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Atomization energies of gaseous molecules of Li with Bi and Pb

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In continuation of an analysis of the saturated vapor over condensed phases of Li–Bi and Li–Bi–Pb alloys by mass spectrometry, the atomization energies of recently detected polyatomic molecules were determined. The following results were obtained:

Molecule	Atomization energy [kJ/mol]
Bi_2Li	367.4 ± 7.0
LiBiPb	341.2 ± 6.0
$BiLi_2$	326.0 ± 10.0
Bi_2Li_2	583.0 ± 15.0

These experimental values were compared with those calculated according to Pauling's rule.

INTRODUCTION

From a thermodynamic viewpoint, the knowledge of bond energies and their variation with cluster size is of fundamental importance for the understanding of the transition between the atomic state and the bulk metal or alloy. Experimentally derived atomization energies provide a basis for improving or testing models.

In a recent investigation of the vaporization of the alloys of lithium with bismuth and lead, which have been proposed as blanket materials for tritium breeding in fusion reactors, we have found the diatomic molecules BiLi and PbLi as the most abundant respective heteronuclear molecules and have determined their dissociation energies.[1] In addition, traces of polyatomic bismuth lithides could be detected in the vapor above the Bi–Li alloy. In the present investigation, we have extended these studies with the purpose to obtain atomization energies of the observed molecules $BiLi_2$, Bi_2Li, and Bi_2Li_2. In addition, the vaporization of a ternary Bi–Pb–Li alloy was investigated, and the molecule BiPbLi was identified and its atomization energy determined. To our knowledge, it is the first triatomic intermetallic compound observed composed of three different elements. During these experiments the previously reported molecule BiPb[2] was reinvestigated.

Prior to the present study, the polyatomic lithium intermetallic compound with silicon, Li_2Si_2,[3] and the bismuth compounds with tin, $SnBi_2$ and $SnBi_3$,[4] has been reported.

EXPERIMENTAL

The mass spectrometer used in the present investigation was a MS 702 (AEI) instrument with Mattauch Herzog geometry. It is equipped with an electron impact source and an ion counting system described elsewhere.[5]

The Knudsen cells were made of molybdenum. The orifices had a diameter and a length of 0.5 mm each. For convenience, inner liners made of Armco iron were used, which had an inner diameter of 8 mm.

Initial compositions of the alloys Li : Bi = 3 : 1 or Li : Bi : Pb = 1 : 1 : 1 were found appropriate with respect to the activities of the constituents. Relative ion currents of the observed species are given in Table I. All these species were identified by their m/e ratio, and if the intensities were sufficiently high, also by their isotopic composition. They were all found to be completely shutterable. Using the ionization potentials of Li^+ (5.39 eV),[6] Pb^+ (7.42 eV),[6] and Bi^+ (7.29 eV),[6] those of $BiPb^+$, Bi_2Li^+, $BiLi_2^+$, $BiPbLi^+$, and $Bi_2Li_2^+$ were found to be 7.1, 5.7, 7.0, 5.9, and 5.5 eV, respectively, applying the linear extrapolation method. The error is estimated to be ± 0.5 eV in all cases. Because these ionization potentials lie between those of the atomic species, we assume the molecular species to be parent ions.

The following reactions were studied to determine the atomization energies of the molecules:

$Bi_2Li(g)$:

$$2\,Bi(g) + Li(g) = Bi_2Li(g) \ ,$$

$$2\,BiLi(g) = Bi_2Li(g) + Li(g) \ .$$

$LiBiPb(g)$:

$$Li(g) + Bi(g) + Pb(g) = LiBiPb(g) \ ,$$

$$Bi_2Li(g) + Pb(g) = LiBiPb(g) + Bi(g) \ .$$

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TABLE I. Relative intensities observed above various alloys of Li, Bi, and Pb at 1200 K.

