YU ISSN 0015-3206
FZKAAA 21 (1) 25 (1989)

DENSITY OF STATES AND FERMI ENERGY OF THE BCC ALKALI METALS: Li, Na AND K

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Received 30 June 1988

UDC 538.915

Original scientific paper

The density of states and the Fermi energy of the bcc metals: Li, Na and K are calculated by using the tetrahedron method and utilising results from our previous energy bands calculations. The occupied bandwidth, thermal mass ratio, and electron-phonon coupling parameter are computed and compared with available theoretical and experimental results. For Li, Na and K, respectively, the occupied bandwidths in Ry are 0.253, 0.223 and 0.149 for the energy independent calculation and 0.287, 0.255 and 0.179 for the dependent one. The thermal mass ratio for the three metals respectively are 1.49, 1.10 and 1.07. These results compare well with other theoretical results, and are in fairly good agreement with experiment. Our procedure is, therefore, justified and even favoured since it economises computing time.

1. Introduction

For a further investigation of the band structure of the alkali metals Li, Na and K, we calculate in the present paper their density of states (DOS) and the Fermi energy E_F. This enables us to obtain a number of theoretical results, such as the occupied bandwidth and the effective thermal mass, which can be measured experimentally. The search for additional theoretically predicted quantities which could be compared with experimental results is of great importance in judging the theoretical model adopted and the procedure of calculation.

We have used the results of the energy bands calculated by one of us[1-3] for Na, Li and K using Shaw optimized model potential, where the energy dependence of the potential was treated as a perturbation. DOS was computed by the tetrahedron method of Lehmann and Taut[4], which gave reliable results when applied to Al and the intermetallic compound $CaAl_2$[5].

2. *Density of states and Fermi energy*

After completely specifying the energy bands, DOS can be determined from the expression:

$$D(E_k) = \frac{V}{4\pi^3} \int_{E=E_k} \frac{ds}{|\nabla_k E_k|} \tag{1}$$

where V is the atomic volume and the integral goes over the constant energy surface defined by $E_k = E$ in the Brillouin zone (BZ).

The integral of Eq. (1) was solved using the tetrahedron method[4]. The irreducible part (1/48) of BZ is divided into a mesh of points. Energy values are calculated at those points, and the whole space is scanned by tetrahedra each of them being formed by four points of this mesh. The value of the integrand at any point inside the tetrahedron is obtained by linear interpolation utilizing the values of E_k at the corners. In this manner, the integration can be done analytically avoiding the histogram method. Obviously, the accuracy improves by choosing a larger number of points for the mesh in the BZ.

Once the density of states $D(E)$ is obtained, the Fermi energy E_F can then be computed using the equation:

$$\int_0^{E_F} D(E)\, dE = N/V \tag{2}$$

where N/V is the number ot valence electrons per atom.

The density of states at the Fermi surface, $D(E_F)$, is related to the coefficient γ of the electronic specific heat, and thus, to the thermal effective mass m_{th} by the relation:

$$D(E_F)/D_0(E_{F0}) = \gamma/\gamma_0 = m_{th}/m \tag{3}$$

i. e., the ratio of metal DOS to the free electron one at the Fermi surface yields the ratio m_{th}/m of the thermal effective mass to the free electron mass m (in atomic units $m = 1$). The electron-phonon coupling parameter λ can be determined by comparing the experimental and theoretical thermal effective masses according to the relation:

$$(m_{th}/m)_{exp.} = (1 + \lambda)(m_{th}/m)_{theor.} \tag{4}$$

λ is also known as the mass-enhancement factor.

3. *Results and discussion*

The lattice constants of Li, Na and K were taken (in atomic units) to be[6] $a = 6.632$, 7.984 and 9.873, respectively. The irreducible part (1/48) of BZ is divided into 91 points leading to 230 tetrahedra. This choice is a compromise between an acceptable accuracy and a reasonable calculation time, since the next possible choice would be 140 points. The energy values at the 91 points are taken from previous band structure calculations[1-3]. The resulting DOS curves for Li, Na and K are shown in Figs. 1,2 and 3, respectively, where $D(E)$ is given in (states/ /Ry-atom) and E is measured from the bottom of the band (in Ry).

