Calculated strain dependence of the Fermi surface of rhenium



1991 J. Phys.: Condens. Matter 3 9033

(http://iopscience.iop.org/0953-8984/3/46/005)

J. Phys.: Condens. Matter 3 (1991) 9033–9039. Printed in the UK

# Calculated strain dependence of the Fermi surface of rhenium

V I Smelyansky, A Ya Perlov and V N Antonov
Institute of Metal Physics, Academy of Sciences of Ukraine, 252680 Kiev 142, USSR

Received 7 September 1990, in final form 19 March 1991

**Abstract.** The response of the Fermi surface of the HCP transition metal rhenium on hydrostatic pressure and on uniaxial stress and homogeneous dilational strain is determined for the first time using *ab initio* fully relativistic LMTO band-structure calculations. Calculated extremal cross section areas of the Fermi surface of unstrained rhenium as well as the cross section derivatives with respect to the pressure and to the stress and strain along the *c* axis are in good agreement with experimental data. The nature of the observed differences in the strain response of the various sheets of the Fermi surface is briefly discussed.

## 1. Introduction

Experimental studies on the stress and strain dependence of the Fermi surfaces of metals provide information directly related to important properties such as ultrasonic attenuation and thermal expansion at low temperatures, elastic moduli, cohesive energy and electron–phonon interaction. These data are also connected with the pressure, stress and strain dependence of the properties governed by the electron density of states at the Fermi level, namely the superconducting transition temperature, the electronic specific heat, etc. In addition to the various experimental techniques, theoretical methods are developed to calculate the volume and strain dependences of the energy band structure, the electronic density of states and the Fermi surface (FS) (for a review of experimental studies and theoretical models for the study of the effect of strain on the FS, see [1] and references therein; a comprehensive survey is given in [2]). However, a thorough theoretical investigation of the effect of strain on the Fermi surface has previously only been done for cubic metals. A considerable amount of experimental work has also been done on anisotropic metallic elements.

For instance, the strain response of the FS of a hexagonal close-packed (HCP) 5d transition metal rhenium has been extensively studied experimentally. The shape of the FS of rhenium has been established in great detail by investigation of the de Haas–van Alphen (DHVA) effect [3, 4], magnetoacoustic effect [5, 6], and radio-frequency size effect [7]. Several experiments have determined the derivatives of the FS cross sections with respect to the hydrostatic pressure [8, 9] using both the solid-helium and the fluid-helium DHVA phase shift technique and also with respect to the uniaxial stress and strain along the hexagonal axis [9, 10] using simultaneous measurements of quantum oscillations in magnetostriction and torque, and in the velocity of sound and torque, respectively. The corresponding experimental results of the FS strain dependence for

0953-8984/91/469033 + 07 $03.50  

cubic transition metals molybdenum and tungsten have been interpreted in terms of the parametrized KKR band-structure calculations [11, 12]. In this approach, the rigid muffin-tin (MT) approximation is used and phase shifts at the Fermi energy of the metal are deduced by fitting the cross section areas of the FS as determined in DHVA experiments. It would be of considerable interest to carry out similar calculations on an anisotropic HCP metal with its band structure strongly influenced by spin–orbit interaction.

The only previous band-structure calculations for rhenium were made by the non-self-consistent relativistic augmented-plane-wave (APW) method using the Slater $X_\alpha$ exchange–correlation potential [13]. It is the purpose of the present paper to employ the state-of-the-art local-density approximation (LDA) scheme to the density-functional formalism [14, 15] for ground-state properties in order to calculate the dependence of the FS of Re on the lattice parameters. Similar first-principle calculations of pressure dependence have previously been performed, for example, on the cubic transition metal palladium with rather good agreement between the theory and experiment [16], and even on the actinide thorium with complete success in the explanation of the unusual pressure dependence of the FS found experimentally in this metal [17].

## 2. Results and discussion

### *2.1. Method of calculation*

We have employed for band-structure calculations a fully relativistic version [18] of the linear muffin-tin orbital (LMTO) method developed by Andersen [19] with the exchange–correlation potential in the form suggested by von Barth and Hedin [20].

Equilibrium lattice parameters $a = 2.760$ Å and $c = 4.458$ Å giving a $c/a$ ratio of 1.615 have been chosen according to the experimentally observed equilibrium values quoted in [21]. Lattice parameters corresponding to the hydrostatic pressure $P$ and uniaxial stress $\sigma_3$ along the hexagonal axis have been determined using the experimental rhenium elastic constant values [22] in the following way.

