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STRUCTURAL ENERGIES OF LIGHT METALS

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For the first time, an exact model potential calculation of the structural energies of Li, Na, Be and Mg is carried out without using any form of interpolation to avoid any possible error. The influences of using different model potential parameters and of applying effective mass approximation are examined. The observed HCP structure is found to have the lowest structural energy in all cases. Calculated and observed axial ratios are in good agreement.

1. Introduction

The structural energy per ion E_{st}, i. e., the structural dependent part of the total energy, is calculated at $T = 0$ K using the optimized model potential of Shaw[1] (OMP) and second order perturbation theory. E_{st} is calculated at a constant volume, the experimentally observed one, for the three common crystal structures FCC, BCC and HCP with ideal and variable axial ratio c/a.

E_{st} is the sum of the electrostatic energy E_{es} and the band structure energy E_{bs}, through which the crystal potential is presented[2]

$$E_{st} = E_{es} + E_{bs}. \tag{1}$$

E_{bs} is a summation in k-space over the energy wave number characteristic $F(\mathbf{q})$ multiplied by the square of the structure factor $S(\mathbf{q})$:

$$E_{bs} = \sum_{\mathbf{q}\neq 0} |S(\mathbf{q})|^2 F(\mathbf{q}). \tag{2}$$

The results are usually expressed as the dimensionless coefficient $a = 2r_0E/Z^2$, where r_0 is the radius of the atomic sphere of volume V_0 and Z is the effective valence. In literature a_{bs} is usually calculated by interpolating the tabulated $F(\mathbf{q})$ to find $F(\mathbf{g}_i)$, where $\mathbf{g}_i$ are the reciprocal lattice vectors of the crystal structure under consideration. However, interpolation is always associated with some inaccuracy regardless of the interpolation scheme used. This can lead to erroneous results since the relative energies ΔE_{bs} of the different crystal structures are usually very small. ΔE_{bs} are highly sensitive to the crystal potential used$^{3)}$. That is why calculations of E_{st} and hence determination of stable crystal structures represent a very critical test of the crystal potential.

To remove any possible uncertainty due to interpolation, $F(\mathbf{q})$ and hence E_{bs} are calculated exactly at the reciprocal lattice vectors $\mathbf{g}_i$ in the present paper. Contrary to all existing calculations, this is the first paper where no interpolation schemes are used at all.

Another feature of the present calculation is the treatment of exchange and correlation of $F(\mathbf{q})$, which differs from that of Shaw$^{4)}$. Our approach$^{5)}$ is based on the diagrammatic representation of the many electron interactions and takes into account the screening of $h(\mathbf{q})$, which was not done by Shaw$^{4)}$.

The model potential parameters used in the present calculation of E_{bs} are those of Shaw$^{1)}$ (SH), Ese and Reissland$^{6)}$ (ER) and Appapillai and Heine$^{7)}$ (AH). The effective mass approximation$^{7)}$ was also applied (in AH potential only) for sake of comparison and is denoted by AH*. For Li and Be a second value$^{7)}$ of m_k (AH**) was obtained by modelling both $l = 0$ and $l = 1$ components of the potential using the scheme suggested by Evans$^{8)}$.

2. *Convergence of band structure energy*

The calculation of the very small structural energy differences between FCC, BCC and HCP needs a well-converged sum in Eq. (2). A critical test of the convergence of a_{bs} in k-space was carried out for Li, Na, Be and Mg (Figs. 1 to 4). The summation was calculated up to the very long range $q = 12\ k_f$ (Li, Na) and $q = 16.5\ k_f$ (Be, Mg) to ensure a good convergence of at least six decimals in a_{st} for all crystal structures. This was achieved at $q/k_f = 8.4$, 11, 14.3 and 14.9 for Li, Na, Be and Mg, respectively. This extraordinary long range summation is essential to obtain accurate quantitative values of a_{st} because the convergence of Eq. (2) is very slow. In literature the summation is terminated usually at $q = 7$ to $8\ k_f$, which gives correct qualitative results only.

A great deal of care was given to the Gauss numerical integration involved in the calculation of $F(\mathbf{q})$, especially at q close to $2k_f$, because of the logarithmic singularity at $q = 2k_f$. In the present calculation, we used $N = 20$ to 32 Gauss points for q close to the singularity and $N = 10$ to 12 otherwise.

