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# Calculations of Molecular Structures and Processes Important for Hydrogen Behaviour in the Li-Amide/Imide System

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Lithium amide ($LiNH_2$) and imide ($Li_2NH$) have recently attracted much attention as part of the Li-H-N system suitable for hydrogen (H) storage applications. However, the ground-state imide structure is still unknown with at least six candidate structures, with ground state energies all very close to one another. In order to discover possible pathways for the imide-amide-imide transformations during the hydrogen absorption/desorption cycles, we have examined the molecular structures involved (along with their changes during these processes) using *ab-initio* calculations based on the linear combination of atomic orbitals (LCAO). In addition, the influence of Li substitution by some other elements of interest on the system behaviour was investigated. These analyses were complemented by density functional theory (DFT) calculations of several crystal structures appearing in the processes. In this way a thorough insight into the structures and the processes taking place at atomic level is attained, providing a starting point for understanding these complicated systems, and the mechanisms governing their transformations.

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## 1. Introduction

The extensive search for hydrogen storage materials suitable for remote applications has recently turned its attention to the Li-N-H system [1-7]. The principal reactions are [1]:

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH \quad (1)$$

The low enthalpy (estimated to range between 45 and 73 kJ/mol), i.e. the temperature ($\approx 170\,^{\circ}C$) of the second reversible reaction, and the hydrogen content of 6.5% are close to fulfil the requests for practical applications. Besides the two principle hypotheses (i.e. that dehydrogenation proceeds either due to a high affinity of $H^+$ coming from $LiNH_2$ and $H^-$ coming from LiH to form $H_2$ [2], or that the reaction is mediated by $NH_3$ [3, 4, 6]), the role of some intermediate, non-stoichiometric structures [7, 8] has been also investigated. In attempt to lower the dehydrogenation temperature of the system the replacement of Li by suitable elements in a wide range of concentrations [9–11] has been performed, giving encouraging results, especially for the replacement of Li by Mg. Experimental investigations have been accompanied by various types of calculations [9, 11–16] that provided valuable results about the electronic structure and the energetics of the involved structures. However, many doubts concerning the mechanism of reactions (1), and their relation with the crystalline and molecular structures and their transformations still persist. For this reason we have performed linear combination of atomic orbitals (LCAO) *ab-initio* calculations of some principal molecular structures appearing in the systems, and investigated effects of deformation of their optimal conformations to those they actually adopt in the crystals, as well as the effects of the replacement of Li by M = Na, K, Mg and Ca, using the HyperChem software package [17]. In addition, we have performed density functional theory (DFT) calculations on the amide and imide crystalline structures using the WIEN2k software package [18], have related the results obtained by the two methods, and discussed them in the light of the most important unresolved questions appearing in the literature.

## 2. Results and discussion

In all the molecular calculations the 6-311-G** basis set has been used, with electron correlation effects considered according to the Moller-Plasset approximation of the second order. The investigated molecular parameter was fixed to a set of appropriate values, and the rest of the molecule was fully relaxed for each of these values up to an energy gradient lower than 0.01 kcal/molÅ. DFT calculations of the amide crystalline structure were performed using the augmented plane waves method with additional local orbitals (APW+lo), and Perdew-Burke-Ernzerhof exchange-correlation functional in generalised gradient approximation, as implemented in the WIEN2k

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code. The $R_{MT}K_{max}$ parameter of the basis set completeness was set at 7.0. The sampling of k-space was done using 100 k-points (4x4x4 grid), or 12 k-points in the irreducible part of the Brilouin zone. The magnitude of the largest vector in the Fourier expansion of the charge density was 16.0.

The destabilisation (defined as increase of the molecular ground state energy relative to the optimal conformation value) of $LiNH_2$ and $Li_2NH$ molecules due to the changes of the Li-N distance $d_{Li-N}$, from the optimal molecular values (1.726 Å in $LiNH_2$, 1.731 Å in $Li_2NH$) to the actual values they attain in the crystalline structures (2-2.3 Å) [19, 15] is presented in Fig. 1 a.

