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Structural evolution of ammonia borane for hydrogen storage

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We have studied the crystal structure of fully deuterated BH_3NH_3 using powder neutron diffraction at different temperatures. It is evident that an order-disorder phase transition occurs around 225 K. At low temperature, the compound crystallizes in the orthorhombic structure with space group $Pnm2_1$ and gradually transforms to a high temperature tetragonal structure with space group $I4$ mm above 225 K. At 16 K, the BD_3-ND_3 unit stacks along the c axis with a tilt angle of about $16°$ between the N–B bond and the c axis. As the temperature is increased, the BD_3-ND_3 groups start to reorient along the c axis and the deuterium atoms become disordered, leading to the tetragonal phase transition. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2889535]

Ammonia borane (BH_3NH_3) is a promising hydrogen storage material because of its high gravimetric (19.6 wt % H_2) and volumetric hydrogen density and moderate decomposition temperature.[1–8] It has been shown that BH_3NH_3 can release hydrogen in the temperature range of 350–410 K.[5,9] Hydrogen can be readily released from BH_3NH_3 either by hydrolysis or by heating. Recent studies indicated that the kinetics of the hydrogen desorption can be improved by using silica as a catalyst or by milling and doping with additives.[2,7,8]

In order to improve the kinetics of the hydrogen absorption and desorption in BH_3NH_3, it is critical to understand the geometric and electronic factors that govern the stability, reactivity, and inter- and intramolecular interactions. Therefore, it is very important to determine the accurate crystal structure of BH_3NH_3. The structure of BH_3NH_3 has been investigated by several groups using x-ray diffraction[10–14] (XRD) and neutron diffraction (ND).[15] The previously reported structures determined using XRD and ND on hydrides show discrepancies in the bond lengths and atomic coordinates. X-ray studies[11,12] found a body-centered tetragonal unit cell for BH_3NH_3 at room temperature, whereas Hoon and Reynhard[13] suggested that the structure is face-centered orthorhombic. At approximately 225 K, a phase transition from tetragonal to orthorhombic occurs.[12] Recent studies confirmed the tetragonal unit cell at room temperature and the orthorhombic cell at low temperature.[14,15] However, there are significant differences among the atomic coordinates and lattice parameters of BH_3NH_3 in the results of Refs. 14 and 15, even taking into account the temperature effect. The distance between the nearest nitrogen and hydrogen atoms at low temperature d_{N-H} is only 0.80 Å,[14] considerably shorter than 1.07 Å.[15] One would expect bond distances, as determined by XRD to be shorter than those obtained from ND due to the fact that x-rays are scattered by extranuclear electrons, whereas the neutrons are scattered by the nucleus. Nevertheless, this extremely short bond distance cannot be entirely rationalized on the above basis. Therefore, a further systematic study is required to clarify these ambiguities in

the crystal structures of BH_3NH_3 at different temperatures. Knowledge of the fundamental properties of BH_3NH_3, especially the accurate location of the hydrogen atoms is critical to an understanding of and improvement in the hydrogen absorption and desorption ability in the BH_3NH_3 system. In this paper, the crystal structure of fully deuterated BH_3NH_3 was studied using powder neutron diffraction with high sensitivity at different temperatures.

A sample of BH_3ND_3 was first prepared by the method of Hu *et al.*[16] The BD_3ND_3 sample was obtained by dissolving BD_3NH_3 in D_2O and stripping off the D_2O under vacuum. The resulting powder of BD_3ND_3 was then placed into a vanadium container (5 mm diameter) and sealed in a glovebox under an argon atmosphere to avoid moisture. The ND experiments were performed at the University of Missouri-Columbia research reactor using neutrons of wavelength $\lambda = 1.478\ 961$ Å. The refinement of the data was carried out using the FULLPROF program.[17]

