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Calculation of the vibrational properties of LiMgAs

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Abstract

We have studied the vibrational properties of the filled tetrahedral semiconductor LiMgAs and its binary analog AlAs by using the plane-wave pseudopotential method within density functional theory. The calculated lattice constants for the studied compounds are in good agreement with previous theoretical and experimental results. The phonon dispersion curves and phonon density of states are calculated by using density functional perturbation theory. The sound speeds in different directions are quantitatively similar in LiMgAs and AlAs. The assignment of the zone center modes to the relative motion of the atoms shows that the lower optic modes are due to the Mg–As pair vibrations, while for the upper ones the Li–Mg pair dominates, which is attributed to the smaller Mg atom mass. The longitudinal interatomic force constant of Mg–As is about 66% higher than that of Li–As, showing the relatively high covalency of the former bond.

1. Introduction

The filled tetrahedral compounds (FTC) $A^I B^{II} C^V$, where the Roman numerals indicate the appropriate column of the periodic table, e.g. LiMgAs, form an interesting class of stable semiconductors closely related to the more familiar III–V compounds such as AlAs. They were synthesized and structurally characterized by Nowotny [1] and Juza [2] a long time ago. Interest in this compound family has been renewed since the prediction of Wood *et al* [3] and Carlsson *et al* [4] that LiZnP and LiZnN exhibit semiconducting behavior with a direct-wide energy gap, which makes them very prominent materials for technological applications. This prediction has stimulated many other works [5–11], and has been confirmed experimentally by Kuriyama and his group [12–15] and Bacewicz and Cizek [16, 17].

The FTC crystal structure can be derived from the zinc-blende (ZB) $D^{III}C^V$ compound structure by transmuting the group III atom into its isovalent pair $A^I + B^{II}$, in this context the $B^{II}C^V$ forms a zinc-blende lattice and A^I can occupy either the $(1/2, 1/2, 1/2)a$ position (where a is the lattice parameter) and forms the α phase, or the $(3/4, 3/4, 3/4)a$ position which is the β one.

Structural studies [18–21] revealed that the most stable of these cubic arrangements of atoms is the α -phase and that the ternary lattice parameter is greater than the binary one, resulting in a smaller bulk modulus for the former. Theoretically, band structure modification of zinc-blende semiconductors has been considered by an interstitial insertion rule [4], which states that: ‘substitution of the filled tetrahedral interstitial sites in zinc-blende semiconductor by He- or Li^+ -like species (i.e. repulsive s core potentials, attractive non- s core potentials) raises (lowers) the energy of the conduction bands that have s (non- s) character on these sites’. In this context, an FTC; $A^I B^{II} C^V$ is viewed as a hypothetical $(B^{II}C^V)^-$ lattice partially filled with $(A^I)^+$ interstitial. Analysis of the ground state charge density [22] and the force constants [23–25] indicates the existence of a strong $B^{II}C^V$ covalent bond and a pronounced $A^I C^V$ ionic one in the same structure. Recently, the Raman scattering measurement from LiMgAs has been reported by Kuriyama and his group [26]. Theoretical *ab initio* calculations of the phonon spectra for LiZnAs and LiZnP [8] and LiCdP and LiCdAs [28] have been reported. The long wavelength acoustic modes of the ternaries resemble those of the binaries; i.e. LiZnAs and GaAs. The same results have been obtained by calculating sound speeds in different directions from the computed elastic constants [18, 20].

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Table 1. Lattice parameter a_0 (in Å), ε_∞ and ε_0 of LiMgAs and its binary analog AlAs.