Initial composition Li : Bi : Pb	Intensities										
	Li^+	Li_2^+	Bi^+	Bi_2^+	BiLi	Bi_2Li	$BiLi_2^+$	Bi_2Li_2	PbLi	BiPbLi	Pb
1 : 1 : 1	3.2		100	7.6		0.003			0.03	0.005	22.4
3 : 1 : 0	100	0.02	46.0	4.1	0.48	0.05	0.007	0.006			

$BiLi_2(g)$:

$$2\,Li(g) + Bi(g) = BiLi_2(g) \ ,$$

$$Li_2(g) + Bi_2(g) = BiLi_2(g) + Bi(g) \ .$$

$Bi_2Li_2(g)$:

$$2\,Li(g) + 2\,Bi(g) = Bi_2Li_2(g) \ ,$$

$$Li_2(g) + Bi_2(g) = Bi_2Li_2(g) \ .$$

The partial pressures p_i were calculated according to

$$p_i = F \cdot \frac{I_i T}{\sigma_i n_i} \ ,$$

where I_i means the ion current, σ_i the ionization cross section, n_i the isotopic abundance of species i, and T the cell temperature. The proportionality factor F was determined by measurements of the equilibrium constants for the reactions $Li_2(g) = 2\,Li(g)$[7] and $Bi_2(g) = 2Bi(g)$,[8] and by comparison with calculated values. The ionization cross sections of the atoms were taken from Mann[9]; for the molecules: $\sigma = 0.75\ \Sigma\ \sigma_i$ was used.

The ion current I_{Li}^+ has been measured at an electron energy 2 eV above threshold. This ion current corresponds to a certain fraction of that at maximum ionization cross section. The ion currents of the other spe-

TABLE II. The thermodynamic functions $\phi_0^\circ = -(G_T^\circ - H_0^\circ)/T$ (J/mol/K) and $(H_T^\circ - H_0^\circ)$ (kJ/mol) of the molecules Bi_2Li, BiPbLi, $BiLi_2$, and Bi_2Li_2.

Structure / Molecule	γ / α	180°				110°			
		1/10		1/100		1/10		1/100	
	T/K	ϕ_0°	$H_T^\circ - H_0^\circ$	ϕ_0°	$H_T^\circ - H_0^\circ$	ϕ_0°	$H_T^\circ - H_0^\circ$	ϕ_0°	$H_T^\circ - H_0^\circ$
Bi_2Li	298	···	13.8	···	14.9	···	13.4	···	14.2
	1000	326.1	56.5	342.4	57.9	347.8	53.3	356.7	54.2
	1100	331.6	62.7	348.0	64.1	353.0	59.0	361.9	60.0
	1200	336.6	68.9	353.1	70.3	357.7	64.8	336.7	65.8
	1300	341.2	75.1	357.8	76.5	362.1	70.6	371.1	71.6
BiPbLi	298	···	14.1	···	15.2	···	13.7	···	14.3
	1000	321.7	56.9	337.6	58.2	343.5	53.6	352.3	54.4
	1100	327.2	63.1	343.1	64.4	348.7	59.4	357.5	60.2
	1200	332.1	69.3	348.2	70.6	353.4	65.2	362.3	66.0
	1300	336.8	75.6	352.9	76.8	357.7	71.01	366.7	71.8
$BiLi_2$	298	···	12.0	···	13.8	···	12.2	···	13.1
	1000	282.7	53.7	300.1	56.1	304.6	51.3	313.3	52.5
	1100	288.0	59.9	305.6	62.2	308.1	57.1	318.3	58.2
	1200	292.8	66.0	310.5	68.4	314.1	62.8	323.0	64.0
	1300	297.3	72.2	315.1	74.6	318.3	68.6	327.3	69.7
		Li–Bi≡Bi–Li				$Bi{\equiv}Bi\langle^{Li}_{Li}$			
	α	1/10		1/100					
Bi_2Li_2	298	···	18.8	···	21.3	···	17.5		
	1000	344.6	81.2	379.9	84.1	371.4	73.6		
	1100	352.0	90.4	387.6	93.3	378.5	82.0		
	1200	358.8	99.2	394.6	102.1	385.0	90.0		
	1300	365.1	108.4	401.1	111.3	391.0	98.3		
	1400	371.0	117.6	407.2	120.5	396.6	106.7		
BiPb	298	···	10.3						
	1000	295.3	36.4						
	1100	298.8	40.2						
	1200	302.0	43.9						
	1300	304.9	47.7						
	1400	307.7	51.5						

