The electronic structure, chemical bonding and ionic conductivity of Li_6MoN_4 and Li_6WN_4

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The calculations of the electronic structure, chemical bonding and energy of transition for lithium ions in Li_6MoN_4 and Li_6WN_4 have been carried out using the LMTO method; a possible model of lithium transport for these crystals has been suggested.

The binary nitrides of lithium and transition metals (Cr, Mo and W) possess a high ionic conductivity and stability against melted lithium. Therefore, they are promising materials for lithium cells. However, the transport properties of these compounds have been studied insufficiently.

For a better understanding of ionic conductivity, we evaluated the electronic structure and chemical bonding for Li_6MoN_4 and Li_6WN_4 by the first-principle linear muffin-tin orbital method in the tight-binding representation (LMTO-TB)[1] and the semi-empirical extended Hückel method (EH).[2] The results of calculations have been used to analyse the mechanism of lithium ion migration in the anti-fluorite structure of these nitrides.

The calculations of the electronic structure and total energy of Li_6MoN_4 and Li_6WN_4 crystals have been carried out by the LMTO-TB method. We have employed a tetragonal unit cell (space group $P4_2/nmc$, $Z = 2$) with 20 atoms per cell: $Li_{12}M_2N_6E_{10}$, where M = Mo, W; E are empty spheres. The LMTO-ASA method has a higher precision for closely packed crystals; therefore, in our calculations additional spheres (empty spheres) with an *s*-orbital basis have been introduced into interstitial positions. These spheres were located at the octahedral and tetrahedral interstitial positions. The experimental lattice constants $a = 6.673$ and 6.679 Å, $c = 4.925$ and 4.927 Å for Li_6MoN_4 and Li_6WN_4, respectively, have been used.[3] The optimised lattice constant for pure Li_6MoN_4 was 4.1% bigger than the experimental value. The valence 2*s*-, 2*p*-states of lithium and nitrogen; the *ns*-, *np*-, $(n-1)d$-states of Mo, W, with $n = 5$, 6 and the *s*-states of empty spheres E were included in the atomic orbital basis used to construct the Bloch functions of crystals. The calculations were fulfilled for 128 *k*-vectors in the first Brillouin zone (30 *k*-vectors in the irreducible wedge). We found that the electronic structures of Li_6MoN_4 and Li_6WN_4 are close to each other. The total and partial densities of states for a Li_6MoN_4 phase are presented in Figure 1. The separation of the electronic energy spectrum into four zones

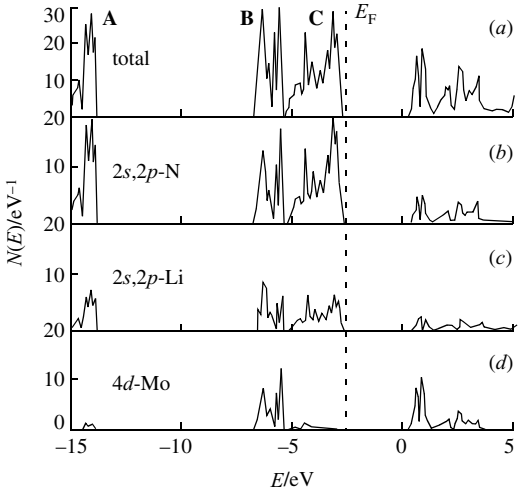

Figure 1 The (*a*) total and (*b*)–(*d*) partial densities of states [*N*(*E*)] for a Li_6MoN_4 crystal.

Table 1 The characteristics of the electronic structure and chemical bonding in the crystals of Li_6MoN_4 and Li_6WN_4.