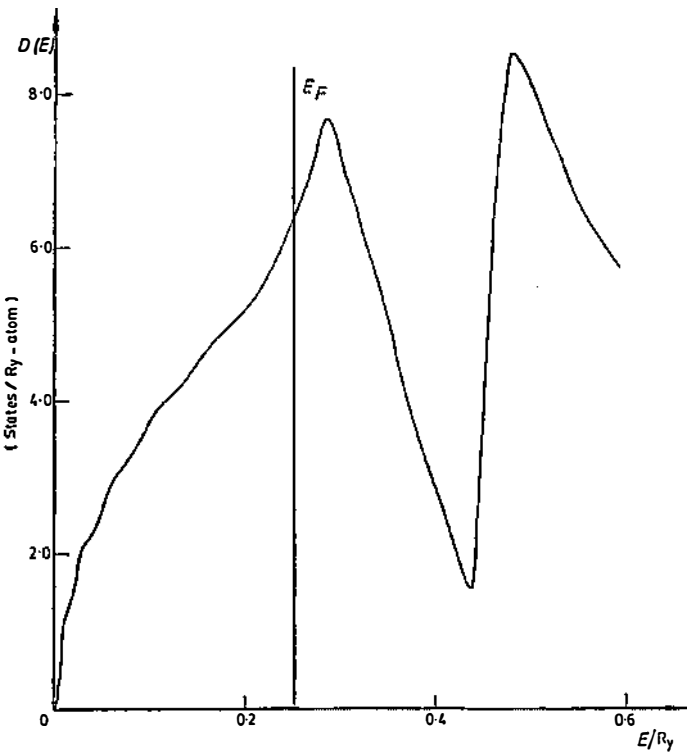

Fig. 1. Density of states for Li.

DOS of Li (Fig. 1) exhibits very strong oscillations which become much weaker in the case of Na (Fig. 2) and even more weak in the curve for K (Fig. 3). This is due to the fact that the model potential parameters[6] of Li are larger than those of Na, which in turn are larger than those of K. Our DOS curves of Li and Na are in very good agreement with those of Moruzzi et al.[7] calculated using the Gilat-Raubenheimer method[8] with 1440 K-points in the irreducible wedge of BZ and the results of a KKR band structure calculation. In the Gilat-Raubenheimer method the K-space is divided into cubes with equal volume and the contri-

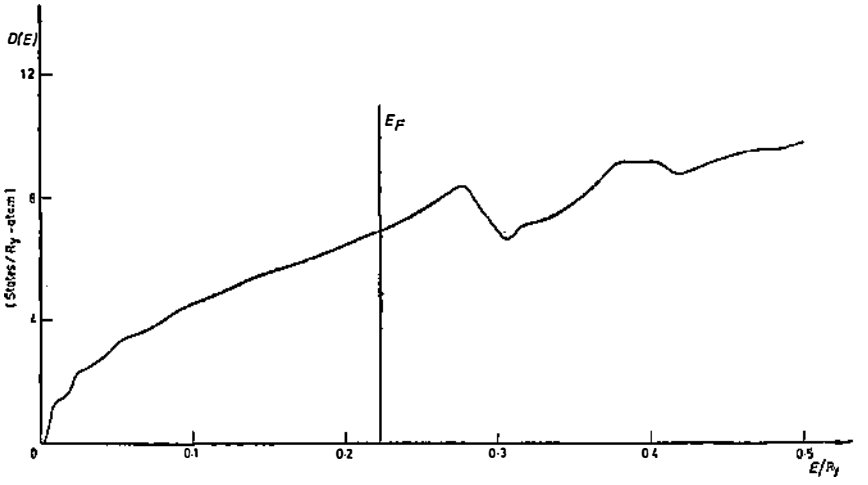

Fig. 2. Density of states for Na.

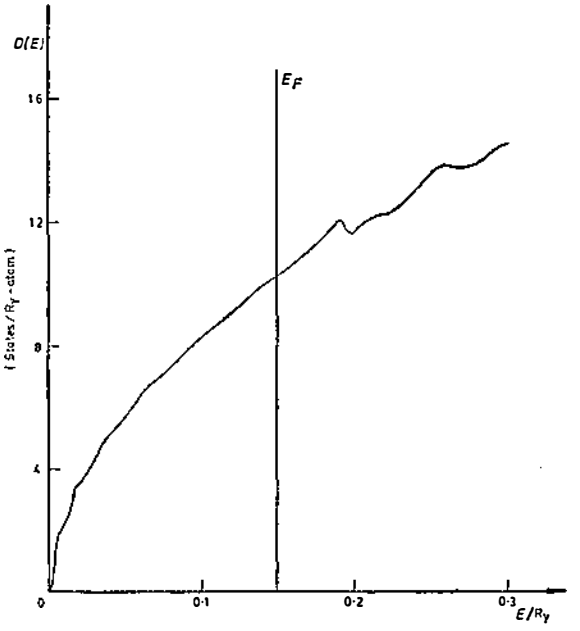

Fig. 3. Density of states for K.