TABLE III. Equilibrium constants and enthalpies (kJ/mol) of the homogeneous reactions (1) $2\,Bi(g) + Li(g) = Bi_2Li(g)$ and (2) $2\,BiLi(g) = Bi_2Li(g) + Li(g)$, involving the molecule Bi_2Li ($p_0 = 101\,325$ Pa).

			180°				110°			
	γ									
	α		1/10		1/100		1/10		1/100	
T/K	$\ln K_1 \cdot p_0^2$	$\ln K_2$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$
1091	17.21	4.34	−374.2	−69.7	−356.3	−51.8	−350.8	−46.3	−341.1	−36.6
1121	16.09	4.16	−374.2	−69.7	−355.8	−51.3	−350.3	−45.8	−340.3	−35.8
1157	14.66	3.83	−372.6	−68.5	−353.6	−49.4	−348.0	−43.4	−337.7	−33.6
1180	14.01	3.85	−373.8	−69.8	−354.3	−50.4	−348.8	−44.8	−338.2	−34.3
1214	12.71	3.61	−371.6	−69.1	−351.5	−49.1	−346.0	−43.9	−335.1	−32.7
1249	12.12	3.54	−376.3	−70.1	−355.7	−49.4	−350.1	−43.9	−338.9	−32.7
1197	13.28	3.65	−372.0	−68.7	−352.2	−49.0	−346.7	−43.4	−335.9	−32.7
1197	13.35	3.62	−371.7	−68.4	−352.9	−48.7	−347.4	−43.1	−336.6	−32.4
1115	16.25	4.05	−373.7	−68.4	−355.4	−50.1	−349.8	−44.5	−339.9	−34.6
Average ΔH_0°, third law			−373.3	−69.1	−354.2	−49.9	−348.6	−44.3	−338.2	−33.9
			±1.5	±0.7	±1.7	±1.1	±1.7	±1.1	±2.1	±1.5
ΔH_0°, second law			−374.9	−67.4	−376.1	−68.6	−371.1	−63.6	−371.9	−64.4
			±11.6	±5.6	±11.6	±5.6	±11.6	±5.6	±11.6	±5.6

$\Delta H_T^\circ(1)$, second law $= -381.1 \pm 11.6$; $\Delta H_T^\circ(2) = -58.6 \pm 5.6$

cies are measured at electron energies which correspond to this same fraction of the respective maximum ionization probability.

From the partial pressures p_i, the equilibrium constants K and then the enthalpy changes of the various reactions cited above were calculated by the second and third law methods according to the relations:

$$\Delta H_T^\circ(\mathrm{II}) = -R\, d \ln K / d(1/T) \ ,$$

$$\Delta H_0^\circ(\mathrm{II}) = \Delta H_T^\circ(\mathrm{II}) - \Delta(H_T^\circ - H_0^\circ) \ ,$$

$$\Delta H_0^\circ(\mathrm{III}) = -RT \ln K + T\Delta\phi_0^\circ \ .$$

Values of the heat content $H_T^\circ - H_0^\circ$, and the Gibbs energy function $\phi_0^\circ = -(G_T^\circ - H_0^\circ)/T$, were taken from the literature for $Bi(g)$, $Bi_2(g)$, and $Pb(g)$,[8] $Li(g)$ and $Li_2(g)$.[7] Those for $BiLi(g)$ were recalculated using a ground state multiplicity $g = 1$,[10] while the other parameters were left unchanged.[1] The functions for $BiLi_2(g)$, $Bi_2Li(g)$, $LiBiPb(g)$, $Bi_2Li_2(g)$, and $BiPb(g)$ were computed from estimated molecular parameters and assuming various geometries: for the triatomic molecules Li–Bi–Li, Li–Bi–Bi, and Li–Bi–Pb bond angles $\gamma = 180°$ and 110° were chosen; for the tetratomic molecule Li–Bi–Bi–Li the linear, and a structure

