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Hydrogen mediated affinity of ions found in compressed potassium amidoborane, K[NH₂BH₃]

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The paper reports on experimental and theoretical investigation of bonding properties of potassium amidoborane, (K[NH₂BH₃]) – one of the most promising compounds for hydrogen storage material among metallated derivatives of ammonia borane (NH₃BH₃). For 10 that purpose *in situ* Raman spectroscopy, synchrotron X-ray diffraction measurements and complementary *ab initio* calculations study have been performed under static pressure conditions in the range from ambient pressure up to 25 GPa. Unusual interplay between strong electrostatic and weak dispersive interactions has 15 been revealed resulting in experimental observation of pressure induced formation of relatively strong conventional hydrogen bonding between negatively charged molecular ions. This finding provides new insight for tailoring materials with desirable properties for various uses.

20 First discovered in 1955 [1] ammonia borane (NH₃BH₃) has increasingly attracted attention as one of promising candidates for chemical hydrogen storage materials being undoubtedly in the spotlight of this hot research field [2]. High temperature of hydrogen desorption (from ~110 to >300 ℃) and release of 25 substantial amount of contaminating byproducts are main drawbacks precluding large-scale practical application of ammonia borane so far. This intensifies experimental efforts aiming at destabilization of ammonia borane in order to get material with lower temperature of hydrogen desorption. This is 30 mostly realized by chemical doping or catalysis, usually on the basis of "empirical rules" or by "trial and error" method. At the same time there is still evident gap in understanding the mechanism beyond the decomposition, better knowledge of which should significantly facilitate the design of new material 35 with reduced emission of unwanted byproducts.

Ammonia borane also represents an interesting case of compound wherein dispersive interactions, such as dihydrogen bonds (N-H^{δ+}---^{δ-}H-B), largely define the structure and dynamics of the material at ambient pressure [3]. The dihydrogen bonds, i.e. 40 protonic-hydridic, are known to have strength and directionality comparable with those found in conventional hydrogen-bonded systems [4, 5]. Relatively strong dihydrogen bond interaction plays also an important role in decomposition of ammonia borane, allowing dimerization of NH₃BH₃ molecules and 45 formation of diammoniate of diborane [6]. Recent high-pressure study has revealed a key role of dihydrogen bonds in formation of new polymorphic phases [7].

Ammonia borane derivatives called metal amidoboranes (MAB) have been recently developed as novel hydrogen storage 50 materials, where a cation Me⁺ (Me = Li, Na, etc.) replaces one of the protons (H⁺) of '-NH₃' group leading to ionic molecular crystal M⁺[NH₂BH₃]⁻ [8, 9]. Alkali metal amidoboranes (LiNH₂BH₃, NaNH₂BH, KNH₂BH₃) exhibit improved performance with respect to hydrogen desorption. They were 55 recently shown to release 10.9, 7.5, and 6.5 mass % H₂, respectively, at temperatures of 80–90 ℃, and all show improved desorption kinetics. Furthermore, there is no apparent release of borazine or diborane from these materials [8, 10,11].

A necessary step towards understanding the stability and 60 therefore towards a rational design of ammonia borane derivatives for hydrogen storage is study of structural and vibrational properties response due to changing temperature and pressure, which for the most of ammonia borane derivatives has not yet been accomplished. External pressure has been proved to 65 be an effective means to tune the electronic, optical, magnetic and mechanical properties of materials for novel applications [12]. In general, applying pressure to molecular crystals with weak intermolecular interactions can induce substantial compression of interatomic distances and therefore significantly enhance intra- 70 and intermolecular interactions. This may also lead to changes of bonding as well as symmetry relationships between the molecular entities of the unit cell [13, 14]. More specifically, in a conventional hydrogen-bonded system, X-H---Y (where X and Y stand for donor and acceptor atoms, respectively), experimentally 75 measured vibrational frequencies are strongly dependent on the X---Y distance [15]. By compressing it is possible to reduce the distance in a wide range without chemical doping. Pressure is thus regarded as a clean tool for investigation. Up to date LiNH₂BH₃ (LiAB), the only metallated ammonia borane 80 derivative experimentally studied under pressure, revealed the absence of dihydrogen bonding in the pressure range up to ~20GPa [16].