It could be easily shown that for the HCP lattice the individual strains $\varepsilon_1$ along the $a$ axis and $\varepsilon_3$ along the $c$ axis under the hydrostatic pressure $P$ are given by

$$\varepsilon_1 = P(s_{11} + s_{12} + s_{13})$$

$$\varepsilon_3 = P(s_{33} + 2s_{13})$$

and under the uniaxial tensile stress $\sigma_3$ by

$$\varepsilon_1 = \sigma_3 s_{13}$$

$$\varepsilon_3 = \sigma_3 s_{33}$$

where $s_{ij}$ are the elastic compliances from table 1.

In the case of homogeneous dilational strain, only $\varepsilon_3$ should be taken into account. Note that under all these strains the symmetry of the HCP lattice is conserved.

For every set of lattice parameters the self-consistent energy band structure has been calculated on 936 $k$-points in the irreducible wedge (one twentyfourth) of the HCP Brillouin zone. When iterating to self-consistency, the mesh of 196 $k$-points was used and terms with $l$ up to 2 were included. To improve the accuracy of the eigenvalue calculations, combined-correction terms to the atomic sphere approximation (ASA) have been included in the LMTO Hamiltonian and overlap matrices, since it was shown to be

**Table 1.** Rhenium elastic stiffness constants $c$ at 4.2 K from [22] and respective elastic compliance constants $s$ used in this work.

| $c$ ($10^{12}$ dyn cm$^{-2}$) | $s$ ($10^{-12}$ dyn$^{-1}$ cm$^2$) |
|---|---|
| $c_{11} = 6.344$ | $s_{11} = 0.199$ |
| $c_{33} = 7.016$ | $s_{33} = 0.164$ |
| $c_{12} = 2.660$ | $s_{12} = -0.072$ |
| $c_{13} = 2.020$ | $s_{13} = -0.037$ |

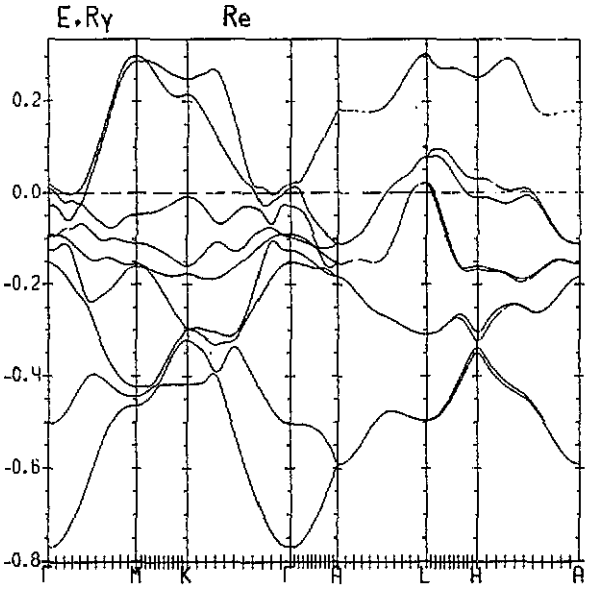


**Figure 1.** Fully relativistic self-consistent energy band structure of rhenium.

indispensable for precise calculations such as the present ones [16]. The areas of the extremal cross sections of the FS were calculated by linear interpolation using the well known tetrahedron method [23]. The pressure, stress and strain derivatives were obtained from calculated cross sections corresponding to the changes in lattice spacings of the order of 1% of the initial equilibrium values.

## *2.2. The Fermi surface*

The model of the FS of rhenium proposed by Mattheiss [13] has been established experimentally [3–7]. It was found to consist of five different sheets: closed hole surfaces $h_5$ (ellipsoids), $h_6$ ('dumbbells') and $h_7$ (distorted spheres) all centred at L, large electronic surface $e_8$ (corrugated cylinder open in the [0001] direction), and hole 'void' $h_8$ at Γ. There has been much controversy concerning the existence of the set of $e_9$ ellipsoids centred at the ΓM line which appeared in calculated FS topology [13]. However, from the analysis of the DHVA frequencies these ellipsoids were later shown not to exist.