TABLE IV. Equilibrium constants and enthalpies (kJ/mol) of the homogeneous reactions (1) $Li(g) + Bi(g) + Pb(g) = LiBiPb(g)$, and (2) $Bi_2Li(g) + Pb(g) = LiBiPb(g) + Bi(g)$, involving the molecule LiBiPb. $\alpha = 1/10$ and $\gamma = 180°$ were used for $Bi_2Li(g)$ in reaction (2) ($p_0 = 101\,325$ Pa).

			180°				110°			
	γ									
	α		1/10		1/100		1/10		1/100	
T/K	$\ln(K_1 \cdot p_0^2)$	$\ln K_2$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$
1018	19.22	−0.923	−358.5	15.10	−342.3	31.3	−338.2	37.3	−329.3	46.2
1056	17.90	−0.560	−360.5	12.6	−343.7	29.3	−339.6	35.4	−330.2	44.7
1080	17.05	−0.323	−361.2	10.6	−344.0	27.8	−339.9	34.0	−330.4	43.5
1111	15.70	−0.338	−359.2	11.7	−341.5	28.9	−337.4	35.0	−327.5	44.9
1141	14.66	−0.359	−359.2	11.6	−341.0	29.9	−336.9	35.0	−326.8	46.2
1152	14.26	−0.225	−358.8	10.5	−340.4	28.9	−335.4	35.0	−326.2	45.3
1155	14.28		−360.0		−341.5		−337.5		−327.2	
1188	13.39	−0.394	−361.7	12.4	−342.7	31.4	−338.7	37.7	−328.6	48.3
1213	12.70	−0.344	−362.5	11.8	−343.0	31.6	−339.1	37.9	−328.2	48.7
1212	12.35	−0.346	−358.6	11.8	−339.2	31.6	−335.3	37.9	−324.4	48.7
1253	11.48	−0.220	−361.8	9.8	−341.7	31.5	−337.8	37.7	−326.6	48.9
1309	10.44	−0.082	−366.4	7.05	−345.9	31.4	−341.5	37.7	−329.7	49.5
Average ΔH_0°, third law			−360.7	11.3	−342.2	30.3	−338.1	36.4	−328.8	46.8
			±2.3	±2.0	±1.9	±1.4	±1.8	±1.5	±3.5	±2.1
ΔH_0°, second law			−340.9	21.6	−341.9	20.6	−337.2	25.3	−338.0	24.5
			±7.3	±5.4	±7.3	±5.4	±7.3	±5.4	±7.3	±5.4

$\Delta H_T^\circ(1)$, second law $= -346.4 \pm 7.3$; $\Delta H_T^\circ(2)$, second law $= 22.0 \pm 5.4$

TABLE V. Equilibrium constants and enthalpies kJ/mol of the homogeneous reactions (1) $2\,Li(g) + Bi(g) = BiLi_2(g)$, and (2) $Li_2(g) + Bi_2(g) = BiLi_2(g) + Bi(g)$, involving the molecule $BiLi_2$ ($p_0 = 101\,325$ Pa).