In this communication we report results of high-pressure study on potassium amidoborane (KNH₂BH₃, KAB), which revealed an 85 interesting case of the compound being on the verge of hydrogen bonding formation.

A pressure generation technique using diamond anvil cell (DAC), transparent for visible light and X-ray radiation, provides a convenient tool for *in situ* studies of vibrational and structural 90 properties under hydrostatic pressure.
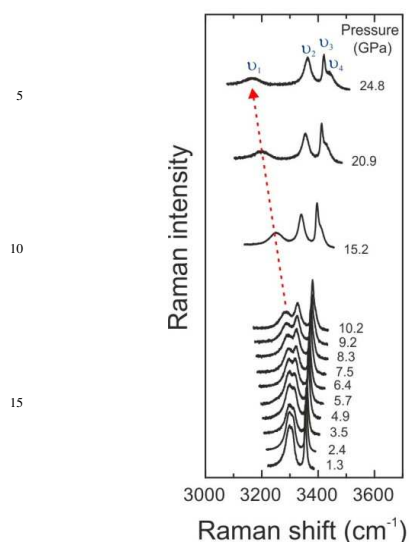
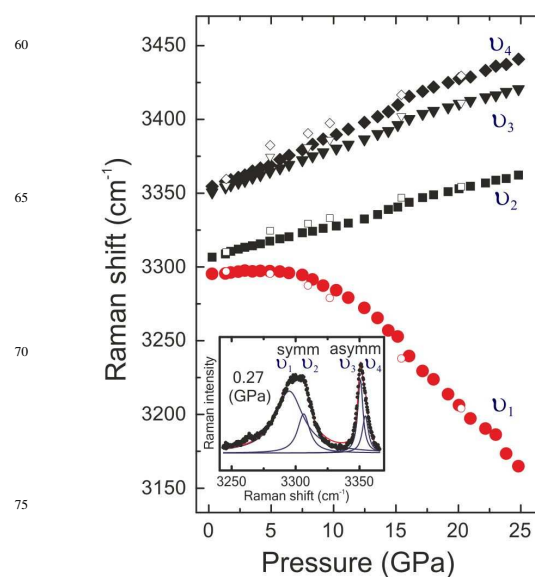Figure 1. Evolution of "N-H" stretching modes of KAB under pressure.

Figure 2. Measured frequencies (solid symbols) as a function of pressure. Inset presents the deconvolution of the measured signal at pressure ~0.27 GPa. Open symbols represent data taken during pressure unloading.

We have conducted *in situ* room temperature Raman spectroscopy, synchrotron powder X-ray diffraction (PXRD) experiments using DAC and complementary first-principles calculations (within the density functional theory (DFT)) in order to investigate the bonding behavior and phase stability of potassium amidoborane at pressure range from ambient to ~25 GPa.

Detailed investigation of the spectral region of 'N-H' molecular vibrations revealed unexpected features about potassium amidoborane. Figures 1, 2 show the behaviour of particular modes under pressure.

In general, there is clear pressure induced differentiation of 'N-H' stretching fundamental modes in compressed material. Application of external pressure, as low as 0.3 GPa, induced clear splitting of 'N-H' modes. There are 4 modes (2 doublets) clearly visible upon deconvolution of measured signal in KAB. This is in contrast to LiAB compound where stretching modes of 'N-H' are represented by 2 modes: symmetric and asymmetric one detected at lower and higher energy, respectively [16]. Apparent difference of 'N-H' vibration spectra reflects more complex crystal structure of KAB featuring two inequivalent positions of atoms as detected in single crystal X-ray diffraction (SXRD) [11] and more recent NMR studies [17].

Compression to ~ 25 GPa resulted in almost complete separation of all four 'N-H' modes. Remarkable behaviour is detected for the mode with the lowest frequency (v_1) which showed pronounced decrease (softening) under pressure.