Characteristic		Li_6MoN_4	Li_6WN_4
Width and centre of band **A**/eV		1.45; –14.62	1.79; –14.80
Width and centre of band **B**/eV		1.21; –6.07	1.68; –5.79
Width and centre of band **C**/eV		2.66; –3.95	2.30; –3.63
Width of a forbidden gap/eV		2.87	3.42
Averaged bond populations by Mulliken	M–N, M=Mo, W	0.837	0.849
	Li–N	0.047	0.046

is observed. A low-energy band **A** at about –15.0 eV was attributed to the 2*s*-states of nitrogen. The next band **B** is a band of hybrid N 2*p* and Mo 4*d*-states with some contributions of Li 2*s*-, 2*p*-states. The calculations of the overlap population of crystalline orbitals for the Mo–N bond showed that the antibonding partner of the band **B** is located at the bottom of the conductivity zone, which is a band with an energy of ~1.6 eV. The valence states in the range from –5.2 to –2.6 eV (band **C**) are hybridised N 2*p* and 2*s*-, 2*p*-states of Li, with the admixtures of Mo 4*d*-states. The presence of a forbidden gap confirms a semiconducting character of conductivity detected experimentally for similar phases.[4] The main characteristics of the electronic energy spectrum for Li_6MoN_4 and Li_6WN_4 phases are presented in Table 1. The *ab initio* band calculations of the electronic structure for binary lithium nitrides were not studied previously. However, these results agree in the main features with the band structure for LiN_3 obtained by Blaha and co-authors[5] using a linearised augmented plane wave (LAPW) method. There are differences in the positions of the N-2*s* and N-2*p* bands and in their widths. The band appears, which consists of hybrid N 2*p* and Mo 4*d*-states.

We also calculated the indices of chemical bonding for the considered compounds using the extended Hückel approach (Table 1). The averaged overlap population of crystalline orbitals is rather high for the Mo–N and W–N bonds. The Li–N interactions are characterised by a high degree of ionicity and an insignificant contribution of covalency. The low covalency of the Li–N bond corresponds to the high lithium mobility in the anti-fluorite structure.

The investigations of the energy of defect formation using the *ab initio* LMTO calculations allowed us to offer a model of

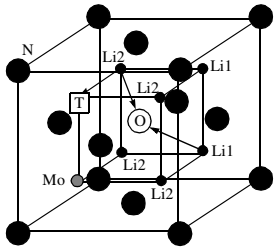

Figure 2 The structure of a perfect crystal of Li_6MoN_4. Arrows show possible transitions for lithium ions into octahedral interstitial position (O) and through structure tetravacancies (T).

the ionic transport in Li_6MoN_4 and Li_6WN_4. The transport of the lithium ions is possible through the octahedral and tetrahedral interstitial positions in the anti-fluorite structure of these phases. The scheme of possible transport of the two crystallographically nonequivalent lithium atoms (Li1, Li2) is given in Figure 2. It is known[3] that the lithium atoms Li1 have no tetravacancies in the nearest environment. Therefore, the Frenkel defect formation energy was calculated for the transport of Li2 into a tetraposition only. This energy was determined as the difference between the total energy of a perfect crystal (when a lithium atom is in a normal position) and the energy of a defect crystal (the lithium atom is located in octahedral or tetrahedral interstitial positions). The calculated energies are presented in Table 2. They show that the jump of lithium ions into a tetrahedral position requires an energy smaller by about 1.3 eV, than the jump of a lithium ion into octahedral positions. For both phases, the energy of transition of Li2 from a normal position into an octahedral position is a little lower than that of Li1. These energies, averaged over Li1 and Li2 atoms, within the limit of the errors of the method (0.1 eV) are practically identical for the Li_6MoN_4 and Li_6WN_4 crystals.

Thus, the *ab initio* calculations of the electronic structure and energy of transition allow us to suggest a possible mechanism of lithium transport for the above crystals. The migration of lithium ions is more probable through the tetrahedral position, whereas the migration through the octahedral interstitial positions should be excluded.

Table 2 The energy of transition for Li1 (ΔE_{oct1}) and Li2 (ΔE_{oct2}) into an octahedral position and that for Li2 into a tetrahedral interstitial position (ΔE_{tetr2}) in Li_6MoN_4 and Li_6WN_4 crystals.

Crystal	ΔE_{oct1}/eV	ΔE_{oct2}/eV	$\Delta E_{average}$	ΔE_{tetr2}/eV
Li_6MoN_4	4.77	4.47	4.62	3.16
Li_6WN_4	4.99	4.21	4.60	3.37

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