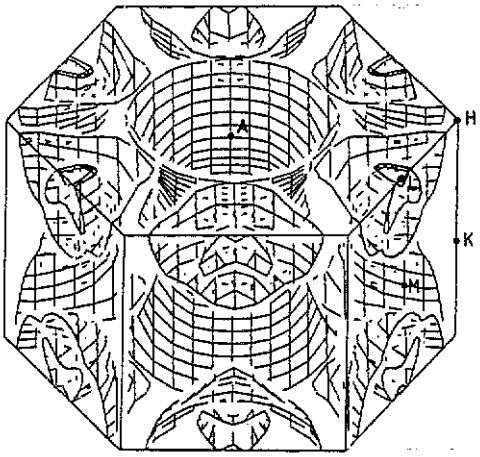


**Figure 2.** The FS of rhenium in the first Brillouin zone. The $h_8$ 'void' in the centre of zone is not seen.

Our calculated FS topology supports this model (figures 1 and 2). The present calculations also give good quantitative agreement with experimental data for extremal cross section areas of all FS sheets except the $h_8$ 'void' (see table 2). The difference between calculated and experimental cross section areas is less than 1% for larger sheets of the FS ($h_7$ and $e_8$) and less than 5% for smaller sheets ($h_5$ and $h_6$) and is always within the experimental uncertainty, which could be regarded as very satisfactory. The relatively large differences for the $h_8$ sheet are not surprising, since its dimensions were shown to be extremely sensitive to the position of $E_F$ [13]. Moreover, as we shall see below, the pressure, strain and stress derivatives of the cross sections of this sheet are the highest observed, especially in directions lying in the basal plane, where the discrepancies between the calculated and observed cross section values are especially noticeable.

### *2.3. Strain dependence of the FS*

The response of the rhenium FS to the hydrostatic pressure is typical for a non-magnetic transition metal with relatively low compressibility. The values of pressure derivatives are generally quite low, with strong anisotropy of the values representing the different magnetic field orientations. This anisotropy cannot be related to the anisotropy of lattice deformations under pressure, because the equilibrium $c/a$ ratio is essentially the same for the rhenium lattice under the hydrostatic pressure applied. Calculated pressure derivatives agree well, within experimental errors, with experimentally determined values for larger orbits on $h_6$, $h_7$ and $e_8$ sheets but somewhat underestimate the response of smaller orbits on ellipsoids $h_5$ and overestimate the response of 'void' $e_8$ orbits, especially for directions lying in the basal plane. The same should be referred to the calculated stress and strain derivatives, where the anisotropy is more pronounced and the deviations in strain and stress derivatives for different FS sheets are higher. The overall accuracy of calculations of the FS strain response for HCP rhenium achieved in the present work is no less than that of other calculations for cubic transition metals [11, 12, 16].

**Table 2.** Calculated and experimental values [8–10] of extremal cross sections $F$, effective masses $m^*$, pressure $\partial(\ln A)/\partial P$, stress $\partial(\ln A)/\partial\sigma_3$ and strain $\partial(\ln A)/\partial\varepsilon_3$ derivatives in high-symmetry directions.

