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FERMI SURFACE DISTORTIONS OF THE BCC METALS Li, Na AND K

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Fermi surface distortions of the BCC alkali metals Li, Na and K are calculated. Whereas, our results for Na have the best agreement with the experimental values compared to published theoretical results, the agreement in case of Li is also reasonable. Although the present results for K, being too small, are not as satisfactory, they are not worse than those obtained by other authors using different crystal potentials.

1. Introduction

The success of any theoretical calculation can be measured through its agreement with experimental results. It is essential to calculate physical quantities that can be measured experimentally. Distortions of Fermi surface of solids are such quantities which represent the most critical test of the band structure, since they are very sensitive to both the crystal potential and the calculated Fermi energy E_F[1-3]. Calculation of Fermi surface distortions is far more sensitive than calculation of other band structure properties such as density of states and related physical quantities. This can be easily demonstrated even in case of light alkali metals like Li and Na. In literature calculated radial distortions of Fermi surfaces of Li and Na are in reasonable agreement with experiment, while the agreement is not satisfactory in case of K[1-3]. Usually, the distortions calculated using a certain crystal potential may be very close to the experimental result in one direction only, but not in the other two directions.

In the present paper we intend to use the observed shape of the Fermi surface as a probe to examine the crystal potential employed in band calculations of the alkali metals Li, Na and K. The radial distortions of the Fermi surface are calcula-

ted and compared with theoretical and experimental results. Then, from comparison of the calculated results with experimental results, we examine the applicability of the present formalism for calculating actual physical quantities to characterize metal properties.

2. *Method of calculations*

Within the model potential formalism, the energy E_k of a conduction electron of wave vector $\mathbf{k}$ may be determined in general by the secular equation

$$\det |\langle \mathbf{k} + \mathbf{g}_i | T + W | \mathbf{k} + \mathbf{g}_j \rangle - E_k \delta_{ij}| = 0 \tag{1}$$

where $\mathbf{g}_i$ is the reciprocal lattice vector, $|\mathbf{k} + \mathbf{g}_j\rangle$ are plane waves, and T and W are, respectively, the kinetic energy and model potential operator. We have used the optimized model potential of Shaw[4]. The matrix elements of Eq. (1) are given in detail in Ref. 5. Solving Eq. (1), we can determine the Fermi energy E_F and then find the wave vector $\mathbf{k}$ in each direction which satisfies the relation $E_k = E_F$. The values of $\mathbf{k}$ thus determined describe the shape of the Fermi surface. However, for simplicity, in this work we calculate E_F by the equation

$$E_F = (3E_{100} + 4E_{111} + 6E_{110})/13 \tag{2}$$

as in the work of Inoue et al.[1] and Matsuura et al.[3]. Here E_{100}, E_{111} and E_{110} are the energy at the $|\mathbf{k}| = k_F$, k_F being the free electron Fermi vector, in the principal directions (100), (111) and (110), respectively. This calculation is believed to be a good approximation in the free electron type materials such as alkali metals, which have nearly perfect spherical Fermi surfaces. Then the radial distortions of the Fermi surface are measured by the equation:

$$\delta_i = (k_i - k_F)/k_F \times 10^4 \tag{3}$$

where i stands for the three principal directions. However, as shown by Dagens and Perrot[2], the δ_i's are more sensitive to errors in the calculation of E_F. Consequently, the quantities X and Y defined by

$$X = (k_{100} - k_{111})/k_F \times 10^4 \tag{4a}$$

$$Y = (k_{110} - k_{111})/k_F \times 10^4 \tag{4b}$$

are also used in the study of the radial distortions of the Fermi surface and perhaps are better quantities to be compared with the experimental results[1, 2, 6].

3. *Results and discussion*

The present calculations were carried out using an unsymmetrical set of 26 plane waves for all three metals, because the convergence is reasonably good[7].

However, the convergence is not perfect in some cases, but we have not pursued the perfect convergent results because it requires unnecessarily long computer times. Nevertheless, the main conclusions of the present calculation will not be affected by this small lack of the perfect convergence. The exchange and correlation function is taken from the paper of Singwi et al.[8]. The model potential parameters for Li, Na and K are those of Appapillai and Williams[9], denoted by AW. In addition, we have used for Li the potential parameters of Ese and Reissland[10], denoted by ER, because they are calculated at $k_F = 0.589$, which is closer to $k_F = 0.5908$ of the experimental results[6] than $k_F = 0.5877$ of AW. Also in case of K the calculations were performed two times, once with the effective valence of the formal theory[9], namely, $Z = 1 - d$ and the second time with $Z = 1 + d$[11], where d is the charge of the depletion hole and 1 is chemical valence of K. The reason is that by taking $Z = 1 + d$, we were able to predict the observed BCC structure for K, while using $Z = 1 - d$ yields the HCP structure as the most stable one[11]. We have solved the 26×26 secular determinant numerically. Our results for the radial distortion of the Fermi surfaces in the alkali metals Li, Na and K, calculated as described above, are listed in Table 1.