We now consider in detail the behavior of 'N-H' stretching mode showing a spectacular "redshift" – negative pressure dependence of vibration frequency. Figure 3 shows the pressure-induced softening of 'N-H' stretching mode. Three pressure regions exhibiting different regimes of v_1 behavior are clearly identified: below ~5 GPa, from 5 to 15 GPa and above 15 GPa. Below 5 GPa the frequency (v_1) is virtually pressure insensitive while a gradual decrease of frequency is noted in the second

pressure region. Above 15 GPa strong softening of mode is detected which frequency shows the linear trend with pressure. At the same time, according to our powder XRD study, major features of crystal structure of potassium amidoborane showed no substantial changes in all three pressure regions (Figure 4).

This behaviour is remarkably different from the parent compound as well as LiAB [16]. The observed soft behaviour of all N-H stretching modes in ammonia borane is accounted for strengthening of dihydrogen bonding (N-H$^{\delta+}$---$^{\delta-}$H-B) under pressure.

In case of LiAB, a continuous positive pressure dependence of both symmetric and assymetric 'N-H' stretching modes up to ~ 19 GPa suggests the absence of considerable enhancement of dispersive interactions (dihydrogen or conventional hydrogen bonding) in the material.

The remarkable differentiation of 'N-H' bonds found in potassium amidoborane under pressure discloses a significant gap in up-to-date understanding of bonding properties of ammonia borane based materials.

In order to gain better insight into bonding properties we have theoretically examined the effect of external pressure on structural properties of potassium amidoborane, with particular attention to dispersive interactions, which are usually neglected in calculations. For *ab initio* calculations we used crystal structure parameters obtained by the Rietveld refinement of normal pressure experimental powder XRD data (Figure S1). Resulting calculated data were consistent with our experimental powder XRD data, single crystal XRD data presented in Ref.[11] as well as theoretical data from Ref. [17]. Calculations for higher pressure showed the stable character of the initial crystal structure up to 25 GPa which was consistent with our high-pressure experimental synchrotron structural study. Based on the
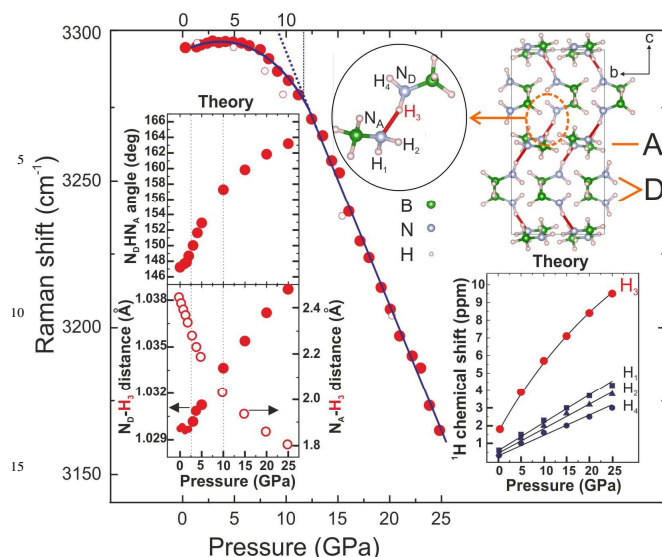
Figure 3. Frequency of ν_1 vibration as a function of pressure. Open symbols represent data taken during pressure unloading. Encircled fragment of the unit cell schematically depicts the formation of hydrogen bonding (red line). Left side inset shows calculated changes of N_D-H---N_A angle (upper panel), N_D-H and N_A-H distances (lower panel: solid and open circles, respectively) with pressure. Right side inset shows the change of ^{1}H NMR chemical shift for particular hydrogen atoms. For clarity the model of the unit cell is shown without sublattice of potassium atoms. "A" and "D" denote two types of layer containing molecular moieties. The arrangement is due to two crystallographic inequivalent sites.

consistency of experimental and calculated data we took theoretical structural data for further analysis.

Detailed investigation of calculated structural data revealed progressive of elongation of certain type of 'N_D-H' (D stands for "donor") interatomic distance above ~ 2.5 GPa (Figure 3 inset (lower panel)). Normally, vibrational frequencies increase with increasing pressure, but in the case of a hydrogen or dihydrogen bonding the frequency may decrease. The stretching frequency of the proton-donor pair will decrease as a function of pressure resulting from a lengthening of the proton-donor bond length. In contrast, the stretching frequency of the proton-acceptor pair will increase with pressure, as do most bond types becoming shorter, i.e. under compression. In present case "NH_2" groups from "D"-type layer seem "donating" one of H atom for nitrogen atoms, N_A, of molecules forming the "A" layer.