| Field direction | Band, orbit type and centre | $F$(MG) | | $m^*/m_0$ | | $\partial(\ln A)/\partial P$ ($10^{-12}$cm$^2$ dyn$^{-1}$) | | $\partial(\ln A)/\partial\sigma_3$ ($10^{-12}$cm$^2$ dyn$^{-1}$) | | $\partial(\ln A)/\partial\varepsilon_3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Theory | Experiment | Theory | Experiment | Theory | Experiment | Theory | Experiment | Theory | Experiment |
| [0001] | $h_5$ (L) | 4.9 | 4.6 | 0.23 | — | 0.76 | 0.94 | 1.0 | 1.1 | 3.6 | 3.7 |
| [0001] | $h_6$ (L) | 8.4 | 7.6 | 0.31 | — | 0.91 | 0.94 | 0.4 | 0.0 | −8.7 | −5 |
| [0001] | $h_6$ (maximum) | 16.0 | 15.8 | 0.35 | — | 0.52 | 0.62 | 0.07 | 0.05 | −0.55 | 0 |
| [0001] | $h_7$ (L) | 96.6 | — | 1.72 | — | 0.04 | — | 0.03 | — | 0.3 | — |
| [0001] | $e_8$ (Γ) | 93.1 | 93.3 | 0.88 | — | 0.31 | 0.31 | 0.16 | — | 1.0 | — |
| [0001] | $h_8$ | 3.30 | 4.90 | 0.34 | — | 2.29 | 0.80 | −8.3 | −4.8 | −52 | −29 |
| [10$\bar{1}$0] | $h_5$ (L) | 0.82 | 0.78 | 0.05 | — | 0.27 | 0.72 | 0.66 | 1.7 | 3.3 | 7.0 |
| [10$\bar{1}$0] | $h_5$ (L′, L″) | 1.34 | 1.45 | 0.09 | — | 0.43 | — | 0.81 | 1.1 | 3.9 | 8.0 |
| [10$\bar{1}$0] | $h_6$ (L) | 18.0 | 16.5 | 0.40 | — | 0.55 | 0.70 | −0.58 | −0.35 | −3.5 | −3.1 |
| [10$\bar{1}$0] | $h_6$ (L′, L″) | 15.1 | 14.5 | 0.36 | — | 0.58 | 0.70 | −0.13 | −0.09 | −1.3 | −1.7 |
| [10$\bar{1}$0] | $h_7$ (L) | 83.9 | — | 1.07 | — | 0.27 | 0.0 | −0.64 | — | −3.8 | — |
| [10$\bar{1}$0] | $h_7$ (L′, L″) | 64.7 | 64.1 | 0.68 | — | 0.32 | 0.0 | −0.28 | — | −2.0 | — |
| [10$\bar{1}$0] | $h_8$ | 4.83 | 6.63 | 0.15 | — | 1.97 | 1.87 | −13 | −12.5 | −83 | −62 |
| [11$\bar{2}$0] | $h_5$ (L, L′) | 0.87 | 0.91 | 0.06 | 0.12 | 0.34 | 0.6 | 0.87 | 3.0 | 4.4 | 11 |
| [11$\bar{2}$0] | $h_5$ (L″) | 3.0 | 2.8 | 0.16 | 0.45 | 0.66 | 0.87 | 0.68 | 2.2 | 3.8 | 12 |
| [11$\bar{2}$0] | $h_6$ (L, L′) | 16.6 | 15.6 | 0.42 | 0.68 | 0.52 | 0.68 | −0.24 | −0.2 | −2.6 | −2.2 |
| [11$\bar{2}$0] | $h_6$ (L″) | 14.6 | 13.5 | 0.32 | 0.45 | 0.59 | 0.87 | −0.11 | −0.2 | −1.0 | −2.6 |
| [11$\bar{2}$0] | $h_7$ (L, L′) | 67.3 | 67.5 | 0.63 | 1.10 | 0.32 | 0.36 | −0.45 | — | −2.7 | — |
| [11$\bar{2}$0] | $h_7$ (L″) | 66.8 | 66.9 | 0.68 | 1.33 | 0.34 | — | −0.09 | — | −1.1 | — |
| [11$\bar{2}$0] | $h_8$ | 5.73 | 6.62 | 0.17 | 0.37 | 2.14 | 1.67 | −15 | −10 | −89 | −58 |

**Table 3.** Local partial densities of states at the Fermi level.

| Symmetry character | LPDOS ($E_F$) (states Ryd$^{-1}$ atom$^{-1}$) | | | |
|---|---|---|---|---|
| | Band 5 | Band 6 | Band 7 | Band 8 |
| $s_{1/2}$ | 0.0 | 0.01 | 0.09 | 0.01 |
| $p_{1/2}$ | 0.0 | 0.09 | 0.36 | 0.03 |
| $p_{3/2}$ | 0.0 | 0.11 | 0.62 | 0.08 |
| $d_{3/2}$ | 0.01 | 0.16 | 1.09 | 0.51 |
| $d_{5/2}$ | 0.01 | 0.27 | 1.88 | 1.77 |

In order to understand the nature of the FS pressure response let us consider the following expression [16] for the volume derivative of a Fermi surface area in the pure (unhybridized) l band, which comes from the canonical band theory:

$$\mathrm{d}(\ln A_l)/\mathrm{d}(\ln \Omega) = -\tfrac{2}{3} + [(E_F - C_l)\pi m_l^*/3A_l]\{\mathrm{d}[\ln(E_F - C_l)]/\mathrm{d}(\ln S) + \mathrm{d}[\ln(\mu_l S^2)]/\mathrm{d}(\ln S)\}$$

where $C_l$ is a centre of the $l$ band, $\mu_l$ is the $l$-band mass, $S$ is the atomic sphere radius and $m_l^*$ is the effective mass of the orbit in question.