	γ		180°				110°			
	α		1/10		1/100		1/10		1/100	
T/K	$\ln(K_1 \cdot p_0^2)$	$\ln K_2$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$
1213	9.20	2.05	−330.5	−37.4	−309.0	−15.9	−304.6	−11.5	−293.9	−0.75
1295	7.59	1.98	−336.1	−38.8	−313.0	−15.8	−308.8	−11.6	−297.2	0.02
1325	6.49	1.87	−331.9	−38.4	−308.3	−14.8	−304.1	−10.6	−292.2	1.26
Average ΔH_0°, third law			−332.8	−38.2	−310.1	−15.5	−305.8	−11.2	−294.4	0.2
			±2.9	±0.7	±2.5	±0.6	±2.6	±0.5	±2.5	±1.0
ΔH_0°, second law			−298.2	−21.6	−300.7	−24.1	−295.3	−18.7	−296.5	−19.9
			±53.4	±8.2	±53.4	±8.2	±53.4	±8.2	±53.4	±8.2

$\Delta H_T^\circ(1)$, second law = 308.0 ± 53.4; $\Delta H_T^\circ(2)$, second law = −19.1 ± 8.2

$$Bi-Bi\begin{matrix}\diagup Li \\ \diagdown Li\end{matrix} \quad \text{(point group } C_{2v}\text{)}$$

with $\gamma(Li-Bi-Li) = 110°$, were used.

The bond distances r_1 and r_2 and the stretching force constants k_1 and k_2 were assumed to be the same as for the corresponding diatomic molecules. The bending force constants were taken as $k_\gamma/r_1 r_2 = \alpha(k_1 + k_2)/2$, where $\alpha = 1/10$ or $1/100$ was used. The statistical weights chosen for the electronic ground states were 1 for Bi_2Li_2, 2 for Bi_2Li, and 1 for LiBiPb. For BiPb, the parameters $r_e = 3.01$ Å, $\omega_e = 155.3$ cm^{-1}, and a multiplicity of the electronic ground state $g = 2$, were used. The calculated values of Φ_0° and $H_T^\circ - H_0^\circ$ are listed in Table II.

RESULTS

The enthalpies and the equilibrium constants of the reactions involving each of the polyatomic intermetallic molecules are presented in Tables III–VI. The measured second law reaction enthalpies are given at the bottom of each table. The results for the reactions involving the BiPb molecules are listed in Table VII.

From Tables III–V, the effects of the various assumed geometries and bending force constants on the enthalpy values can be seen. The spread in the resulting third law enthalpies is up to 40 kJ/mol (linear structure with $\alpha = 1/10$, as compared with the bent structure with $\alpha = 1/100$). It is also noteworthy that for reactions involving a triatomic molecule, the assumed bent structure with $\alpha = 1/10$ results in an enthalpy change that is similar to that obtained when based on a linear structure of the same molecule with $\alpha = 1/100$.

To find the most probable structure of a molecule, the agreement between the third law and second law results for the various structures has been examined. For Bi_2Li, (Table III), good agreement is found for $\gamma = 180°$ and $\alpha = 1/10$. For LiPbBi (Table IV), the best agreement is obtained for the direct reaction (1) for the structure $\gamma = 180°$ and $\alpha = 1/100$, while the results for the exchange reaction (2) do not allow a decision to be made. Therefore the structure $\gamma = 180°$ and $\alpha = 1/100$

TABLE VI. Equilibrium constants and enthalpies (kJ/mol) of the homogeneous reactions (1) $2\,Li(g) + 2\,Bi(g) = Bi_2Li_2(g)$ and (2) $Li_2(g) + Bi_2(g) = Bi_2Li_2(g)$, involving the molecule Bi_2Li_2 ($p_0 = 101\,325$ Pa).