bution of each K-mesh cube to DOS is found for a range of energies about the energy at the cube centre. This means that the linear interpolation performed there employs the values of E_k at the centres of the cubes. However, the tetrahedron method applied here reduces the numerical effort by using for the interpolation the energy values at the corners rather than the centre. The present DOS of Li (Fig. 1) agrees fairly well with that of Ham[9] calculated using an interpolation

formula suggested by the nearly free electron model. Our DOS of Na (Fig. 2) agrees fairly well with that obtained by Gupta and Freeman[10] using the same method[4] and APW calculation at a fine mesh of 285 points in 1/48 of BZ, i. e., three times the number of points in our mesh. Ganin and Shirokovskiy[11] have calculated DOS for Li and K by means of the 4 point linear interpolation[12,13] using also 285 datum points in the basic polygon of BZ. The energies at these points were calculated by Green's function method with a priori crystalline potential. Their DOS is in fair agreement with our curve for Li, which agrees also reasonably with that of Borland and Cooper[15] obtained by the method of Gilat and Raubenheimer[8]. A far less agreement is found with DOS of Shaw and Smith[16] for Li. However, their DOS has been calculated by determining the distortion of energy surfaces due to the first few zone planes using perturbation theory without resorting to a full band structure calculation.

The Fermi energy E_F was calculated using Eq. (2). Consequently, the occupied bandwidth $E_F - E(\Gamma_1)$, denoted here by E, and $D(E_F)$ are determined and hence the quantities m_{th}/m and λ are calculated.

The occupied bandwidth E, thus obtained, corresponds to the energy-independent calculation E of Ref. 1. We recall from Ref. 5 that the energy-dependent results EE are obtained from the energy-independent results E by the linear transformation

$$EE_k = [E_k - E_F(\overline{\partial f}_{E_F}/\partial E_F)]/[1 - \overline{\partial f}_{E_F}/\partial E_F] \tag{5}$$

TABLE 1a.

Ref.	17)	9)	Pres. E	18), 19)	20)	7)	21) 22), 23) $\alpha = 1$; KS	24) $0.9\,K_0$	Pres. EE	22) $\alpha = 2/3$	23) HF
Li	.200	.248	.253	.254	.260	.261	.268	.278	.285	.287	.289	.294
Ref.	Press. E	21)	17)	25)	10)	19)	20)	9)	Press. BE	7)	Free el.	
Na	.223	.228	.229	.234	.237	.238	.239	.243	.252	.255	.238	
Ref.	17)	Press. E	11)	21)	20) KS	26)	20) HF	9)	7)	Press. EE	Free el.	
K	.142	.149	.150	.157	.159	.163	.164	.165	.176	.179	.156	

Occupied bandwidth $E_F - E(\Gamma_1)$ of different theoretical calculations (in Ry; 1 Ry = 13.6 eV).

where $\overline{\partial f}_{E_F}/E_F$ is the mean value in K-space of the derivative $\partial f_{E_F}(k, 0)/\partial E_F$ of the model potential. Table 1a shows our bandwidths E and EE of Li, Na and K compared with other theoretical results[7,9-22,17-26].

The experimental conduction bandwidths are obtained from soft X-ray emission spectrum. However, due to many body effects both the bottom of the con-

TABLE 1b.

Ref.	27)	28)	29)	30)*
Li	0.221 ± 0.007	0.237	0.247	0.252 ± 0.007
Ref.	**31)**	**32)**		**33)**
Na	0.184 ± 0.022	0.191 ± 0.022		0.224 ± 0.011
Ref.	**34)**		**35)**	
K	0.119 ± 0.003		0.140 ± 0.015	

*) Photo-absorption measurements

Experimental conduction bandwidths (Ry).

duction band $E(\Gamma_1)$ as well as the Fermi edge E_F are obscured. A refined interpretation of the experimental emission spectrum taking many-body effects into account is necessary to locate $E(\Gamma_1)$ as well as E_F and hence to measure the bandwidths given in Table 1b for Li, Na and K[27-35]. The value 0.252 ± 0.007 Ry in case of Li is obtained from photo-absorption measurements[30].