Figure 1 shows the neutron powder diffraction pattern of BD_3ND_3 collected at different temperatures. It is obvious that the diffraction pattern at 16 K shows more peaks and complexity as compared to the pattern at RT. Some peaks are merged and disappear as the temperature increases. At about 225 K, additional peaks appear and the number of the peaks is greatly reduced, indicating that a phase transition of much higher symmetry has occurred. The pattern at 16 K can be indexed in an orthorhombic cell with space group $Pnm2_1$, and with $a = 5.553\ 95(29)$, $b = 4.610\ 48(21)$, and $c = 5.000\ 04(21)$ Å. The unit cell has 2 fu. The pattern at room temperature can be indexed as a body-centered tetragonal unit cell with space group $I4$ mm, and with lattice parameters $a = b = 5.228\ 14(64)$ and $c = 5.021\ 82(61)$ Å. The atomic coordinates proposed by Bowden *et al.*[14] were used as starting parameters in the refinement for data at 16 K. In Table I, we list the refined atomic positions. The positions of hydrogen atoms are significantly different from those values,[13–15] which significantly changes the bond distances between N and H. This is likely due to the fact that our ND patterns allow us to more accurately locate both boron/nitrogen and hydrogen/deuterium positions. The main problem in the x-ray structural analysis for compounds, such as
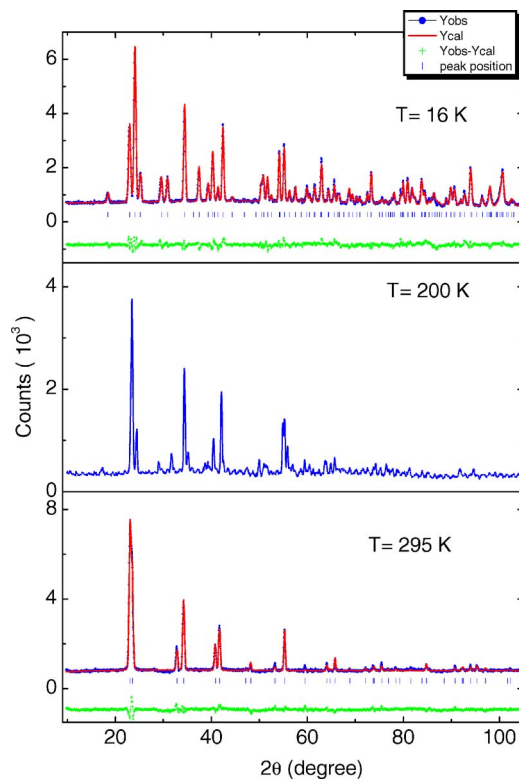
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FIG. 1. (Color online) Neutron diffraction patterns of BD_3ND_3 at different temperatures. In the patterns, the bottom curves (Y_{obs}-Y_{cal}) are the difference between xperimental data and refinement data. The vertical bars indicate Bragg peak positions.

light metal hydrides with low atomic numbers, is their poor scattering ability for the incident x-rays. The intensity of coherently diffracted x-rays is proportional to the square of the atomic number and falls dramatically with the decrease of this value. In contrast, neutron scattering from the hydrogen proton (or ideally, the deuteron) gives a reliable measurement of the hydrogen location and occupation. The replacement of hydrogen with deuterium increases the scattering ability. The bond lengths between the nearest nitrogen and deuterium are 1.011 and 0.972 Å, and the B–D bond lengths are 1.208 and 1.222 Å at 16 K, which are

longer than those obtained by previous XRD and ND studies.[14,15] These values are close to those of $LiND_2$ ($d_{N–D}$=1.01 Å)[18] and $LiBD_4$ ($d_{B–D}$=1.214 Å).[19] The bond angles of D1–N–D2 and D3–B–D4 are 105.8° and 114.4°, respectively. We have tried to compare our results with ND data collected at 200 K.[15] It is found that our atomic coordinates are considerably different from those of Ref. 15. This may be caused by the variation of the sample's compositions (our sample is polycrystalline, theirs is a single crystal).

It was proposed by Hoon and Reynhard[13] that the room temperature structure is disordered where the vertices of the hydrogen triangle in the BH_3 and NH_3 group can point in four mutually perpendicular directions, so that each hydrogen can occupy any of the 12 possible positions. However, Bowden *et al.*[14] have proposed a model with eight hydrogen positions around each of the boron and nitrogen atoms. In order to conserve the stoichiometry, the occupancy of each hydrogen position is 3/8. We have tried to refine the structure with 12 hydrogen or eight hydrogen positions around each of the boron and nitrogen atoms. The best refinement with χ^2=3.21% was obtained for the model with eight hydrogen positions. We list the results of the refined structure in Table I. The atomic coordinates are significantly different from those obtained in Ref. 14. The bond lengths between the nearest nitrogen and deuterium atoms are 0.950 and 0.951 Å, and B–D bond lengths are 1.20 and 1.199 Å. As expected, these values are longer than the single crystal XRD study, where the N–H bond is found to be 0.85 Å.

Figure 2 shows the dependence of the lattice parameters on the temperature from 16 to 370 K. It can be seen that the c cell parameter remains unchanged in the orthorhombic phase from 16 to 225 K. The lattice parameter a decreases from 5.553 to 5.336Å, while the length of the b axis increases from 4.610 to 5.018 Å from 16 to 225 K. The cell parameters a and b and the unit cell volume have abrupt changes at the phase transition region. It is interesting to note that there is a kink in the curve of the unit cell volume around 225 to 250 K. The reason for this kink is still under investigation.