	Geometry		Li–Bi–Bi–Li				$Bi-Bi\begin{matrix}\diagup Li \\ \diagdown Li\end{matrix}$	
	α		1/10		1/100			
T/K	$\ln(K_1 \cdot p_0^3)$	$\ln(K_2 \cdot p_0)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$	$\Delta H_0^\circ(1)$	$\Delta H_0^\circ(2)$
1178	22.0		−598.2		−556.0		−567.3	
1226	19.3		−594.8		−550.9		−563.3	
1275	17.3		−597.5		−551.6		−565.0	
1327	15.1		−598.3		−550.4		−564.2	
1159		11.8		−279.2		−237.8		−249.0
1165		11.6		−279.1		−237.4		−248.4
1174		11.5		−279.6		−237.6		−249.3
1195		11.0		−279.7		−236.9		−248.7
Average ΔH_0°, third law			−597.2 ± 1.6		−552.2 ± 2.5		−564.9 ± 1.7	
				−279.4 ± 0.3		−237.3 ± 0.4		−248.8 ± 0.4
ΔH_0°, second law			−593.7 ± 20.0		−596.6 ± 20.0		−585.3 ± 20.0	
				−257.3 ± 21.1		−260.3 ± 21.1		−249.0 ± 21.1

$\Delta H_T(1)$, second law = −595.3 ± 20.0; $\Delta H_T(2)$, second law = −247.3 ± 21.1

TABLE VII. Equilibrium constants and enthalpies (kJ/mol) of the homogeneous reactions: (1) $Bi(g) + Pb(g) = BiPb(g)$ and (2) $Bi_2(g) + Pb(g) = Bi(g) + BiPb(g)$, involving the molecule BiPb ($p_0 = 101\,325$ Pa).

T/K	$\ln(K_1 \cdot p_0)$	$\ln K_2$	$\Delta\phi^\circ_0(1)$	$\Delta\phi^\circ_0(2)$	$\Delta H^\circ_0(1)$	$\Delta H^\circ_0(2)$
989	7.70	−4.29	−75.51	24.70	−138.0	59.7
965	7.91	−4.58	−75.39	24.69	−136.2	60.6
931	8.65	−4.76	−75.22	24.69	−137.0	59.8
913	9.32	−4.79	−75.13	24.68	−139.3	58.9
903	9.25	−5.03	−75.08	24.68	−137.2	60.0
951	8.31	−4.60	−75.32	24.69	−137.3	59.8
993	7.51	−4.29	−75.53	24.70	−137.0	59.9
1028	6.77	−4.01	−75.70	24.70	−135.7	59.7
1064	6.42	−3.83	−75.87	24.71	−137.5	60.2
		Average ΔH°_0, third law			−137.2 ± 1.0	59.8 ± 0.5
		ΔH°_0, second law			−143.7 ± 6.8	57.3 ± 3.1

$\Delta H^\circ_T(1)$, second law = −149.5 ± 6.8;
$\Delta H^\circ_T(2)$, second law = 57.5 ± 3.1

was selected. For $BiLi_2$ (Table V), no well-founded decision with respect to a structure is possible because of a lack of data. A linear structure with $\alpha = 1/10$ was arbitrarily selected for this molecule. In the case of Bi_2Li_2 (Table VI), the linear structure with $\alpha = 1/10$ is favored.

The value for the atomization energy of a molecule is then found by calculation of the mean of the four individual values obtained for this molecule from the two reactions using the second and third law method. Here, the structure selected above was used. In these calculations, a weight of 2 was given to the third law values, because of their smaller errors. The atomization energies found for the various molecules are collected in Table VIII. Table VII shows the results obtained for BiPb. The atomization energy found agrees well with that determined by Rovner *et al.*[2]

TABLE IX. Comparison of experimental and calculated atomization energies (kJ/mol).