From Tables 1a and 1b we see that:

1. The theoretical values for the bandwidths of Li have a considerable deviation of 47% followed by those of K (24%) and finally Na (12%). The experimental bandwidths of Li lie within the range of the theoretical ones, especially the latest experimental results of Bross[29] and Haensel et al.[30]. However, in case of Na and K some experimental results[31,32,34] are about 20% smaller than the theoretical values, while the others[33,35] are much closer.
2. The present bandwidth E of Li is almost identical to both the photo absorption result[30] and to the theoretical results[18,19] and is very close to Ham's value[9] and to the experimental bandwidth.[29] On the other hand, the EE bandwidth of Li is very close to the results of Rudge[22] (with $\alpha = 2/3$) and Bross and Bohn[24].
3. In case of Na, our E bandwidth, being the smallest among theoretical results, is almost identical to the experimental value[33] and is very close to the results of Refs. 21 and 17. The EE value is in very good agreement with that of Moruzzi et al.[7].
4. For K, the bandwidth E is almost identical with the result of Ref. 11 and is close to that of Ref. 17 and to the experimental result[35]. The EE value, being the largest among theoretical results, is again in very good agreement with the bandwidth of Moruzzi et al.[7].

$D(E_F)$ are given (in states/Ry-atom) in Table 2 with the few published results for Li, Na and K.

Table 2 shows that:

1) The present $D(E_F)$ of Li is almost identical to the very recent result of Sundqvist et al.[36] and to those of Moruzzi et al.[7] and Ching and Callaway[19].

TABLE 2.

Ref.	26)	11)	Pres.	36)	7)	19)	9)	18)	23)
Li	6.11	6.26	6.49	6.50	6.53	6.54	6.80	7.00	7.06
Ref.	7)	9)	25)	19)	10)	20)	17)	Pres.	
Na	6.12	6.29	6.42	6.50	6.53	6.54	6.88	6.92	
Ref.	26)	7)	Pres.	11)					
K	9.19	9.93	10.28	12.63					

$D(E_F)$ (states/Ry-atom) of Li, Na and K.

2) $D(E_F)$ of Na is very close to the result of Stockes and Young[17], but is about 7% higher than the average of other theoretical results.

3) Our $D(E_F)$ for K is in very good agreement with that of Moruzzi et al.[7]. However, $D(E_F)$ of various authors show more deviation in case of K than in that of Li or Na.

Table 3 contains: a) theoretical and b) experimental results for the thermal mass ratio (m_{th}/m) of Li, Na and K. The experimental value $m_{th}/m = 1.10$ of K is derived indirectly from experimental paramagnetic spin susceptibilities by Knecht[41]. It can be directly compared with theoretical results, since it does not include the mass enhancement due to the electron-phonon coupling.

TABLE 3.

a) Theoretical results of different authors

Ref.	37)	16)	26)	38)	24) $0.9\,K_0$	Pres.	39)	19)	
Li	1.19	1.27	1.40	1.41	1.44	1.49	1.50	1.53	
Ref.	22)	7)	40)	9), 20)	23)	18)	17)		
Li	1.55	1.60	1.61	1.64	1.65	1.67	1.81		
Ref.	9)	25)	17)	19)	20)	7)	40)	Present	
Na	1.00	1.02	1.03	1.033	1.04	1.047	1.05	1.10	
Ref.	26)	37)	40)	Pres.	20)	9)	41)* Exp.	7)	17)
K	0.95	0.99	1.04	1.07	1.07—1.15	1.09	1.10	1.13	1.47

*) Value derived from experimental paramagnetic spin susceptibilities

b) Experimental values (electron-phonon interaction is maintained)

Ref.	42)	43)	44)	45)	38)	46)	47)
Li	2.00	2.168	2.176	2.19	2.20	2.30	2.31

Ref.	48)	40)	49)
Na	1.24 ± 0.02	1.26	1.27

Ref.	46)	9)*	43)	38)	50) [3]
K	1.20	1.21 ± 0.02	1.234	1.24	1.25

*) Cyclotron mass measured by A. F. Kip and C. C. Grimes and quoted by Ham[9].

Thermal mass ratio m_{th}/m of Li, Na and K.

We have the following remarks on the thermal mass ratios of Table 3:

1. For Li, we found $m_{th}/m = 1.49$. MacDonald[51] using a density functional approximation for the quasi-particle properties of simple metals has obtained the following results for the density of states mass of Li:

$$m^{NL} = 1.39, \quad m^{LE} = 1.51, \qquad m^{L} = 1.55$$

m^{NL} is the DOS mass calculated with a non-local and energy-dependent mass operator, m^{LE} is calculated by means of a local but energy-dependent potential and m^{L} is a further approximation to m^{LE} in that the energy-dependence is removed. As for experimental results the specific heat mass $m^* = 1.55 \pm 0.2$[51] was obtained utilizing the result of Martin[45], however, the electron-phonon coupling parameter has been divided out using the value recommended by Grimvall[52]. Bross and Bohn[24] estimated roughly a value of $m_{th}/m = 1.59 \pm \pm 0.05$ after subtraction of electron-phonon interaction. We see that our result is very close to m^{LE}, and also to the values given by Perdew and Vosko[39], Ching and Callaway[19], and Rudge[22]. Moreover, it lies exactly between m^{NL} and the estimated value of Ref. 24.