Figure 3 plots the evolution of the crystal structures of BD_3ND_3 at 16, 200 K, and RT. It was found that at 16 K, the

TABLE I. Refinement parameters of BD_3ND_3 at 16 K and RT. Space group is $I4\,mm$ at RT and $Pmn\,2_1$ at 16 K. x, y, and z are the fractional position coordinates, a, b, and c are the lattice parameters, and n is the occupation number. χ^2 is $(R_{wp}/R_{expt.})^2$.

| Atom	site	x	y	z	n	B (Å^2)
T=16 K, a=5.553 95(29), b=4.610 48(21), and c=5.000 04(21) Å, χ^2=3.03%
B	2a	0	0.156 90(144)	0	0.5	0.602(119)
N	2a	0	0.248 21(75)	0.304 32(113)	0.5	0.095(63)
D1	2c	0	0.456 68(128)	0.333 44(141)	0.5	2.042(156)
D2	4b	0.147 14(66)	0.171 98(69)	0.400 67(130)	1.0	1.763(82)
D3	2c	0	−0.105 44(124)	−0.004 48(145)	0.5	2.152(138)
D4	4b	0.179 64(80)	0.268 23(86)	−0.096 74(165)	1.0	4.049(131)
T=295 K, a=b=5.228 14(64) Å, c=5.021 82(61) Å, χ^2=3.21%
B	2a	0	0	0	0.125	3.966(382)
N	2a	0	0	0.670 33(243)	0.125	3.871(217)
D1	8d	0	0.167 88(141)	0.605 45(312)	0.1875	7.060(273)
D2	8c	0.118 70(100)	0.118 70(100)	0.605 45(312)	0.1875	7.060(273)
D3	8d	0	0.227 49(140)	0.037 47(349)	0.1875	7.060(273)
D4	8c	0.160 67(99)	0.160 67(99)	0.037 47(349)	0.1875	7.060(273)
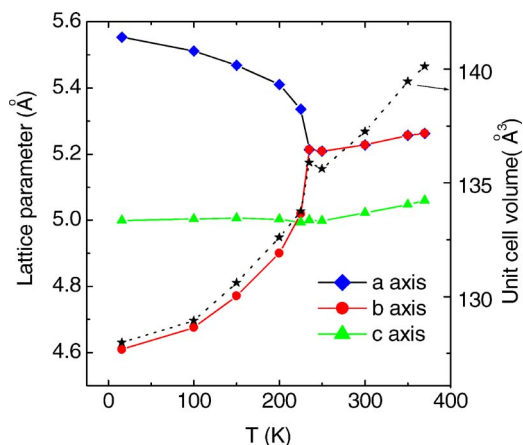
FIG. 2. (Color online) The lattice parameters and unit cell volumes of BD_3ND_3 at different temperatures.

BD_3-ND_3 unit stacks along the c axis with tilt angles of $16°$ and $74°$ between the N–B bond and the c axis and between the N–B bond and the b axis, respectively. The B–N bond is almost perpendicular to the a axis, and the B–D and N–D bonds are stretched along the a-b plane. As the temperature is increased, the BD_3-ND_3 groups start to reorient along the c axis with an increase in the N–B bond length, and the deuterium atoms become disordered, leading to the tetragonal phase transition around 225 K.

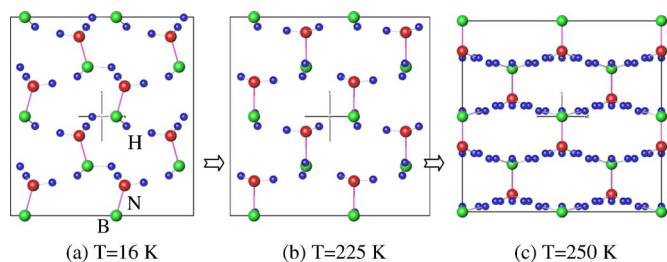In summary, the structure of fully deuterated BH_3NH_3 has been investigated using ND. It is found that the atom coordinates, lattice parameters, as well as bond lengths are different from previous studies. It is found that at 16 K, the BD_3-ND_3 unit stacks along the c axis with tilt angles of $16°$ and $74°$ degrees between the N–B bond and the c axis and between the N–B bond and the b axis, respectively. The B–N bond is almost perpendicular to the a axis, and the B–D and N–D bonds are stretched along the a-b plane. The BD_3-ND_3 groups start to reorient along the c axis as the temperature is increased. The lattice parameter b increases while a decreases from 16 to 225 K. The deuterium atoms become disordered around 225 K, leading to the tetragonal phase transition.

FIG. 3. (Color online) The evolution of the crystal structure of BD_3ND_3 with temperature (projection on the b-c plane) (a) $T=16$ K, (b) $T=225$ K, and (c) $T=250$ K.

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