For comparison purposes, we also list in Table 1 the results obtained from different methods using various crystal potentials, namely: i) Augmented plane wave APW method with Wigner-Seitz (WS), Hedin (H), Hartree (Ha) and Heine-Hedin (HH) potentials[1] or using Kohn-Sham exchange (KS)[2], ii) Shaw's optimized model potential OMP[3], iii) Energy-independent model potential EIMP[3], iv) Modified augmented plane wave MAPW method[12], v) Korringa-Kohn-Rostoker KKR method allied with the quantum defect method[13], vi) Heine-Abarenkov model potential HAMP[14], vii) Linear combination of atomic orbitals LCAO method[15], and viii) Local orbitals LO[16]. The experimental values for the Fermi surface distortions were obtained from the measurements of positron annihilation for Li and the de Haas-van Alphen effect for Na and K[6].

Analysis of the results in Table 1 shows that:

1. Li has the largest Fermi surface distortions, followed by K and Na. This is a clear demonstration of the fact that Li has the strongest potential, then comes K and finally Na. In general, the deviations between theoretical and experimental results of Li are much higher than in case of K or Na.

2. The different results obtained by the present OMP (AW) and OMP[3], though using the same model potential parameters[9], arise because: i) we use in our calculations an unsymmetrical set of plane waves which are closer to the origin of the irreducible part of the Brillouin zone, and ii) different exchange and correlation functions are used.

3. For Li, the agreement of our results and experiment is fair but not significant. However, if we take the sum of the deviations between calculated and observed distortions (in percents %) as a criterion to examine and judge the different theoretical results, we find that: the present (AW) results are the closest to experiment followed by LCAO[15], LO (HF)[16], LO (KS)[16] and present (ER), respectively. We note that no single set of results has best fit to all of the measured values. The δ_{110} of HAMP[14] is definitely wrong. The EIMP[3], MAPW[12], KKR[13] and APW (KS)[2] results give too deformed Fermi surface in the 100 and 111 directions, but their deformations in the 110 direction are far less than experiment.

Ref.	Meth.	δ_{100}	δ_{111}	δ_{110}	X	Y
Li						
3)	EIMP	−281	−128	276	−154	403
12	MAPW ($\sqrt{2}k_0$)	−280	−150	260	−130	410
13)	KKR	−270	−170	230	−100	400
2)	APW (KS)	−254	−137	236	−117	373
14)	HAMP	−247	−115	−307	−132	422
1)	APW (WS)	−226	−111	307	−115	418
15)	LCAO	−220	−110	380	−110	490
1)	APW (H)	−218	− 97	290	−121	387
3)	OMP	−192	− 92	206	−100	299
Pres.	OMP (ER)	−180	− 88	204	− 92	292
Pres.	OMP (AW)	−170	− 88	188	− 82	276
16)	LO (KS)	−166	− 58	325	−108	383
16)	LO (HF)	−136	− 41	264	− 95	305
6)	Expt.	−100	−100	400	− 80	722
Na						
3)	OMP	− 16.42	5.76	− 12.42	− 10.7	18.2
1)	APW (H)	− 12.7	− 5.1	8.2	− 7.6	13.3
Pres.	OMP (AW)	− 8.87	− 1.66	7.89	− 7.21	9.54
3)	EIMP	− 9	− 0.1	4.7	− 8.9	4.8
14)	HAMP	− 8.3	0	3.7	− 8.3	3.7
1)	APW (WS)	− 5.6	− 2.9	4.8	− 2.7	7.7
2)	APW	− 4.6	− 0.7	3.3	− 3.9	4.0
6)	Expt.	− 7.83	− 1.54	9.27	− 7.1	10.3
K						
1)	APW (Ha)	25.8	− 32.3	8.9	58.1	41.2
1)	APW (HH)	30.6	− 22.6	− 1.8	53.2	20.8
14)	HAMP	25.3	− 12.4	− 9.2	37.7	7.8
3)	EIMP	15.4	− 9.8	− 1	25.2	8.8
3)	OMP	− 2.4	0.5	0.9	− 2.9	0.4
Pres.	OMP (AW1)	0.8	0.6	− 0.1	0.2	− 0.7
Pres.	OMP (AW2)	− 10.5	− 4.5	10.2	− 6.0	14.6
13)	KKR	− 60	− 60	70	0	130
6)	Expt.	14.7	− 11.0	10.8	25.7	25.0

Various theoretical and experimental values of the radial distortions of the Fermi surfaces, δ_{100} δ_{111}, δ_{110}, X and Y given in text, for the alkali metals Li, Na and K. Present results are denoted by AW and ER (for Li only). For K, AW1 and AW2 denote results calculated with $Z = 1 - d$ and $Z = 1 + d$, respectively (see text for other details).

