD at 295 K and 1.5 K, over a Q-range of $0.85\ \text{Å}^{-1} \leq |\vec{Q}| \leq 3.75\ \text{Å}^{-1}$, observed no obvious indications of anion ordering. For the low-temperature 1.5 K NPD data, two very small peaks at low Q were interpreted by Renaudin et al. [2] as a possible indication of a superstructure lattice due to an order-disorder transition. These earlier diffraction studies, including the somewhat tentative low-Q results, motivated our further investigation of a potential order-disorder phase transition.

In this work, we have used a combination of NVS to verify the presence of a phase transition in an isotopically-enriched $Rb^{11}BD_4$ powder sample; NPD over a larger Q-range ($0.21\ \text{Å}^{-1} \leq |\vec{Q}| \leq 8.09\ \text{Å}^{-1}$) to confirm the structure and investigate the behavior across the order–disorder transition; and lastly, additional low-Q diffraction measurements with higher statistical precision than in previous experiments, in an attempt to corroborate the presence of weak, long-range-order-induced superstructure peaks below the phase transition.

2. Materials and methods

The deuterated rubidium borohydride was prepared through a metathesis reaction between ^{11}B-enriched sodium borodeuteride ($Na^{11}BD_4$) and rubidium hydroxide (RbOH). The RbOH was dissolved in deionized H_2O to give a 9 mol/L solution. The $Na^{11}BD_4$ was synthesized from 99.83% ^{11}B-enriched boric acid as previously

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[*] Corresponding author at: NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102, USA.
E-mail address: nina.verdal@nist.gov (N. Verdal).

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reported [7], and was added in a 2:1 mol ratio ($Na^{11}BD_4$:RbOH) in order to ensure all the rubidium hydroxide was converted by the following reaction:

$$RbOH + Na^{11}BD_4 \rightarrow Rb^{11}BD_4 + NaOH$$

The solution was shaken vigorously for ≈1 min. The reaction resulted in an aqueous solution containing unreacted $Na^{11}BD_4$, the NaOH byproduct, and the $Rb^{11}BD_4$ as a precipitate. The precipitate was collected using a fine-glass-frit Büchner funnel and was rinsed with two separate 50 mL portions of isopropanol, which served to remove any $Na^{11}BD_4$ or NaOH that co-precipitated with the product. The finely divided powder was collected and dried with diethyl ether to remove excess H_2O. The product was then dried under vacuum at 523 K for ≈24 h. The final $Rb^{11}BD_4$ product was verified by FT-IR and XRD. The final isotopic composition of the sample was determined to be $Rb^{10}B_{0.040 \pm 0.005}{}^{11}B_{0.960 \pm 0.005}D_{3.83 \pm 0.03}H_{0.17 \pm 0.03}$ by prompt gamma neutron activation analysis performed at the Oregon State TRIGA Reactor [8]. Natural boron and polyethylene samples were used as standards. Since the isotopic composition is directly related to the sample scattering length density, it was utilized in the refinement of the structural models. (N.B., for the sake of simplicity, we will refer to the sample as $RbBD_4$ throughout the rest of this paper.)

NVS data were collected between 4 K and 58 K with the Filter-Analyzer Neutron Spectrometer [9] at the NIST Center for Neutron Research (NCNR). The Cu(2 2 0) monochromator was used with pre- and post-collimations of 40′ and 20′, respectively, over an energy transfer range of 25–46 meV (1 meV=8.066 cm^{-1}). The pyrolytic graphite (0 0 2) monochromator was used with both 20′ pre- and post-collimations over an energy transfer range of 15–33 meV. The DAVE software package was used to reduce the data [10].

NPD data were collected using the BT-1 32-detector neutron powder diffractometer[11] at the NCNR. A Cu(3 1 1) monochromator with a 90° take-off angle, yielding a neutron wavelength of 1.5403(2) Å, and in-pile collimation of 15 min of arc were used. Data were collected over a 2θ range of 3–168° (a Q range of 0.2–8.1 $Å^{-1}$) with a step size of 0.05°. The sample was sealed in a vanadium container of length 50 mm and diameter 9.2 mm inside a dry He-filled glovebox. A closed-cycle He refrigerator was used for temperature control. NPD data were collected at 5 K and 60 K, below and above the reported 48.5 K phase transition. Low-Q diffraction measurements were performed at 4 K, 38 K, and 58 K with 4 Å neutrons, using the cold-neutron, Spin-Polarized Triple-Axis Spectrometer (SPINS) instrument [12] at the NCNR with a large flat analyzer to enhance the data collection rate.

