

Structural Quantum Isotope Effects in Amorphous Beryllium Hydride

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Introduction

Light and heavy liquids or noncrystalline solids fabricated by hydrogen-deuterium substitution chemistry are known to exhibit measurable changes in their thermodynamic properties and structure. The differences in zero point librations and intermolecular binding between isotopically enriched samples are usually reflected in subtle changes in both intermediate range order and local structure. Although these quantum isotope effects are usually small, the extracted information is important for understanding fundamental hydrogen bond interactions and developing realistic interatomic potentials, which include quantum contributions. The magnitude of the quantum component depends on the nuclear masses and the coupling between them. Consequently, there are only a few hydrogenous systems that are likely to show a quantum isotope effect that is larger than that observed for water. Perhaps the most promising candidate is amorphous beryllium hydride (Fig. 1). Its molecular weight increases 18% when it changes from BeH_2 to BeD_2 . The molecular weight of water increases 11% when it changes from light water (H_2O) to heavy water (D_2O).

Because of their unusually low mass and high hydrogen content, beryllium hydride and its derivatives

have historically received much attention for their potential applications in fields such as rocket fuel technology and nuclear materials. Beryllium hydride has also served as a popular test bed for several recent electronic structure calculations that used *ab initio* methods, and it has been the focus of numerous theoretical studies in both gas and condensed phases. However, very few experimental data are available. An accurate experimental measurement of the Be-H bond length for the linear gas-phase BeH_2 molecule has only recently been determined [1]. The standard temperature and pressure phase of BeH_2 is an amorphous solid, which can transform into two known crystalline phases at higher temperatures and pressures, both of which are composed of network-forming tetrahedral structures. Early models suggested amorphous BeH_2 was composed of edge-shared tetrahedra in a polymeric chain structure, similar to that of beryllium chloride (BeCl_2) and dimethyl beryllium [$\text{Be}(\text{CH}_3)_2$]. This has been superseded, however, by more recent modeling of low-resolution neutron diffraction measurements, which suggest that the structure of amorphous BeH_2 is composed of corner-sharing tetrahedra, similar to the structure found in the tetragonal crystalline phase (Fig. 2). Consequently, BeH_2 is analogous to other classic network-forming glasses such as amorphous H_2O , BeF_2 , SiO_2 , and GeO_2 . In comparison, the average intertetrahedral $\angle\text{Be-D-Be} = 135 \pm 1^\circ$ for BeD_2 (calculated from peak positions), whereas $\angle\text{Be-F-Be} = 139^\circ$ in BeF_2 , $\angle\text{Si-O-Si} = 146^\circ$ in SiO_2 , $\angle\text{Ge-O-Ge} = 132^\circ$ in GeO_2 , and $\angle\text{O-H-O} = 165^\circ$ in H_2O . Consequently, the interesting variation of BeH_2 from the other vitreous systems is that it is a hydride, indicating some potential analogy to H_2O .

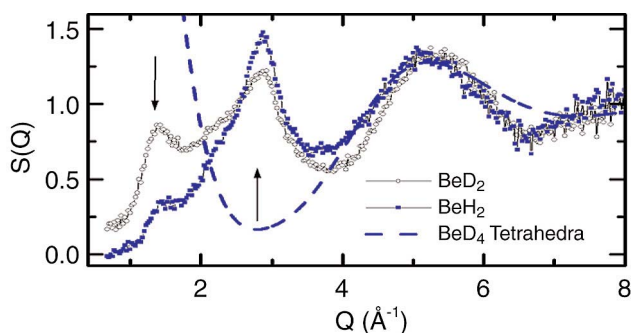


FIG 1. The pseudo-nuclear x-ray structure factor for amorphous BeD_2 (circles) and amorphous BeH_2 (squares). The dashed line represents the calculated signal from an isolated BeD_4 tetrahedra. Note that the first sharp diffraction peak decreases and the second peak increases when BeD_2 changes to BeH_2

Methods and Materials

Amorphous BeH_2 and BeD_2 were synthesized by using standard methods. The purity of both samples was determined to be $\geq 95\%$ by using infrared and Raman spectroscopy as well as elemental analysis. The only difference between the samples was the isotopic enrichment of $\geq 98\%$ D in the deuteride sample. High-energy x-ray measurements were performed on the weakly scattering BeD_2 and BeH_2 samples by using a

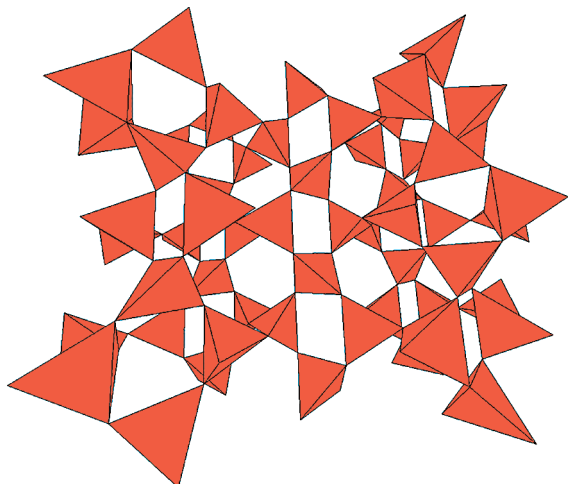


FIG. 2. Perspective 3-D view of crystalline tetrahedral corner-shared BeH_2 network.

~115-keV beam on the BESSRC ID-11-C beamline at the APS. The data were analyzed by standard analysis routines [2].

Results and Discussion

The observed trend has been interpreted as increased intermediate range ordering of the cation correlations in beryllium deuteride compared to the hydride [3]. This is in good agreement with earlier measurements on other materials. The surprising result here is the magnitude of

the measured isotopic structural difference between the light and heavy materials. The marked increase in intermediate range order is probably due to the propensity of amorphous BeD_2 to form an extended network compared to BeH_2 . It may be less likely (but cannot be ruled out) that it is a reflection of the polymorphism that is conjectured in the crystal structures. Nonetheless, the magnitude of the measured effect provides the most rigorous test yet in the development of the quantum part of the interatomic potential in a binary amorphous solid.

Acknowledgments

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