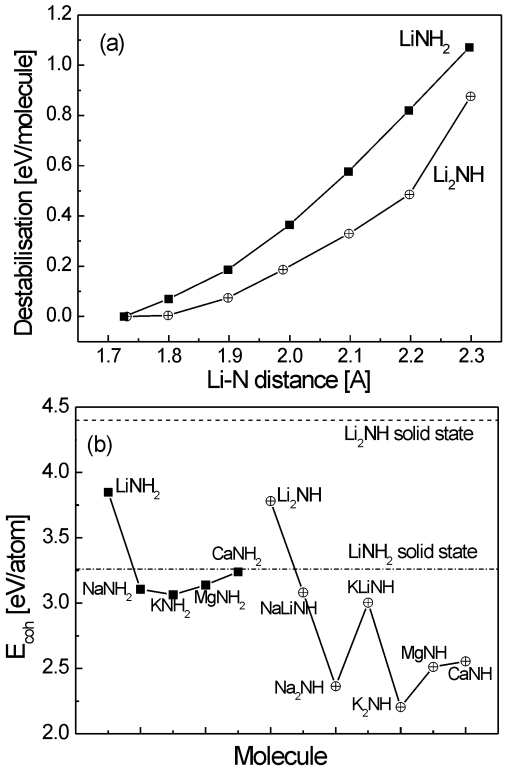


Fig. 1. (a) Destabilisation effect of the Li-N bond elongation on $LiNH_2$ and $Li_2NH$ molecules, (b) Cohesion (atomisation) energies of $LiNH_2$, $Li_2NH$ and corresponding molecules with Li substituted by Na, K, Mg and Ca.

The destabilisation is quite large, especially for distances $d \geq 2$ Å, observed in the crystals, and larger for $LiNH_2$ than for $Li_2NH$, where the elongation of the one is compensated by the shortening of the other Li-N bond. The effect is about 1/32 eV/Å$^3$ for both compounds, which makes about 9 eV/(unit cell) for the amide. As a matter of fact, $LiNH_2$ molecule becomes unstable for $d_{Li-N} \approx 2.1$ Å, and $Li_2NH$ for $d_{Li(1)-N} \approx 2.2$ Å, which is proved by the softening of the corresponding Li-N vibrational modes (see Fig. 2 a and b), and for $Li_2NH$, by abrupt changes of $d_{Li(2)-N}$, and the Li charge ($Q_{Li}$), when $d_{Li(1)-N}$ attains the critical value (see Fig. 3 a).

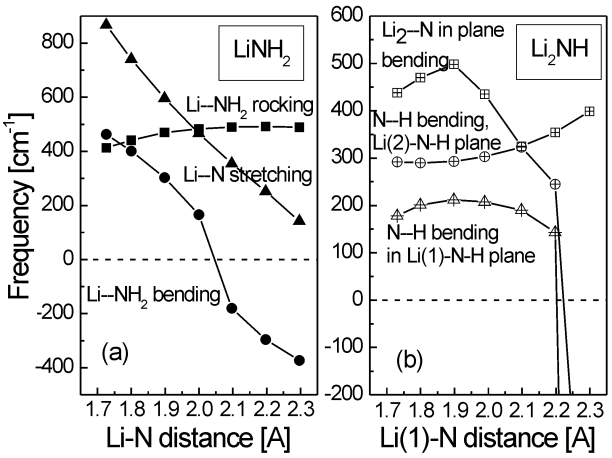


Fig. 2. Dependence of the Li-N vibrations in $LiNH_2$ on the Li-N distance, (b) Dependence of the Li(1)-N vibrations in $Li_2NH$ on the Li(1)-N distance.

Cohesion (atomisation) energies of amide/imide molecules, and of molecules with Li substituted by Na, K, Mg and Ca, are presented in Fig. 1 b, together with the values calculated for Li-amide/imide crystals [12, 15]. The destabilisation of the optimal molecular conformations induced by M → Li substitution is significant, although it should reduce in the solid state due to the fact that the equilibrium $d_{M-N}$ values in substituted molecules are much closer to distances observed in Li amide/imide crystals, than it is $d_{Li-N}$ of the optimal amide/imide molecular conformations.

The dependence of calculated Mulliken charges on $d_{Li-N}$ in amide/imide molecules is presented in Fig. 3 a. The absolute values of both Li ($Q_{Li}$), and N ($Q_N$) charges in $LiNH_2$ monotonically increases (i.e. Li becomes more positive, and N more negative) along with $d_{Li-N}$, indicating that the Li-N bond in the crystal becomes more ionic than in the molecules, which contrasts some earlier findings [11] in favour of an increased covalence of the bond in the solid state. The H-charge ($Q_H = 0.159 \div 0.151$ e) of both hydrogen atoms, as well as the N-H bond lengths ($d_{N-H} = 1.013 \div 1.001$ Å), are quite insensitive to $d_{Li-N}$ changes in the observed range $d_{Li-N} = 1.726 \div 2.3$ Å, suggesting $NH_2^-$ to be a compact entity in the investigated molecular processes.