	LiMgAs			AlAs		
	This work	Others	Expt.	This work	Others	Expt.
a_0	6.10	6.08 ^a , 6.073 ^b , 6.218 ^c	6.181 ^d	5.61	5.64 ^a , 5.6036 ^b	5.66 ^e
ε_∞	8.16	8.55 ^f		10.50	10.05 ^f , 8.83 ^g , 9.2 ^h , 8.167 ⁱ	8.16 ^g , 8.2 ^h , 8.16 ⁱ
ε_0	11.98			12.42	10.06 ⁱ	

^a Reference [18]. ^b Reference [21]. ^c Reference [19]. ^d Reference [14]. ^e Reference [39]. ^f Reference [10].

^g Reference [40]. ^h Reference [35]. ⁱ Reference [41].

Table 2. Phonon frequencies (in cm^{-1}) of LiMgAs and AlAs at the Γ , X and L points.

	LiMgAs		AlAs		
	This work	Expt.	This work	Others	Expt.
TO ₁ (Γ)	255.89	307 ^a	365.50	363 ^b , 365 ^c	361 ^b , 361 ^d , 363 ^e
LO ₁ (Γ)	301.98	329 ^a	397.38	400 ^b , 400 ^c	402 ^b , 404 ^d , 404 ^e
TO ₂ (Γ)	327.87	638 ^a			
LO ₂ (Γ)	343.17	656 ^a			
TA(X)	116.03		89.29	95 ^b , 104 ^c	109 ^b , 103 ^d , 103 ^e
LA(X)	173.52		214.41	216 ^b , 213 ^c	219 ^b
TO ₁ (X)	208.53		337.23	337 ^b , 335 ^c	333 ^b , 340 ^d , 338 ^e
LO ₁ (X)	216.60		390.79	393 ^b , 385 ^c	399 ^b , 400 ^d , 396 ^e
TO ₂ (X)	328.88				
LO ₂ (X)	410.27				
TA(L)	87.39		67.63	71 ^b , 75 ^c	82 ^d , 83 ^e
LA(L)	169.85		210.32	212 ^b , 212 ^c	
TO ₁ (L)	257.73		354.36	352 ^b , 352 ^c	350 ^d , 350 ^e
LO ₁ (L)	263.15		368.72	372 ^b , 375 ^c	386 ^e
TO ₂ (L)	314.92				
LO ₂ (L)	356.89				

^a Reference [26]. ^b Reference [35]. ^c Reference [42]. ^d Reference [43].

^e Reference [44].

In this work we report on the vibrational properties of another member of this class LiMgAs and its binary analog AlAs using the plane-wave pseudopotential method. We found that the sound speeds deduced from the acoustic phonon branches are quantitatively similar in LiMgAs and AlAs. The upper optic modes are due to the Li–Mg pair motion, and not to the Li–C^V as in LiZnP, LiZnAs, LiCdP and LiCdAs. The remainder of the paper is organized as follows: in section 2 the method and details of calculation are described. In section 3 we give the obtained results and discuss them. Finally, a conclusion is given in section 4.

2. Method and details of calculations

The calculations are done using the pseudopotential plane-wave method based on the density functional theory (DFT), using the local density approximation (LDA) with the Ceperley–Alder [29] form of the exchange–correlation energy as parameterized by Perdew and Wang [30]. Norm-conserving Troullier–Martins pseudopotentials [31] are used for all atoms of the studied semiconductors, as supplied in the ABINIT code [32, 33]². The states Li 2s¹, Mg 3s², Al 3s²3p¹, and As 4s² 4p³ are treated as valence states. The phonon dispersion

² The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors, URL <http://www.abinit.org>.

curves and the phonon density of states are calculated by using density functional perturbation theory [34–37] as implemented in the ABINIT code. Brillouin zone integration is performed by k -point sampling with special points obtained by using the standard special technique of Monkhorst and Pack (MP) [38]. In this work $8 \times 8 \times 8$ MP mesh and a cutoff energy of 80 Ryd are used for the ternary and binary semiconductors.

3. Results

In table 1 we present the lattice parameter, the electronic dielectric function, ε_∞ , and the static one, ε_0 , for LiMgAs and its binary analog AlAs, the calculated values compare well with the available experimental data and results of other calculations.