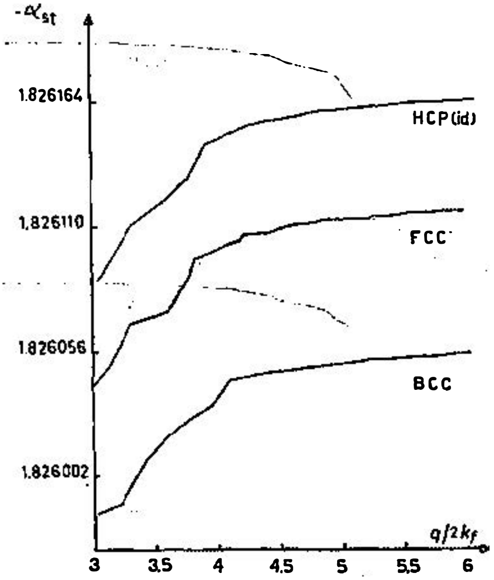

Fig. 1. Convergence of structural coefficient α_{st} for BCC, FCC and ideal HCP structures. Li (ER-potential).

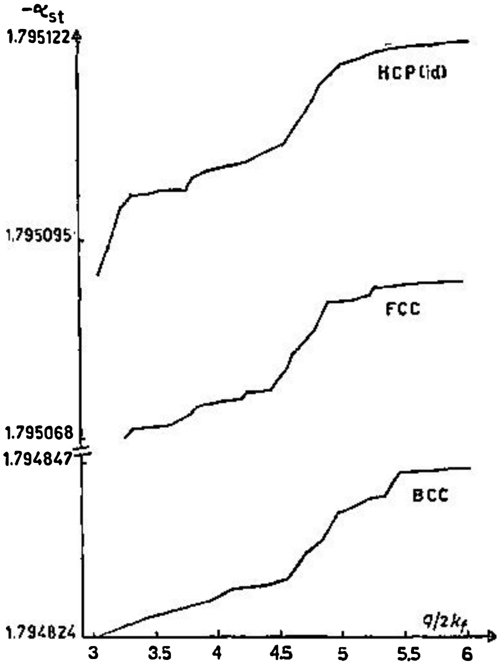

Fig. 2. Convergence of structural coefficient α_{st} for BCC, FCC and ideal HCP structures. Na (ER-potential).

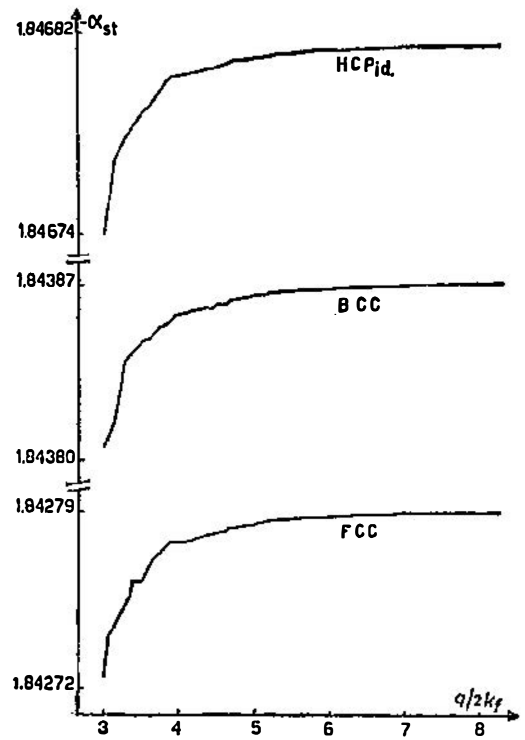

Fig. 3. Convergence of structural coefficient α_{st} for BCC, FCC and ideal HCP structures. Be (ER-potential).

3. *Results*

Our calculated electrostatic constants α_{es} are identical with those of Sholl[9]. To determine α_{es} at various axial ratios c/a in the HCP structure we used the formalism given by Harrison[2]. α_{bs} and hence α_{st} were calculated in the three common crystal structures FCC, BCC and HCP with ideal $c/a = \sqrt{8/3}$. In addition, the variation of α_{st} with the axial ratio c/a in the HCP structure was examined to obtain $(c/a)_{min}$ at which α_{st} is minimum. The whole procedure was carried out several times for each metal using different potential parameters with and without effective mass approximation. We have taken the exchange and correlation function of Singwi et al.[10]. The results are given in Table 1. The variation of α_{st} versus c/a in the HCP structure is shown in Figs. 5 to 8 for Li, Be (ER potential) and Mg (SH potential).

