Pramāṇa – J. Phys., Vol. 31, No. 6, December 1988, pp. 513–517. © Printed in India.

Effect of pressure on the Fermi surface of potassium

M G RAMCHANDANI
Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085, India

MS received 26 May 1988; revised 23 September 1988

Abstract. The complete electronic energy band structure of bcc potassium metal has been calculated using the non-relativistic augmented plane wave method. The density of states has been calculated and results compared with available thermal, optical and X-ray data. The lattice constant has been varied to get the band structures for pressures varying from 1 to 5 kb. The Fermi surface has been studied with varying lattice constants and the results discussed in the light of results of pressure-induced changes of de-Hass van-Alphen frequency obtained by Altounian and Datars.

Keywords. Potassium; Fermi surface; electronic properties; pressure.

PACS No. 71·25

1. Introduction

Alkali metals are the simplest of metals and their electronic properties have been extensively studied both experimentally and theoretically. Potassium presents certain anomalies in its observed properties. In order to explain these properties, the existence of charge density waves (CDW) has been postulated (Overhauser 1978) and it has been argued that the Fermi surface of potassium is a sphere distorted into lemon shape. The shape of the Fermi surface remains the key to understanding the electronic properties. Callaway (1956) calculated a few electronic energy levels using orthogonalised plane wave (OPW) method. His calculations were confined to the few symmetry points of the Brillouin zone. Ham (1962) studied the energy band structure of alkali metals using quantum defect (QD) method and Green's function method for a few values of **k** (propagation vector) points along [100], [111], [110] axes and some symmetry points within the Brillouin zone. He used the interpolation method to construct the Fermi surface and calculated the various parameters based on such calculations. Ham's calculations predicted that for potassium the Fermi surface was distorted from the sphere by about 0·5%. Yamashita *et al* (1969) who studied the band structures of Na and K under a very high pressure predicted large changes in the shapes of the Fermi surface. They also conjectured that highly compressed alkali metals have complex Fermi surfaces. They calculated the band structures for five different lattice parameters which corresponded to the volume ratio of 1·0, 0·5, 0·4, 0·3 and 0·2 respectively. These calculations were not tested against any experimentally known data on Fermi surface. Janak *et al* (1975) studied the ground state thermo-mechanical properties of some of the alkali metals. Their aim was to show how bulk properties like cohesive energy and lattice constants can be calculated from the energy band structure. Skriver (1985)

calculated the crystal structure of metals from one-electron theory and concluded that when subjected to pressure, potassium undergoes a transition from bcc to fcc before transforming into a complex structure. No experimental data exist to test this prediction. Moruzzi *et al* (1978) listed many of the calculated properties of metals. We compare our results with those of Moruzzi *et al*. Shoenberg and Stiles (1964) experimentally studied the de Haas-van Alphen (dHvA) effect in alkali metals using a new method designed to explore very spherical Fermi surface. They did find deviations from a sphere of the order of 1 part in 10^3 in the case of potassium. This was much less than that predicted by Ham (1962). Heine and Abarenkov (1964) constructed a new potential for the energy band structure of alkali metals. Their calculations were in better agreement with experimental values than those of Ham. Altounian and Datars (1980) recently measured the change of frequency of de Haas-van Alphen of potassium with pressure and explained these results in terms of the charge density (CD) model of Overhauser. We have calculated complete band structures of potassium metal for five different lattice parameters using the non-relativistic augmented plane wave (APW) method and studied the effect of pressure on the Fermi surface. We have also compared our results with the available experimental data.

2. Calculations

Using atomic electronic charge densities for potassium atom as computed by Liberman *et al* (1965), we have computed the muffin-tin potential by superposing charge densities from 14 nearest neighbours. We have used Slater's approximation for the exchange part of potential. It was shown earlier (Ramchandani 1971) that Slater's exchange approximation is better for a metal with free electron-like behaviour. The energy eigenvalues were calculated for 55 k points in 1/48th of the Brillouin zone which, by symmetry considerations, amounts to 1024 points. The energy bands along some symmetry directions are shown in figure 1 for normal pressure. The eigenvalues converge up to 0·001 Ry. The histogram of density of states versus energy was computed with energy bar-width of 0·005 Ry. We repeated these calculations for four more lattice constants that correspond to varying pressures up to 5 kbar. The lattice constants at different pressures were based on Monfort and Swenson's (1965) experimental determination of change of volume with pressure. This, in our opinion, will suffice to study the variation of Fermi surface with respect to pressure, the number of electrons at Fermi energy, the band gap at N and the width of the conduction band. The Fermi suface data computed are listed in table 1.

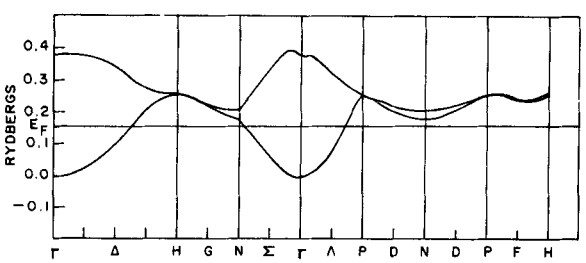

Figure 1. Energy bands for potassium in some symmetry directions.

Table 1. Calculated Fermi surface parameters at different pressures.

Pressure (kbars)	$N(E)$ (per atom/eV)	k_{100}	k_{110}	k_{111}	Band width	Band gap
1	0·834	5·00	5·09	5·02	0·162	0·027
2	0·735	5·00	5·09	5·02	0·165	0·029
3	0·742	5·00	4·95	4·85	0·166	0·031
4	0·735	5·00	5·09	5·02	0·168	0·032
5	0·939	5·00	5·09	5·02	0·171	0·031

$k_{100}, k_{110}, k_{111}$ are in units of $\pi/4a$ where a is the lattice constant corresponding to appropriate pressure. Band gap is at N. Bandwidth and band gap is in Ry units.