The computed values of the phonon frequencies at the high symmetry points are reported in table 2. For AlAs, our calculated values compare well with the available theoretical results and the experimental data which are also included in table 2.

For LiMgAs, the predicted low frequency optic mode values are fairly close to the measured ones [26], whereas the high frequency values are much smaller than the observed data [26]. The calculated values of the latter modes are underestimated by about 48%. In order to assess for the reliability of the obtained results, we calculated the phonon

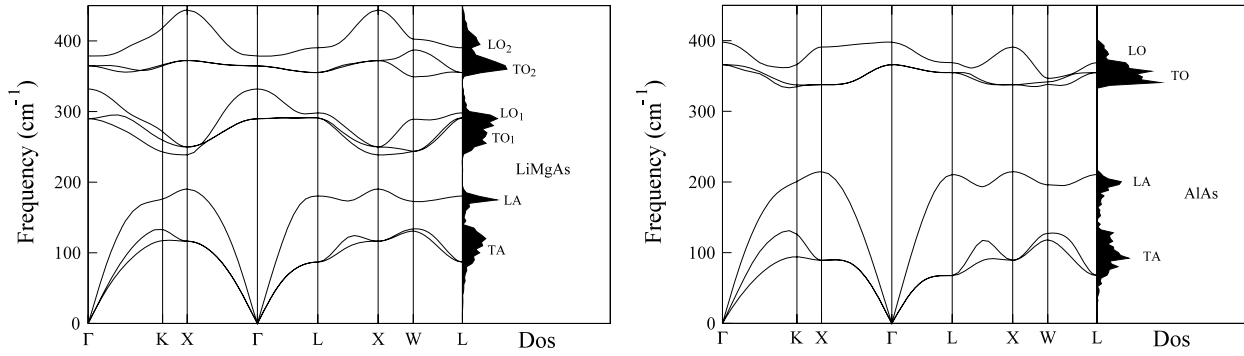


Figure 1. Phonon dispersion spectra and the phonon density of state curves of LiMgAs and AlAs.

Table 3. Comparison between theoretical and experimental optical phonon frequencies at the Γ point for the LiMgAs, LiZnP and LiZnAs compounds.

LiMgAs					
	Our calculation	Expt. [26]	Error (%)	Our calculation ^a	Error (%)
TO ₁ (Γ)	255.89	307	17	240.43	22
LO ₁ (Γ)	301.98	329	8	288.74	12
TO ₂ (Γ)	327.87	638	48	311.57	51
LO ₂ (Γ)	343.17	656	47	327.27	51
LiZnP					
	Our calculation	Expt. [23]	Error (%)	Other [8]	Error (%)
TO ₁ (Γ)	246.90	230	7	242	5
LO ₁ (Γ)	269.60	265	2	266	0.4
TO ₂ (Γ)	388.89	363	7	382	5
LO ₂ (Γ)	431.48	421	3	424	0.7
LiZnAs					
	Our calculation	Expt. [25]	Error (%)	Other [25]	Error (%)
TO ₁ (Γ)	202.03	204	1	190	7
LO ₁ (Γ)	221.70	233	5	217	7
TO ₂ (Γ)	363.94	420	13	340	19
LO ₂ (Γ)	384.49	452	15	370	18

^a At the experimental lattice parameter $a = 6.181 \text{ \AA}$ [14].