Molecule	$\Delta H^\circ_{0,at.}$(expt.)	$\Delta H^\circ_{0,at.}$(calc.) Bond sum	Pauling
Bi_2Li	367.4 ± 7.0	343.4	378
LiBiPb	341.2 ± 6.0	285.0	320
$BiLi_2$	326.0 ± 10.0	292.6	362
Bi_2Li_2	583.0 ± 15.0	489.7	559

CONCLUSION

In Table IX the atomization energies obtained in this work are compared with those calculated by summation of the individual bond strengths occurring in a molecule. On the one hand (column 3), the bond strengths Bi–Bi,[8] Bi–Li,[1] Bi–Pb, (Ref. 2 and this work) used for this calculation are experimental values taken from literature. It is seen that these data, are all lower than the measured atomization energies of the polyatomic molecules, from 24 kJ/mol in the case of $BiLi_2$ up to 93 kJ/mol in the case of Bi_2Li_2. On the other hand (column 4), the strengths of the heteronuclear bonds Bi–Li and Bi–Pb were calculated according to Pauling's rule[11]:

$$D(A-B) = 1/2[D(A-A) + D(B-B)] + 96(X_A - X_B)^2 ,$$

while for the homonuclear bond Bi–Bi again the experimental value was used. The electronegativities were taken from Pauling.[11] Because Bi–Li is singly bonded, "single bond energies"[11] were used for the calculation of the bond Bi–Li. The result is $D(BiLi) = 180.9$ kJ/mol, appreciably higher than the experimental value 146.3 kJ/mol.

To calculate $D(BiPb)$, the experimental values $D(BiBi)$[8] and $D(PbPb)$[12] were used. The result $D(BiPb) = 139.1$ kJ/mol is very nearly the mean of these values because of the small difference in the electronegativities of Bi and Pb, and agrees very well with the experimental value.[2]

TABLE VIII. Selected reaction enthalpies ΔH°_0 and derived atomization energies $\Delta H^\circ_{0,at.}$ of intermetallic molecules of Li with Bi and Pb (kJ/mol).

Reaction	ΔH°_0	$\Delta H^\circ_{0,at.}$	Molecule
$2\,Bi(g) + Li(g) = Bi_2Li(g)$	−373.8 ± 5.0	367.4 ± 7.0	Bi_2Li
$2\,BiLi(g) = Bi_2Li(g) + Li(g)$	−68.5 ± 3.0		
$Li(g) + Bi(g) + Pb(g) = LiBiPb(g)$	−342.1 ± 5.0	341.2 ± 6.0	LiBiPb
$Bi_2Li(g) + Pb(g) = LiBiPb(g) + Bi(g)$	27.1 ± 5.0		
$2\,Li(g) + Bi(g) = BiLi_2(g)$	−321.3 ± 10.0	326.0 ± 10.0	$BiLi_2$
$Li_2(g) + Bi_2(g) = BiLi_2(g) + Bi(g)$	−32.7 ± 8.0		
$2\,Li(g) + 2\,Bi(g) = Bi_2Li_2(g)$	−596.0 ± 10.0	583.0 ± 15.0	Bi_2Li_2
$Li_2(g) + Bi_2(g) = Bi_2Li_2(g)$	−272.0 ± 10.0		
$Bi(g) + Pb(g) = BiPb(g)$	−139.4 ± 3.0	138.7 ± 3.0	BiPb
$Bi_2(g) + Pb(g) = BiPb(g) + Bi(g)$	59.0 ± 1.0		

Auxiliary data used: $\Delta H^\circ_{0,at.}(BiLi) = 146.3$ kJ/mol (recalculated according to Ref. 10)
$\Delta H^\circ_{0,at.}(Li_2) = 100.96$ kJ/mol (Ref. 7)
$\Delta H^\circ_{0,at.}(Bi_2) = 197.1$ kJ/mol (Ref. 8)

Summation of these calculated values yields atomization energies of the molecules, which agree with those found in this work within about 10%. Obviously the bond Bi–Li is stronger, and Pauling's formula gives better results for this bond in the triatomic molecules treated in this work than in the diatomic molecule.

The dimerization energy of BiLi obtained experimentally is about twice the dissociation energy of the monomer. A comparably high ratio of dimerization energy to bond strength has been observed for $2\,SiLi \rightarrow Si_2Li_2$. This is likely to be caused by multiple bond formation between the heavy atoms.

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