From Table 1 we see that the energetically most favoured structure in all cases is HCP, which is also the experimentally observed structure. For Be, however, the BCC structure is more stable than FCC, while for Li, Na and Mg the situation is reversed. The theoretically calculated axial ratio $(c/a)_{min}$, at which α_{st} (HCP) has its minimum, changes slightly according to the potential parameters

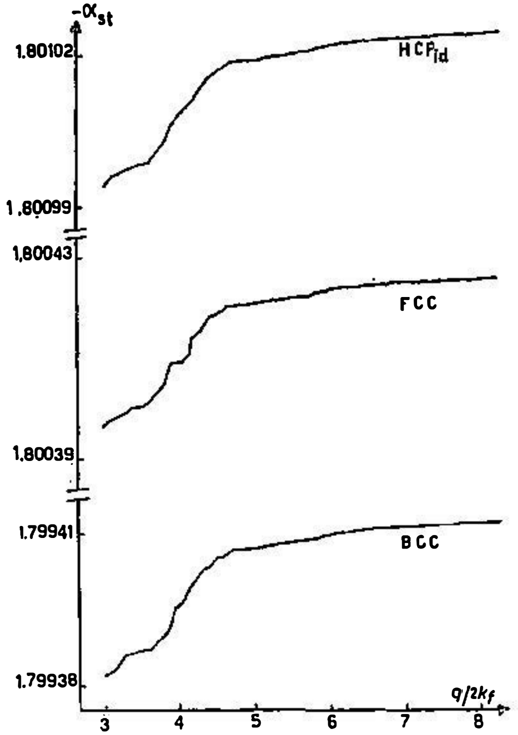

Fig. 4. Convergence of structural coefficient a_{st} for BCC, FCC and ideal HCP structures. Mg (SH-potential).

used. On the other hand the numerical values of a_{st} increase with increasing Z, which is obvious. Comparison of AH* and AH of Table 1 shows that inclusion of effective mass approximation changes the results quantitatively in favour of HCP, however, the order of stable crystal structures is not affected. An increase of 28% (Li), 15% (Na), 33% (Be) and 14% (Mg) in $|E_{bs}|$ is obtained upon inclusion of effective mass corrections, compared to 24% (Li), 15% (Na), 26% (Be) and 11% (Mg) as expected by Weaire's treatment$^{11)}$. In case of Li and Be the AH** values of $|E_{bs}|$ are 6% and 15% less than AH results, while Weaire$^{11)}$ predicted 4% and 11%, respectively.

4. *Discussion and conclusions*

The main purpose of the present paper is to examine the applicability of the optimized model potential and second order perturbation in the sensitive and critical calculation of stable crystal structures for some light metals. To exclude any possible error arising from the interpolation schemes used by other authors, the band structure energy E_{bs} (or a_{bs}) was calculated exactly without using any form of interpolation. This is the major advantage of our results over previous ones.

TABLE 1.

Potential	$(c/a)_{min}$	HCP_{min}	HCP_{id}	FCC	BCC
a) Li					
AH*	1.635	−1.833717	−1.833717	−1.833635	−1.833510
ER	1.630	−1.826166	−1.826166	−1.826118	−1.826056
AH	1.635	−1.824983	−1.824983	−1.824938	−1.824869
AH**	1.635	−1.822681	−1.822681	−1.822643	−1.822576
b) Na					
AH*	1.638	−1.795512	−1.795510	−1.795463	−1.795167
ER	1.633	−1.795122	−1.795122	−1.795089	−1.794847
AH	1.637	−1.795080	−1.795078	−1.795047	−1.794809
c) Be					
AH*	1.604	−1.910789	−1.910707	−1.900769	−1.906595
AH	1.609	−1.882364	−1.882313	−1.874470	−1.878897
AH**	1.612	−1.869876	−1.869837	−1.862967	−1.866722
SH	1.616	−1.851809	−1.851790	−1.847038	−1.848657
ER	1.618	−1.846827	−1.846815	−1.842790	−1.843870
d) Mg					
AH*	1.629	−1.802375	−1.802374	−1.801742	−1.800633
AH	1.629	−1.801223	−1.801223	−1.800630	−1.799607
SH	1.630	−1.801025	−1.801024	−1.800426	−1.799412
ER	1.631	−1.799603	−1.799603	−1.799347	−1.798197

a_{st} of Li, Na, Be and Mg in BCC, FCC and ideal HCP structures. The minimum of a_{st} (HCP) is given together with the corresponding $(c/a)_{min}$.