Table 4. Ratio between sound velocities (deduced from the acoustic phonon spectra) in LiMgAs and its zinc-blende binary analog AlAs for different propagation directions, $r = v_{(\text{FTC})}/v_{(\text{Binary})}$. The subscripts L and T stand for longitudinal and transverse, respectively, and the superscript (hkl) indicates the propagation direction.

	r_L^{001}	r_T^{001}	r_L^{110}	r_{T1}^{110}	r_{T2}^{110}	r_L^{111}	r_T^{111}
LiMgAs versus AlAs	1.03	1.04	0.97	1.29	0.71	0.93	1.2

frequencies at the Γ point for LiMgAs at the experimental value of the lattice parameter and for LiZnP and LiZnAs at the obtained equilibrium one. The results are displayed in table 3 together with the experimental data and the results of other calculations. It is clear that at the measured lattice parameter the frequencies are reduced. For LiZnP and LiZnAs our results compare well with the measured ones and those obtained from other calculations and the error does not exceed 15%.

In this context, one might attribute the discrepancy between the predicted and measured optic mode frequencies to the real state of the LiMgAs crystal, i.e. the crystal growth of

LiMgAs is very difficult and its surface gets damaged rapidly during the Raman scattering experiment [27].

The calculated phonon curves (left panels) and phonon density of states (right panels) of LiMgAs and AlAs are shown in figure 1. It is clear that the acoustic phonon dispersion curves of LiMgAs resemble those of AlAs and the sound speeds are quantitatively similar; the slopes of acoustic branches near the Γ point are calculated and the ratios $v_{\text{LiMgAs}}/v_{\text{AlAs}}$ in different directions are given in table 4. This finding confirms the one obtained using the elastic constants [18]. It is worth adding that the elastic constants have been calculated (not shown here) and they are close to the ones reported earlier, except the values of C_{44} , obtained with relaxation, which are 43.55 and 53.19 GPa (experiment [45], 54.20 GPa for AlAs) and without relaxation were 53.79 and 79.92 GPa for LiMgAs and AlAs, respectively. Bearing in mind that the acoustic modes depend on total masses and the fact that the total mass of (Mg + As) ions differs only by 2.62% from that of (Al + As), the result of quantitative similarity between the sound speeds for the ternary and the binary is

Table 5. Calculated longitudinal interatomic force constants (IFC) in (10^4 dyn cm $^{-1}$) for each pair of atoms and the values of the dimensionless parameter P (see the text for details) for the contribution of different pairs of atoms to the longitudinal and transverse optic modes, LO and TO, respectively.

	B ^{II} -C ^V	Li-B ^{II}	Li-C ^V	B ^{II} -C ^V	Li-B ^{II}	Li-C ^V
	LiMgP			LiMgAs		
P	0.9967(LO ₁)	0.750(LO ₂)	0.576(LO ₂)	0.968(LO ₁)	0.943(LO ₂)	0.263(LO ₂)
	0.9967(TO ₁)	0.750(TO ₂)	0.576(TO ₂)	0.968(TO ₁)	0.943(TO ₂)	0.263(TO ₂)
IFC	4.37	1.39	1.40	4.18	1.16	1.44
	LiZnP			LiZnAs		
P	0.970(LO ₁)	0.100(LO ₂)	0.991(LO ₂)	0.998(LO ₁), 0.988(LO ₁) [8]	0.273(LO ₂)	0.938(LO ₂), 0.988(LO ₂) [8]
	0.970(TO ₁)	0.100(TO ₂)	0.991(TO ₂)	0.998(TO ₁), 0.999(TO ₁) [8]	0.273(TO ₂)	0.938(TO ₂), 0.909(TO ₂) [8]
IFC	4.27	1.17	3.17	4.88	0.94	3.41
	LiCdP			LiCdAs		
P	0.9728(LO ₁)	0.162(LO ₂)	0.978(LO ₂)	0.999(LO ₁)	0.536(LO ₂)	0.782(LO ₂)
	0.9728(TO ₁)	0.162(TO ₂)	0.978(TO ₂)	0.999(TO ₁)	0.536(TO ₂)	0.7816(TO ₂)
IFC	4.89	1.06	1.39	4.66	0.84	1.44

a clear manifestation of the electronic resemblance between (MgAs)⁻ and AlAs compounds.