4. For Na, the present results have the best agreement with observed δ_{111}, X and Y. They have also the second best fitting to δ_{100} after HAMP[14] and to δ_{110} after APW (H)[1]. Thus, our set of results is, by far, the best one obtained for Na. The APW (WS)[1] results tend to a more spherically symmetric Fermi surface than the experiment, whereas the OMP[3] results overestimate the distortions.

5. For K, the KKR results of Ham[13] are the worst compared to experiment, although his potassium band structure results are good. The reason seems to be in the interpolation process, not in the primary calculation. Unlike Li and Na, δ_{100} and δ_{111} calculated by OMP[3] and present OMP (AW2 for δ_{100} and AW1 for δ_{111}) have a different sign than experimental δ_{100} and δ_{111}. For δ_{110}, the results obtained by APW (HH)[1], HAMP[14], EIMP[3] and OMP (AW1) are all negative, while the experimental δ_{110} is positive. The present (AW1) distortions are all too small, thus practically yielding a spherically symmetric Fermi surface, contrary to experiment. On the other hand, the present (AW2) results have much better agreement with the measured values of δ_{110}, Y and δ_{111}, but not so good for X and δ_{100}. The best theoretical results are those of EIMP[3] followed by HAMP[14] and present OMP (AW2), respectively. The worst are KKR[13], OMP[3] and the present OMP (AW1).

We conclude that OMP is capable of producing Fermi surface distortions of Li and Na, which have better agreement with experiment than all other theoretical results obtained using more sophisticated methods like APW or KKR. However, in case of K, the (AW1) results obtained from the formal OMP theory, with $Z = 1 - d$, are not satisfactory. This is in complete agreement with our conclusions on previous band structure calculations of Li[5], Na[17] and K[18]. The other results (AW2) of K, calculated with $Z = 1 + d$, are much better but not sufficiently good, although they are only preceded by EIMP[3] and HAMP[14].

The situation can be explained in a simple way using the energy gap $(N_1 - N_1')$ at point N which is related to Fermi surface distortions[1]. For both Li and Na, $(N_1 - N_1')$ is positive in all band structure calculations including those using OMP[5,17]. However, in case of K, $(N_1 - N_1)$ should be negative, but the OMP band calculation[18] yields a positive value for $(N_1 - N_1')$ similar to Li and Na. Thus using formal theory of OMP, we can not expect such good results for K as those of Li and Na. Even though using OMP with $Z = 1 + d$ leads to a correct prediction[11] of the observed BCC structure of K and to acceptable values of Fermi surface distortions (AW2), no negative value of $(N_1 - N_1')$ could be obtained.

References

1) S. T. Inoue, S. Asano and J. Yamashita, Phys. Soc. Japan **30** (1971) 1546;
2) L. Dagens and F. Perrot, Phys. Rev. **B8** (1973) 1281;
3) M. Matsuura, C. H. Woo and S. Wang, J. Phys. **F5** (1975) 1849;
4) R. W. Shaw, Phys. Rev. **174** (1968) 769;
5) A. M. Radwan, Proc. Math. Phys. Soc. Egypt **54** (1982) 35;
6) M. J. G. Lee, Phys. Rev. **178** (1969) 953;
7) A. M. Radwan, Egypt. J. Phys. **14** (1983) 63;
8) K. S. Singwi, A. Sjolander, M. P. Tosi and R. H. Land, Phys. Rev. B **1** (1970) 1044;
9) M. Appapillai and A. R. Williams, J. Phys. F **3** (1973) 759;
10) O. Ese and J. A. Reissland, J. Phys. F **3** (1973) 2066;
11) A. M. Radwan, *A Study of the Effect of Depletion Charge on the Stable Crystal Structures of Heavy Alkalis*, submitted to NRC Bulletin (1987),
12) H. Bross and G. Bohn, Z. Phys. B **20** (1975) 261;
13) F. S. Ham, Phys. Rev. **128** (1962) 2524;

14) M. Matsuura, Phys. Lett. **50A** (1974) 131;
15) W. Y. Ching and J. Callaway, Phys. Rev. B **9** (1974) 5115;
16) D. R. Jennison, Phys. Rev. B **16** (1977) 5147;
17) A. M. Radwan, Egypt. J. Phys. **12** (1981) 81;
18) A. M. Radwan, Egypt. J. Phys. **14** (1983) 63.

DISTORZIJA FERMIJEVE POVRŠINE U BCC METALIMA Li, Na I K

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Izračunata je distorzija Fermijeve površine volumno centriranih kubičnih metala Li, Na i K. Dok je slaganje za Na najbolje ako se eksperimentalni rezultati usporede s objavljenim teoretskim rezultatima, slaganje za Li je također zadovoljavajuće. Iako su rezultati za K, budući premali, nezadovoljavajući, oni nisu lošiji od onih koje su dobili drugi autori koristeći različite kristalne potencijale.