The situation with $Li_2NH$ is quite different. Although $d_{Li(2)-N}$ is considerably shorter, ($d_{Li(2)-N} = 1.724 \div 1.672$ Å for $d_{Li(1)-N} = 1.8 \div 2.2$ Å), the $Q_{Li}$'s of both Li ions are quite close to each other and vary slowly. However, the change of the sum of the two charges is not negligible. At $d_{Li(1)-N} = 2.2$ Å, Li(1) detaches from the molecule leading to an abrupt charge redistribution among the Li ions, and to the elongation of $d_{Li(2)N}$ up to 1.761 Å. $Q_N$ increases with the $d_{Li(1)-N}$ elongation up to $d_{Li(1)-N} = 2$ Å, but after that, it decreases, following the trend of the $Q_{Li}$'s sum. Like in the case of most changes of both molecular species, $Q_H$ is pretty stable varying

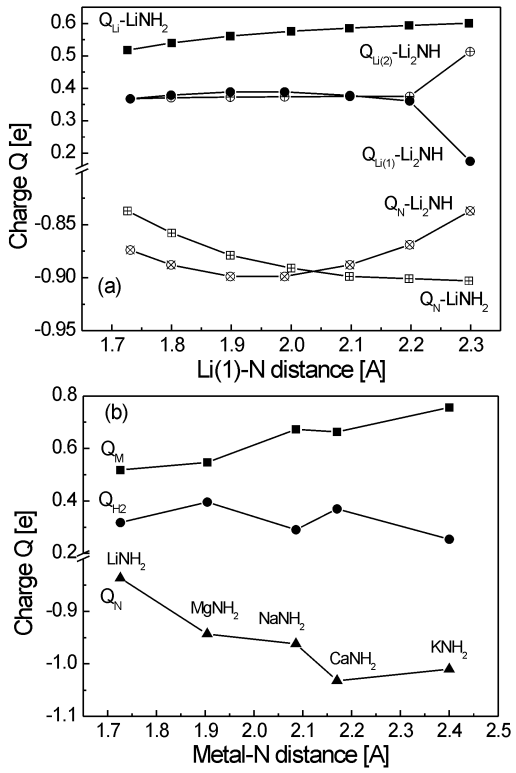


Fig. 3. (a) Dependence of calculated Mulliken charges on the Li(1)-N distance in amide/imide molecules, (b) Influence of the replacement of Li by Na, K, Mg, Ca on the distribution of Mulliken charges in $LiNH_2$ molecule.

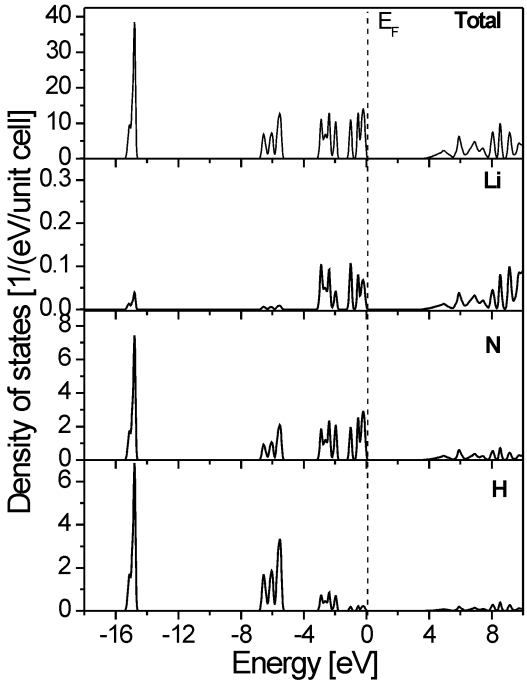


Fig. 4. The $LiNH_2$ (space group I-4) crystal structure DOS, and its atomic decomposition.

only from $Q_H = 0.138$ e for the optimal conformation ($d_{Li(1)-N} = 1.731$ Å, $d_{N-H} = 1.013$ Å) to $Q_H = 0.134$ e, for $d_{Li(1)-N} = 2.2$ Å and $d_{N-H} = 1.007$ Å. After the break-up point of the Li(1)-N bond $Q_{Li(1)}$ takes up the value of $Q_H$ in $LiNH_2$, enabling all the bonds and the charges of the rest of the $Li_2NH$ molecule to assume values close to those of the equilibrium $LiNH_2$ conformation.