In assessing the value of the agreement with the calculation, not only the frequencies but also the eigenvectors have to be taken into account. The phonon spectrum for LiMgAs differs from its binary analogous compound AlAs by three additional optical phonon curves. In order to assign the zone center optic modes to the relative motions of the atoms in LiMgAs, we used the procedure of Wood and Strohmayer [8]. The description of the modes as the relative vibrations of pair of atoms α (α can be {Li, Mg} for example), can be done by introducing for a given optic mode the dimensionless parameters

$$\delta_\alpha \equiv \left(\sum_{i \in \alpha} m_i u_i \right) / \sqrt{m_1^2 u_1^2 + m_2^2 u_2^2 + m_3^2 u_3^2}$$

$$P_\alpha \equiv 1 - 2\delta_\alpha \cdot \delta_\alpha$$

where m_i and u_i are the masses and displacement vectors of atom i in a given normal mode. $P_\alpha = 1$ means a two-atom description perfectly (the pair α) describes the optic mode of the ternary compound.

In table 5, we displayed the values of P for different pairs of atoms for the longitudinal and transverse optic modes in LiMgAs, LiMgP, LiCdAs, LiCdP, LiZnAs and LiZnP. We also included in this table the calculated longitudinal interatomic force constants (IFC) (i.e. along the direction joining the two atoms constituting the pair in question). It is clear from the values of P that the lower optic modes (TO₁, LO₁) are due to the vibrations of the B^{II}-C^V pair in all compounds, while the higher ones (TO₂, LO₂) are due to the Li-C^V pair atoms in LiZnAs and LiCdAs, with a considerable contribution from Li-B^{II} in the latter. However, in LiMgAs the upper optic modes are dominated by Li-Mg motions (i.e. $P = 0.943$). This can be understood by the fact that the Mg atom is lighter than the As one, so it is involved in the higher optic modes. This finding does not agree with the assignment expected by Kuriyama *et al* [26]. Compared with the Li-As bond in LiZnAs, the one in LiMgAs is more ionic.

The polar semiconductors are characterized by the splitting of transverse and longitudinal optical phonons in the center of the BZ. The value of LO-TO splitting is based on the Born effective charges which satisfy the acoustic sum rule (ASR) [35], we find the following results for Li (0.87 e), Mg (1.76 e) and As (-2.63 e), where e is the electron charge. The value of 1.76 e for Mg is comparable to the observed value $\simeq 2.18e$ of Al in AlAs [46], this confirms that the filled tetrahedral structure of LiMgAs is viewed as a hypothetical AlAs-like (MgAs)⁻ lattice partially filled with He-like Li⁺ ions.

The splitting of LO(Γ) and TO(Γ) is found to be 15.30 and 46.09 cm $^{-1}$ for the upper and the lower optic modes, respectively, it has the same trend as the one reported experimentally [26]; 18 and 21 cm $^{-1}$. Furthermore, using the values of longitudinal IFC, we found that the Mg-As IFC is 66% higher than that of the Li-As one, showing the relatively high covalency of the Mg-As bond. In LiZnAs the Zn-As IFC is only 30% higher than that of Li-As IFC, which is close to the value of 23% reported by Kuriyama *et al* [25] using the relation $\omega_{TO} \simeq (C/\mu)^{1/2}$, where ω_{TO} is the transverse phonon frequency at the Γ point, C represents the force constant of the nearest neighbor atoms and μ is the reduced mass.

4. Conclusion

In this paper, we have studied the vibrational properties of the filled tetrahedral semiconductor LiMgAs and its binary analog AlAs by using first principles calculations, based on the application of the plane-wave pseudopotential. The sound speeds evaluated from the acoustic phonon branches in different directions are quantitatively similar in LiMgAs and AlAs. The high frequency modes are assigned to the Li-Mg pair. The calculated interatomic constants reveal that the Li-As bond is ionic whereas the Mg-As one is covalent.

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