3. Results and discussion

Neutron vibrational spectra in the region of the anion torsional bands at 38 K and 55 K are shown in Fig. 1. Three torsional bands are evident, centered near 28.6 meV, 31.7 meV, and 35.9 meV. The 28.6 meV band is associated with the fully deuterated BD_4^- anions. As ≈4% of the D atoms in the nominal $RbBD_4$ sample are replaced by H atoms, the majority of these H atoms contribute to BHD_3^- defect anions within the structure. If one assumes statistical mixing, then a much smaller fraction of anions will alternatively contain two H atoms to form $BH_2D_2^-$ defect anions (and even smaller fractions will contain either three or four H atoms to form either BH_3D^- or BH_4^- defect anions, respectively). Despite the small number of isotopically mixed defect anions compared to BD_4^-, the much larger scattering cross section for H compared to D means that at least the former two defect anions will be observable. Indeed, the prominent 31.7 meV and 35.9 meV torsional bands are associated with BHD_3^- and $BH_2D_2^-$ defect anions, respectively, their higher energies due to their smaller inertial masses.

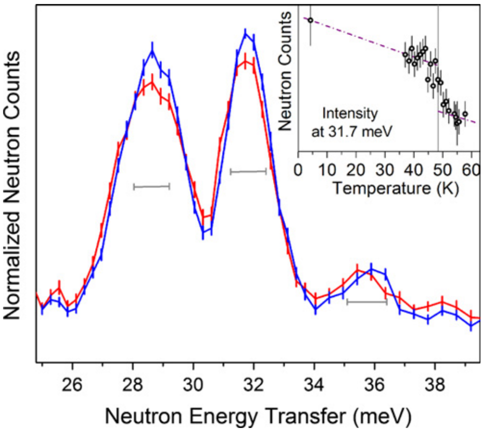

Fig. 1. Neutron vibrational spectra of $RbBD_4$ (with ≈4% H) measured at 38 K (blue) and 55 K (red). The spectral features at 55 K are shifted slightly to lower energies. Horizontal bars denote the instrumental resolution. Inset: neutron scattering intensity at 31.7 meV as a function of temperature. The vertical gray line denotes the phase transition temperature of 48.5 K reported for $RbBH_4$ (Ref. [6]) and the dashed purple line is a guide to the eye. All vertical error bars denote $\pm 1\sigma$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

It is clear from a comparison of the 38 K and 55 K vibrational spectra that all the torsional bands soften in a similar fashion to that observed previously for $RbBH_4$ below and above the 48.5 K phase transition [6], albeit not as dramatically. In particular, as $RbBH_4$ increases in temperature across the phase transition, the BH_4^- torsional band is shown to both soften and broaden. First-principles phonon calculations strongly suggested that this was a direct manifestation of a transition from a structure with orientationally ordered anions, at least on a short-ranged scale, to one with orientational disorder. The 4 K spectrum for $RbBD_4$ is seen to be almost identical to the 38 K spectrum (see Fig. S1 in the Supplementary Material), indicating that the ordering is already complete at this higher temperature. We corroborated the presence of a phase change by measuring the scattering intensity at the BHD_3^- band maximum (at 31.7 meV) as a function of temperature at 4 K and between 37 K and 58 K with approximately 1 K steps. Typically, each point was measured for 15 min with 10 min of equilibration time between measurements. The data is plotted as an inset of Fig. 1. It indicates the presence of an expected step change in intensity near the 48.5 K transition temperature, as observed for $RbBH_4$ previously [6]. This confirms that the $RbBD_4$ phase transition temperature is close to that for $RbBH_4$, and is thus not very sensitive to isotopic composition.

The NPD data collected on the BT-1 diffractometer were analyzed via Rietveld crystal structure refinement [13] using the GSAS [14] computer code as implemented in EXPGUI [15]. Similar to the results of Renaudin et al. [2], the NPD data at both 5 K and 60 K were well fit with a BD_4^- orientationally disordered structural model in the space group $Fm\bar{3}m$ (see Fig. 2). The results of the structural refinements for 5 K and 60 K are illustrated in Fig. 3, and the parameters associated with these fits are provided in Tables S1 and S2 in the Supplementary material.

Finally, in order to further investigate the possibility of long-range order as suggested by the data of Renaudin et al. [2], we measured low-Q diffraction patterns under much better signal-to-noise conditions than for the data in Ref. [2], using the SPINS instrument with 4 Å neutrons. To assure that the $RbBD_4$ sample had the maximum chance to develop a long-range-ordered structure in the low-temperature phase, we lowered the temperature through the phase transition at 48.5 K and kept the sample at 38 K