To show the error in a_{bs} arising from interpolation, we consider a_{bs} of Mg calculated up to $q = 6k_f$ using SH potential. Using 4-point interpolation with interval $q/k_f = 0.05$, we find:

$$a_{bs}(\text{FCC}) = -0.00854862 \text{ and } a_{bs}(\text{HCP}_{id}) = -0.00931738.$$

If no interpolation is used (i. e. exact value) we get:

$$a_{bs}(\text{FCC}) = -0.00827559 \text{ and } a_{bs}(\text{HCP}_{id}) = -0.00931633.$$

It is clear that interpolation causes much greater error in a_{bs} (FCC) that in a_{bs} (HCP$_{id}$) of Mg.

Refs. 10 to 24 represent the most important papers using different forms of pseudo and model potentials in the calculation of structural energies of light metals. Hafner and Heine$^{25)}$ gave a qualitative discussion of the structural trends of the elements, however, they did not attempt to calculate E_{st}.

In Li, Na, Be and Mg there are no d-electrons and these metals are considered to be ideal from the point of view of pseudopotential theory. This is demonstrated clearly in the successful prediction of their stable crystal structures using model or pseudopotentials$^{12-24)}$. Calculated and observed axial ratios are given in

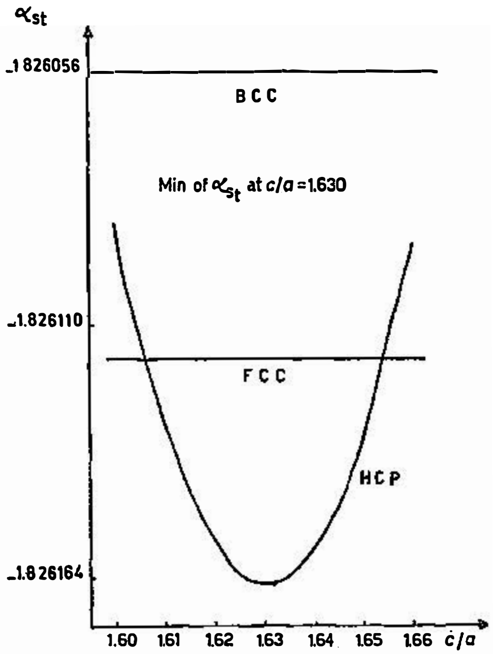

Fig. 5. Variation of structural coefficient a_{st} with the axial ratio c/a in the HCP structure. a_{st} of FCC and BCC structures are also shown.
Li (ER-potential).

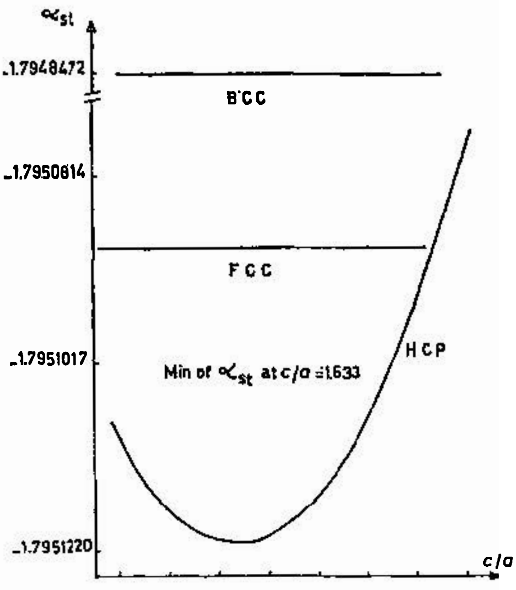

Fig. 6. Variation of structural coefficient a_{st} with the axial ratio c/a in the HCP structure. a_{st} of FCC and BCC structures are also shown.
Na (ER-potential).

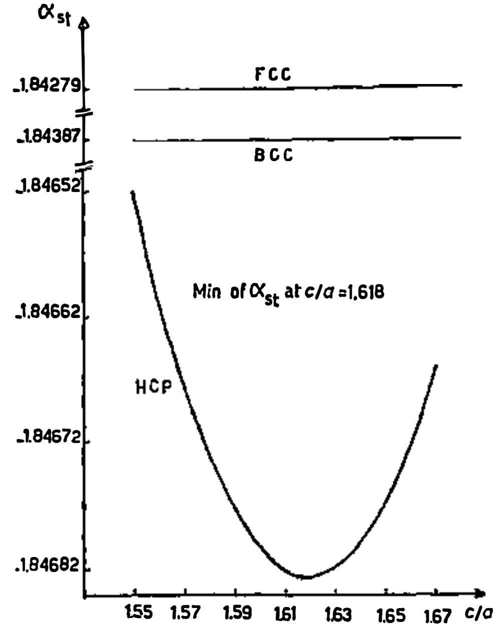

Fig. 7. Variation of structural coefficient α_{st} with the axial ratio c/a in the HCP structure. α_{st} o FCC and BCC structures are also shown.
Be (ER-potential).