The influence of the replacement of Li by M = Na, K, Mg, Ca on the distribution of Mulliken charges in $LiNH_2$ molecule is presented in Fig. 3 b. The charge transfer from M to N ion increases along the series Li–Mg–Na–K–Ca, and is accompanied by the increase of $d_{M-N}$, with an exception $d_{K-N} > d_{Ca-N}$. Again, $Q_H = 0.159$(Li), 0.198(Mg), 0.145(Na), 0.185(Ca), 0.127(K) e is quite uniform, although clearly higher for the formally divalent Mg and Ca ions ($Q_{Mg} = 0.547$ e, $Q_{Ca} = 0.663$ e), accommodating that way a part of the excess charge introduced by them. $Q_H$ decreases uniformly along the alkali series following the increase of charge of M ion ($Q_{Li} = 0.518$, $Q_{Na} = 0.673$, $Q_K = 0.756$ e). $d_{N-H}$ also changes a little: from 1.000 Å in $MgNH_2$ to 1.009 Å in $KNH_2$.

The DOS of $LiNH_2$ (space group I-4) crystal structure and its atomic decomposition, calculated by APW+lo method implemented in WIEN2k software package, are presented in Fig. 4. They are in good agreement with previous calculations [12, 13], and show a pronounced "molecular" character exhibited in the localised, well defined bands. However, it seems that our calculations predict somewhat stronger hybridisation of the N:*s* with the low-laying H:*s* states (around –15 eV), and of the H:*p* states (not explicitly shown or discussed in [12, 13]) with N:*p* and H:*s* states in the central (around –6 eV), and region near the Fermi level ($0 \div -3$ eV). Together with the smaller gap between the two highest energy bands (mainly due to the enhanced N:*p*–Li:*p* hybridisation) these suggest that APW+lo method predicts stronger collective effects in the system than the pseudo-potential methods used in [12, 13].

## 3. Conclusions

The changes of some molecules from their equilibrium gas-phase conformations to those they attain in the amide/imide crystals, and the effects of the replacement of Li by Na, K, Mg and Ca, have been investigated using *ab-initio* LCAO, and APW + lo DFT calculations. The destabilisation of both $LiNH_2$ and $Li_2NH$ molecules is quite large at distances observed in the crystalline phases ($d_{Li-N} \geq 2$ Å), reaching about 1 eV/(formula unit), and more pronounced in $LiNH_2$ due to the fact that in $Li_2NH$ the shortening of Li(2)-N compensates the elongation of Li(1)-N bond. Strictly speaking, at the solid-state Li-N distances, both $LiNH_2$ and $Li_2NH$ molecules become instable, which is proved by the softening of appropriate Li-N vibrations, and in $Li_2NH$, by the abrupt changes of $Q_{Li}$'s and $d_{Li(2)-N}$. In $LiNH_2$, this provides a picture of a compact, negative $NH_2^-$ ion interacting by an increas-

ingly ionic interaction with the neighbouring $Li^+$ ions, in good agreement with the density-of-states calculations of the amide crystalline structure. The tendency of $d_{Li(2)-N}$ to shorten, and that way to compensate the elongation of $d_{Li(1)-N}$, makes the situation in $Li_2NH$ more complicated. At the $Li_2NH$ molecular brake-up point, which takes place at $d_{Li(1)-N} \approx 2.2$ Å observed in the crystalline phase, the more distant Li(1) ion takes up the charge which is very close to $Q_H$ in $LiNH_2$, enabling the other bonds and charges in the $Li_2NH$ molecule to assume values close to those in the equilibrium $LiNH_2$ molecular conformation. The replacement of Li by Na, K, Mg and Ca destabilises the optimal molecular conformations, but the destabilisation is reduced in the solid state because the optimal M-N bond is longer than $d_{Li-N}$, and closer to the crystal values. This issue requires additional calculations of the bond length-energy dependence in the M-replaced molecules. Interestingly, the charges of nominally divalent Mg and Ca ions are lower, and bond lengths are shorter than those of the corresponding alkali metals Na and K, indicating that simple explanations based on electronegativity scale, or valency of the amide/imide impurity destabilisation are not reliable. It appears that LiNaNH and LiKNH are much more stable than $Na_2NH$ and $K_2NH$ ($K_2NH$ being metastable) suggesting that the destabilisation is enhanced by the increase of impurities concentration. In all the investigated cases, except perhaps for MgNH and CaNH, $Q_H$ and $d_{N-H}$ are quite stable and uniform. This implies that disintegration of the $NH_2^-$ molecule during the amide-imide transformation is not probable, supporting the model which predicts the $NH_3$ mediated reaction. In favour of this model is also a very large proton affinity of $NH_2^-$, which exceeds all the Li-N and Li-H bond energies, in molecules, as well as in the solid state.

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