3. Discussion

Most of the experimental data on various electronic properties of potassium are available for the normal pressure. However, only some Fermi surface data are available at different pressures. Lien and Phillips (1960) reported an experimental value of 2·13 mJ/g atom^{0}K^2 for the electronic component of specific heat constant (γ) of potassium. Based on our calculations of density of states of Fermi energy we have obtained a γ value of 2·08 mJ/g atom^{0}K^2. This agreement between calculated and experimental value of γ shows that our choice of initial potential and exchange approximation is reasonable. We have compared some energy levels with those obtained by Moruzzi *et al* (1978) (table 2). However, Fermi surface studies have presented some complications. Shoenberg and Stiles (1964) have pointed out many difficulties in experimenting with potassium and suspected an inhomogeneous strain in the specimen. They also suspected the homogeneity of the sample. Experimentalists have been bewildered by the observation that not only do the results vary from sample to sample, they even vary from run to run for the same sample. According to Shoenberg and Stiles, the Fermi surface sphere is distorted to the extent of 1 part in 10^3 at normal pressure. Our calculations put this distortion at 4 parts in 10^3. This agreement may be regarded as reasonable. Altounian and Datars (1980) have studied the change of de Haas-van Alphen frequency of potassium varying up to 4·6 kbar. They have reported that Fermi surface anisotropy increases from 0·13% at normal pressure to 0·47% at 4 kbar. As seen from table 1, our calculations show that Fermi surface anisotropy which is 1·8% in [110] direction and 0·4% in [111] direction remains the same under various pressures except at 3 kbar. Pressure only changes the size of the Fermi surface through dependence on lattice

Table 2. Comparison of energies at some points of Brillouin zone.

Symmetry point	Present calculation	Moruzzi *et al* (1978)
Γ	−0·005	0·016
H	0·258, 0·258	0·302, 0·302
N	0·180, 0·207	0·221, 0·251
P	0·252, 0·252, 0·252	0·304, 0·304, 0·304

All energies are in Ry units and the constant potential set to zero.

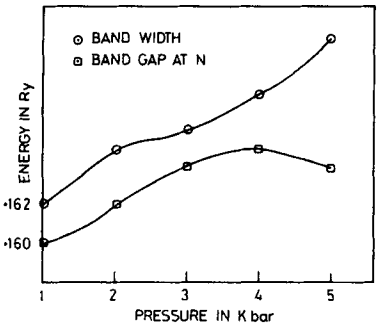

Figure 2. Variation of band width and band gap with pressure.

constant and does not appreciably change the shape. The variation of density of states with pressure cannot be commented upon as variation of specific heat with pressure has not been studied experimentally. In optical studies the interband threshold absorption for potassium has been reported at 1·3 eV for normal pressure. Our calculations gave the gap of occupied to unoccupied states near Fermi level as 1·46 eV at normal pressure. Under pressure the energy gap changes linearly with pressure though the change seems to be very small. However, there exists considerable controversy regarding optical data which do not seem to be reproducible. No data exist on variation of optical absorption when subjected to pressures.

Soft X-ray emission studies by Crisp (1960) and Kingston (1951) give the width of the conduction band as 1·6 and 1·9 eV respectively. Our calculations give the bandwidth as 2·1 eV at normal pressure. We have studied the change in width of the conduction band with respect to pressure. This is plotted in figure 2. The conduction bandwidth varies linearly with pressure up to 4 kb but dips at 5 kb. Under higher pressure, potassium probably becomes softer. In the absence of any experimental data on pressure-dependent lattice constant, we presume that lattice constant changes linearly with pressure. The band gap at the symmetry point N has been reported to be as low as 0·15 eV by Heine and Aberenkov (1964) and as high as 0·5 eV by Ham (1962). Our calculated value of 0·37 eV indicates that our potential is close to reality than Heine's parametrized pseudopotential and Ham's nearly free-electron model. Our calculations on variation of band width and band gap with pressure are the first to be reported and should inspire experimental verification of the same.

Acknowledgement

Thanks are due to Dr G Mukhopadhyay of the Indian Institute of Technology, Bombay for useful discussions.

References

Altounian Z and Datars W R 1980 *Can. J. Phys.* **58** 370
Callaway J 1956 *Phys. Rev.* **103** 1219
Crisp R S 1960 *Philos. Mag.* **5** 1161

Ham F S 1962 *Phys. Rev.* **128** 2524
Heine V and Aberenkov I 1964 *Philos. Mag.* **9** 451
Janak J F, Moruzzi V Ł and Williams A R 1975 *Phys. Rev.* **B12** 1257
Kingston R H 1951 *Phys. Rev.* **84** 944
Lien W H and Phillips N E 1960 *Proc. Seventh Int. Conf. Low Temp. Phys.* (Toronto: Univ. of Toronto Press) p. 675
Liberman D, Waber J T and Cromer D T 1965 *Phys. Rev.* **A137** 27
Monfort C E and Swenson C A 1965 *J. Phys. Chem. Solids* **26** 291
Moruzzi V L, Janak J F and Williams A R 1978 *Calculated electronic properties of metals* (New York: Pergamon)
Overhauser A W 1978 *Adv. Phys.* **27** 343
Ramchandani M G 1971 *J. Phys.* **F1** 69
Shoenberg D and Stiles S J 1964 *Proc. R. Soc. London* **A281** 62
Skriver H L 1985 *Phys. Rev.* **B31** 1909
Yamashita J, Wakoh S and Asano S 1969 *J. Phys. Soc. Jpn.* **27** 1153