TABLE 2.

a) Li

Ref.	12)	21)	14)	18)	16)	19)	Present	17)	Obs., 20), 22)
c/a	1.597	1.62	1.623	1.627	1.63	1.633	1.63, 1.635	1.636	1.637

b) Na

Ref.	12)	15)	21)	17), 18)	14), 15), 22)	Obs., 20)	Present
c/a	1.58	1.625	1.63	1.632	1.633	1.634	1.633—1.638

c) Be

Ref.	Obs.	16), 18)	12)	19)	Present	21)	17)	14)	20)
c/a	1.568	1.585	1.592	1.599	(1.604—1.618)	1.61	1.614	1.621	1.633

d) Mg

Ref.	19)	Obs.	12), 18)	14), 23)	Present	17)	24)
c/a	1.618	1.623	1.625	1.630	(1.629—1.631)	1.631	1.633

Calculated and observed axial ratios of Li, Na, Be and Mg.

ΔE_{st} for Be and Mg. However, we think that the reliability of their estimates is questionable, since they gave the same values for both Be and Mg. A quantitative comparison between theoretical and experimentally estimated structural energy differences is given in Table 3. Due to lack of experimental data, no such comparison was possible for Li.

TABLE 3.

a) Na ($V_0 = 255.19$ au)

Ref.	27), 28)	22)	24)	18)	Present			15)	24)	12)	20)
	Exp.		GPT		ER	AH	AH*		LMT		
BCC-HCP	0.055	0.05*)	0.065	0.071	0.081	0.083	0.108	17**)	0.30	0.40	0.76

*) calculated at volume = $1.07\ V_0$
**) calculated at volume = $0.75\ V_0$

b) Be ($V_0 = 54.70$ au)

Ref.	29)	30)	Present					20)	12)	19)	16)	18)
	Exp.		ER	SH	AH**	AH	AH*					
FCC-HCP	1.48	4.02	7.54	9.27	13.93	15.76	20.2	8.0	8.30	12.57	36.3	44.5
BCC-HCP	0.351	5.11	5.52	6.12	6.36	6.92	8.45	8.4	9.45	8.18	12.6	20.7

c) Mg ($V_0 = 156.8$ au)

Ref.	29)	Present				24)		31)	30)	19)	18)	17)	16)	12)
	Exp.	ER	SH	AH	AH*	GPT	LMT							
FCC-HCP	1.48	0.35	0.83	0.83	0.89	0.6	0.7	0.9	0.5	1.8	1.6	0.4	1.1	1.8
BCC-HCP	3.51	1.94	2.23	2.26	2.46	2	0.9	2.5	1.7	3.2	3.1	1.8	5.4	4.2

Structural energy differences ΔE_{st} expressed in mRy (1 mRy = 0.0136 eV).

The result of Smirnov et al.[22] for Na in Table 3 is calculated at a volume 7% larger than V_0, thus its agreement with the experimental value is not justified. However, ΔE_{st} of McMahan and Moriarty[24] using GPT and of Williams and Appapillai[18] using OMP together with our ER result all have reasonable agreement with experiment.

The quantitative agreement of theoretical results with the experimental estimates for Be are not satisfactory (Table 3). In the present paper and Refs. 16, 18 and 19 the BCC structure is closer to the HCP, whereas in the experimental estimates and Refs. 12, 20 and 30 the FCC structure comes in second place after HCP.