Now to obtain the electron-phonon coupling parameter λ we have to compare our theoretical m_{th}/m with the experimental results of Table 3b. λ has correspondingly the values $\lambda = 0.34$ to 0.55 for Li. Direct calculation of λ using the Heine-Animalu potential yields $\lambda = 0.56$[38]. Pseudopotential calculation of λ for Li performed by Goddard and quoted in Ref. 38 gives λ in the range (0.37—0.56), almost identical with our result. After a review of theoretical and experimental methods of obtaining λ, Grimvall[52] computed λ for Li to be $\lambda = 0.41 \pm 0.15$. These numerical values are the average and statistical standard deviation based on 9 values of λ taken from 4 references[52].

2. In case of Na, the present $m_{th}/m = 1.10$ is somewhat higher than those of other authors (10% at most), the closest results are those of So et al.[40] and Moruzzi et al.[7].

We calculated λ for Na to be $\lambda = 0.13$—0.15 for the experimental values of Table 3b. Allen and Cohen[38] found $\lambda = 0.15$. Energy independent model potential (EIMP) calculation yields $\lambda = 0.14$[40]. Grimvall[52] obtained for Na the value $\lambda = 0.16 \pm 0.04$, as the average of 18 values of λ taken from 11 references. We see that all these values of λ mentioned above are in very good agreement with our results.

3. As for K, we obtained $m_{th}/m = 1.07$, which is in very good agreement with the results of Dagens and Perrot[20], Ham[9], So et al.[40] and the experimental value derived from paramagnetic spin susceptibilities by Knecht[41].

The present value of λ corresponding to $(m_{th}/m)_{exp}$ of K (Table 3b) lies in the range $\lambda = 0.12$—0.17. Allen et al.[53] have determined $\lambda_{exp} = 0.11 \pm 0.02$ for potassium metal from their far-infrared cyclotron resonance experiment, in excellent agreement with our $\lambda = 0.12$ calculated from the most recent value for $(m_{th}/m)_{exp} = 1.2$[46]. Direct calculation of λ[38] yields $\lambda = 0.14$, while in previous calculations[38] λ has values in the range (0.11—0.16), which is almost identical with our results. EIMP calculation gives $\lambda = 0.09$[40]. Grimvall[52] computed λ of K to be $\lambda = 0.13 \pm 0.03$, which is the average of 18 values taken from 9 references. His result is also very close to ours.

We end our discussion by the following final conclusions:

1. Our DOS curves for Li and Na are in good agreement with other theoretical curves, especially those of Moruzzi et al.[7]. However, the present DOS of K shows too weak oscillations and whence the agreement with DOS of other authors is not satisfactory although $D(E_F)$ is quite acceptable.

2. Among all other theoretical results, except Ref. 17 for K, the present occupied bandwidths E have the best agreement with the more realistic experimental values[30,33,35] for Li, Na and K, respectively. Inclusion of the energy dependence of the potential increases the bandwidth E by about 13% for Li and Na and 20% for K. However, the resulting bandwidths EE are very close to those of Rudge[22], Bross and Bohn[24] for Li and Moruzzi et al.[7] for Na and K.

3. Our $D(E_F)$ are almost identical with the more recent result for Li[36] and that of Na[17], while $D(E_F)$ for K is in reasonable agreement with other theoretical results[7]. As for m_{th}/m and λ the present results are very close to other theoretical and experimental ones.

The conclusions mentioned above are all in favour of our procedure.

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GUSTOĆA STANJA I FERMIJEVA ENERGIJA VCK METALA: Li, Na i K

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Originalni znanstveni rad

Koristeći tetrahedronsku metodu i svoje prijašnje rezultate proračuna energetskih vrpci određene su gustoće stanja i Fermijeve energije za volumno centrirane kubične metale Li, Na i K. Izračunati su: širina zaposjednutog dijela vrpce, termalna efektivna masa i parametar elektron-fonon vezanja i uspoređeni sa postojećim teorijskim i eksperimentalnim metodama. Usporedba je pokazala veoma dobro slaganje, a obzirom na vremensku uštedu pri proračunu ovom metodom, njena primjena se pokazala opravdanom.