Furthermore we analyzed the angle in 'N_D-H---N_A' fragment (Figure 3 left side inset (upper panel)) ("A" stands for "acceptor"). It was found that with pressure the angle gradually increased and the molecular fragment deformed towards linear arrangement.

At the same time one can clearly distinguish three pressure ranges with respect to the monotonic change of the considered angle: <2.5, ~2.5 – 10 and >10 GPa, which is quite consistent with experimental observations detected for the frequency (ν_1) of soft

Based on this finding we suggest that the observed pronounced softening of (ν_1) mode is due to progressive formation of hydrogen bonding in KAB between negatively charged molecular
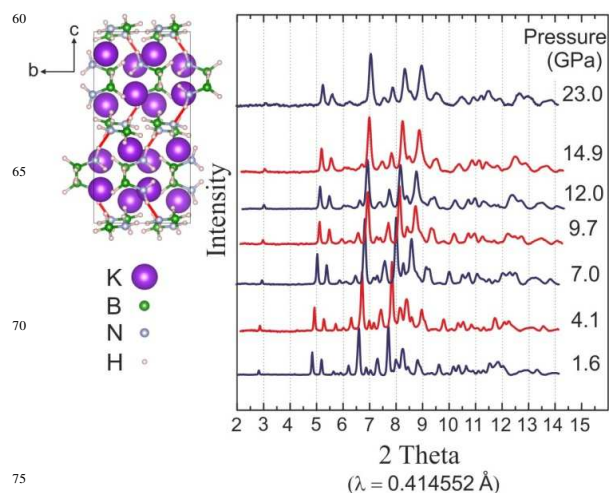

Figure 4. Pressure evolution of room temperature synchrotron X-ray diffraction patterns of KAB.

ions $[NH_2BH_3]^-$ under pressure. For hydrogen bonding to an electronegative acceptor atom such as nitrogen, the hydrogen nucleus involved into hydrogen bond always exhibit a change in the isotropic chemical shift to higher frequencies. Figure 3 (right side inset) presents values of calculated ^{1}H NMR chemical shift for particular hydrogen nuclei as function of pressure (referenced to solid-state L-alanine measurement at ^{1}H shielding of 30.9 ppm.). Hydrogen nuclei H_1, H_2 and H_4 were shown to exhibit a linear change of ^{1}H NMR chemical shift with pressure while the behaviour of H_3 was found remarkably different both in the trend and the magnitude of chemical shift corroborating the assumption of hydrogen bond formation.

This hydrogen bond may be referred as moderate one considering the degree of 'N_D-H' interatomic elongation, values of angle in the 'N_D-H---N_A' group. It is noteworthy to draw attention to the fact, that in the pressure range studied the frequency of the soft mode (ν_1) decreased by ~ 150 cm^{-1}, which is almost three times as much as that of an average change of 'N-H' soft modes in ammonia borane (~50 cm^{-1}) [18, 19].

At the same time to the best of our knowledge there is no example of simple molecular – ionic systems, wherein hydrogen bonding would form between ions of the same polarity. KAB is therefore a unique example of such a material.

In conclusion, our *in situ* Raman spectroscopy, X-ray diffraction studies and complementary DFT calculations revealed unexpected behaviour of potassium amidoborane under pressure, which is remarkably different from that of parent ammonia borane and its lithium derivative. Upon compression initially weak dispersive interactions experience considerable enhancement resulting in dimer-like moieties constituted of hydrogen bonded $[NH_2BH_3]^-$ molecular ions. This is unprecedented example of competition between strong electrostatic and weak dispersive leading to hydrogen bonding between ions of the same polarity.

Tuning of subtle bonding properties of potassium amidobranate without major change of its crystal structure in the wide pressure

range may pave the way towards design of optimal hydrogen storage materials.

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