Thus for Be we conclude that inclusion of third order terms in our OMP calculations may remove this discrepancy and improve the quantitative agreement with both observed axial ratio and experimental ΔE_{st}. However, the results of a band structure calculation of Be[32] carried out using the present OMP are very satisfactory. This is understandable since energy bands are far less sensitive to the crystal potential and perturbation order than structural energies. The fact that Z plays quantitatively an important role in the band structure[32] is also confirmed in the present paper. This means that Z could be used as a parameter to

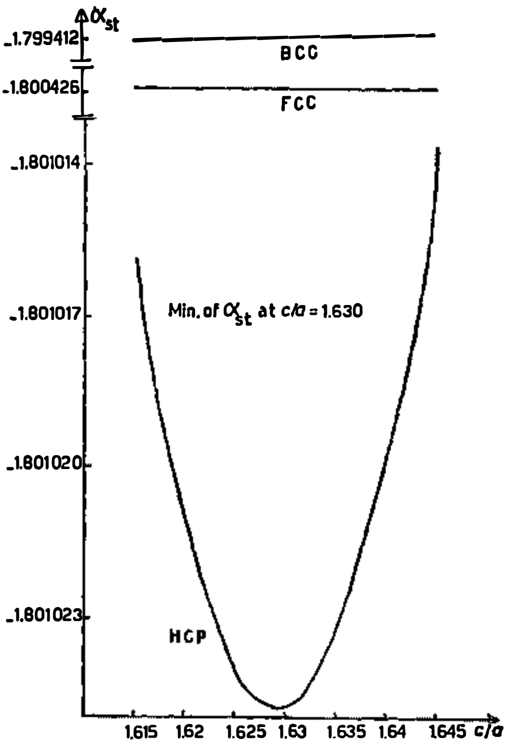

Fig. 8. Variation of structural coefficient a_{st} with the axial ratio c/a in the HCP structure. a_{st} of FCC and BCC structures are also shown.
Mg (SH-potential).

Table 2. All theoretically calculated axial ratios of Li, Na and Mg are in excellent agreement with the observed c/a, except those of Pick$^{12)}$ for Li and Na. In case of Be the agreement is not as good. This can be attributed to the fact that $c/a = 1.568$ of Be is quite far from the ideal value 1.633, while for Li, Na and Mg the observed c/a ratios are very close to 1.633. Actually, Be has the smallest c/a ratio among HCP elements. Be has a very strong and non-local pseudopotential due to the lack of p-states in the ion-cores. Li also has no p-core-states, however, its model potential is weaker than that of Be. The large values of a_{st} of Be and Li show that the band structure contribution to second order is large. Thus third order contributions can be very important for Be and Li, as pointed out by Williams$^{26)}$. This is also in agreement with the conclusions of Mclaren and Sholl$^{20)}$. They found that calculations to second order perturbation in case of Li and Be were not able to predict the observed HCP structure, which was first obtained when third-order terms were included.

An experimental value of structural energy difference ΔE_{st} (BCC — HCP) = = 0.055 mRy for Na is obtained by subtracting the calculated BCC-HCP difference in zero point vibrational energy$^{27)}$ from the measured heat of transformation$^{28)}$. Kaufman and Bernstein$^{29)}$ gave thermodynamically based estimates of obtained theoretical results having better agreement with the experiment. However, the optimal Z for structural energy calculations might not be the best choice in case of energy band structure.

As can be seen from Table 3 the quantitative agreement of theoretical results of Mg with estimated ones is much better than in case of Be. All authors obtained as stable structure HCP then FCC and finally BCC. Calculated ΔE_{st} of different authors are of the same order as magnitude of experimental ΔE_{st}, however, those of Refs. 18, 19 and 12 have the best agreement with estimated ΔE_{st}. However, it should be kept in mind that the experimental estimates for Be and Mg are based only on extrapolations of thermochemical alloy data[29] and are of unknown reliability.

Our conclusion for Li, Na and Mg is that second order OMP calculations are capable of reproducing excellent qualitative and fair quantitative agreement with experiment for Na and Mg. In our opinion, the third order contribution in case of Li will improve the quantitative agreement of ΔE_{st} with experiment, leaving the stable HCP structure and axial ratio calculated in second order practically unchanged.

The conclusions of the present paper are consistent with those of previous papers dealing with band structure calculations of Li and Na[33,34]. This proves the adequacy of the optimized model potential to the calculation of some electronic properties of Li and Na such as band structure and total energy.

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STRUKTURNE ENERGIJE LAKIH METALA

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Po prvi puta je proveden egzaktan račun modelnog potencijala strukturnih energija za Li, Na, Be i Mg bez interpolacijskog postupka. Ispitan je utjecaj izbora različitih parametara modelnog potencijala i primjene aproksimacije efektivne mase. Nađeno je da opažena HCP struktura ima najnižu strukturnu energiju, te da se izračunati omjeri osi c/a dobro podudaraju s eksperimentalnim vrijednostima.