Our calculations show that the relative band centre energies $C_s$, $C_p$ and $C_d$ move very little with lattice parameter changes, while the variation in the band width proportional to $\mu_l S^2$ depends strongly on l. We have calculated the symmetry character of the bands at the Fermi level (table 3). The local partial densities of the states of band 5 are purely and band 8 predominantly of d character, and d electrons are far from being free electron-like, when the states contributing to the bands 6 and 7 are strongly hybridized, mainly of p–d character. The unusual behaviour of the electrons in $h_5$ surfaces, i.e. the non-parabolic form of the band associated with this FS sheet, was stressed in [10], in agreement with the results of the present work. We consider the difference in symmetry character of the bands at the Fermi level to be the main reason for the differences in pressure response of various sheets of rhenium FS. However, it should be noted that in the case of the FS strain and stress response the effect of lattice distortions should also play an important role. The concept of volume dependence of a FS sheet associated with the pure l band cannot be directly applied to the analysis of the observed anisotropies in strain response of various orbits on the same FS sheet. However, this anisotropy could be associated with the local symmetry character of states in given $k$-points representing the particular orbit.

## 3. Conclusions

In conclusion, on the basis of *ab initio* fully relativistic band-structure calculations we have determined the response of the FS of the HCP transition metal rhenium to the hydrostatic pressure, the uniaxial tensile stress and the homogeneous dilatation strain. The calculated extremal cross section areas of the FS of unstrained rhenium, as well as the cross section derivatives with respect to the pressure and to the stress and strain, are in good agreement with the experimental data. The applicability of LDA to the description of the strain response of the FS of a non-cubic transition metal is therefore demonstrated.

The nature of the observed differences in the response of the various sheets of the rhenium FS to the hydrostatic pressure is connected with the symmetry character of the energy bands at the Fermi level while, for the response to uniaxial stress and strain, lattice distortions should also be taken into account.

## References


[1] Fawcett E, Griessen R, Joss W, Lee M J G and Perz J M 1980 *Electrons at the Fermi Surface* ed M Springford (Cambridge: Cambridge University Press) p 278
[2] Joss W, Griessen R and Fawcett E 1983 *Landolt–Börnstein New Series* vol 13b (Berlin: Springer) p 1
[3] Joseph A S and Thorsen A C 1964 *Phys. Rev.* **133** A1546
[4] Thorsen A C and Joseph A S 1966 *Phys. Rev.* **150** 523
[5] Jones C K and Rayne J A 1965 *Phys. Rev.* **139** A1876
[6] Testardi L K and Soden R R 1967 *Phys. Rev.* **158** 581
[7] Ruthruff T L and Goodrich R G 1979 *J. Phys. F: Met. Phys.* **9** 95
[8] Perz J M, Svechkarev I V and Templeton I M 1980 *Can. J. Phys.* **58** 194
[9] Anderson J R, Holroyd F W, Perz J M, Schirber J E and Templeton I M 1983 *Can. J. Phys.* **61** 1428
[10] Fawcett E, Holroyd F M and Perz J M 1980 *Can. J. Phys.* **58** 1191
[11] Griessen R, Lee M J G and Stanley D J 1977 *Phys. Rev.* B **16** 4385
[12] Stanley D J, Perz J M, Lee M J G and Griessen R 1977 *Can. J. Phys.* **55** 344
[13] Mattheiss L F 1966 *Phys. Rev.* **151** 450
[14] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
[15] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[16] Skriver H, Venema W, Walker E and Griessen R 1978 *J. Phys. F: Met. Phys.* **8** 2313
[17] Skriver H and Jan J-P 1980 *Phys. Rev.* **21** 1489
[18] Nemoshkalenko V V, Krasovskii A A, Antonov V N, Antonov Vl N, Fleck U, Wonn H and Ziesche P 1983 *Phys. Status Solidi* b **120** 283
[19] Andersen O K 1975 *Phys. Rev.* B **12** 3060
[20] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
[21] Pearson W B 1958 *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (London: Pergamon) p 831
[22] Shepard M L and Smith J F 1978 *J. Appl. Phys.* **36** 1447
[23] Lehmann G and Taut M 1972 *Phys. Status Solidi* b **54** 469