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The band structure of hexagonal close-packed metals

II. Sc, Ti, Y and Zr

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Abstract. The band structures, density-of-states curves and Fermi surfaces are presented for the hexagonal close-packed configurations of Sc, Ti, Y and Zr, as calculated by the cellular method. A study is made of the effect of the potential field on the band structure and Fermi surfaces of Ti. Heat capacities and bandwidths are discussed.

1. Introduction

We present in this paper the band structures, Fermi surfaces and density-of-states curves for the hexagonal close-packed metals Sc, Ti, Y and Zr, as computed by the cellular method. A full description of the method, as well as a study of the errors involved in it, has been given in a previous paper (Altmann and Bradley 1965 b).

The calculations are of an *ab-initio* nature, the only experimental data required being the lattice constants of the metals. These are shown in table 1.

Table 1. Lattice constants

| Metal | a (A.U.) | c/a | Reference |
|-------|------------|-------|------------------------------|
| Sc | 6.25 | 1.59 | Pearson 1958 |
| Ti | 5.575 | 1.59 | McQuillan and McQuillan 1956 |
| Y | 6.88 | 1.57 | Pearson 1958 |
| Zr | 6.117 | 1.59 | Lustman and Kerze 1955 |

2. Potential fields

The most serious problem in the calculation of the band structure of a transition metal is that of the choice of an appropriate metal field. It is now well known that quite reasonable changes of the potential field can alter the spacing of the energy eigenvalues by factors of 2 or 3. Mattheiss (1964), for instance, on using the augmented plane wave method, obtained such factors when comparing results for two vanadium fields, derived from the atomic configurations $3d^3 4s^2$ and $3d^4 4s^1$ respectively. Admittedly, the order of the levels is unaltered in this case and most of the features of the Fermi surface would presumably be preserved. Nevertheless, this is so only because vanadium has a favourable band structure with well-separated bands. There is no reason whatever to expect this to be the case for other transition metals.

In view of uncertainties of the order of 0.3 ryd in the energy levels arising from the choice of field, we did not consider it would have been consistent to introduce a number of refinements in the field which, however desirable on physical grounds, would nevertheless affect the eigenvalues by a few hundredths of a rydberg. Instead, we tried to achieve some overall consistency over a region of the periodic table as follows.

For a given metal, say A, with n valency electrons, we started from a Hartree-Fock self-consistent field for the ion A^{m+} (m generally equal to n , but in some cases taken to be one of the various integers $m \leq n$). We added to this field the contribution due to a uniform charge distribution of $m-1$ electrons over half the unit cell (since there are two atoms per unit cell in the hexagonal close-packed lattice).

The whole of such a field must be considered as a parameter of the calculations and its goodness can be gauged in two distinct ways. The first is, of course, to compare the resulting band structure with whatever experimental evidence is available for a given metal,

such as bandwidths or de Haas-van Alphen periods. This will provide support for the results obtained from a given field. Secondly, when no such experimental evidence is available for a given metal, we can apply a consistency criterion over a region of the periodic table, since we expect to preserve a certain element of rigidity of the band structure in going from Sc to Ti and from Y to Zr.

Thus, from three fields used for Ti, only one (Ti3) gave a bandwidth in reasonable agreement with experiment (see § 6). For Sc, where experimental evidence is lacking, we

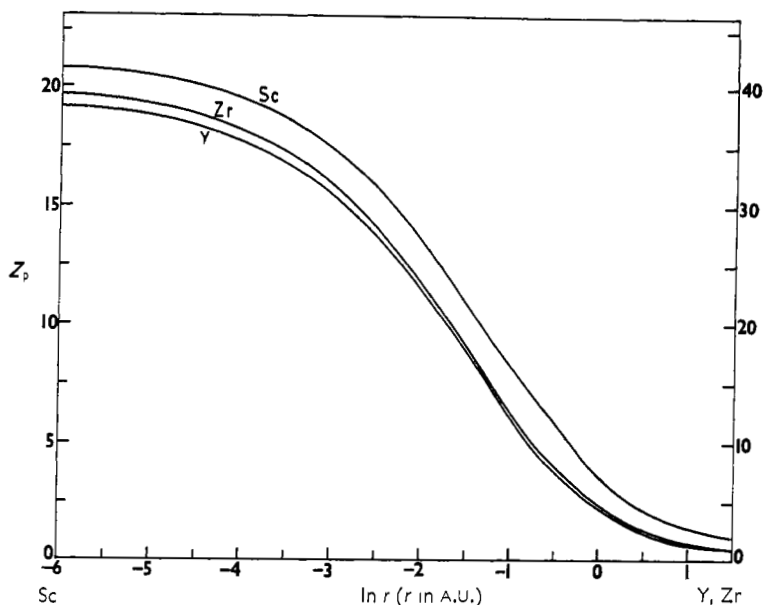


Figure 1. The potential field Z_p for Sc, Y, Zr; the scale on the right is for Y and Zr.

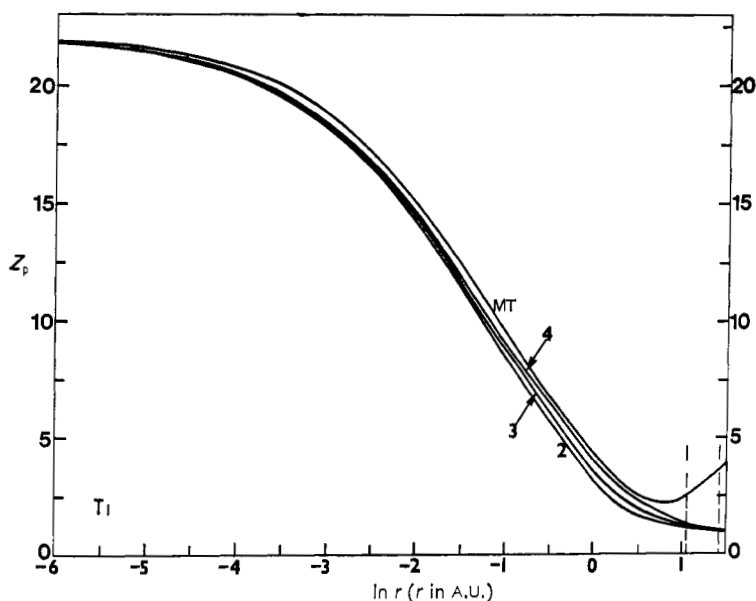


Figure 2. The potential fields for Ti₁; the vertical lines mark the shortest and longest radii of the Wigner-Seitz cell.

observe good consistency of the bands with that of the best Ti field. Likewise, the Zr field used gives a bandwidth, heat capacity and Fermi surface in reasonable agreement with experiment and that for Y is consistent with the Zr band structure. On these grounds, we are reasonably satisfied that the results we present for these metals are of some significance.

We show in figure 1 the potential fields used for Sc, Y and Zr, derived from those of the ions Sc^{3+} , Y^{3+} and Zr^{4+} respectively. In figure 2 we display four fields used for Ti. The number n given in the figure indicates that the field derives from the Ti^{n+} ion. We also investigated a muffin tin field (designated MT) constructed from a field obtained by L. F. Mattheiss and kindly provided by him. Although the basic field is the same as that used for Ti by Mattheiss (1964), the choice of muffin tin is different so that our results cannot be compared directly with his. However, it is interesting to consider this field for the following reason. For the other fields used the potential is not spherically symmetric outside the inscribed sphere, and this might introduce some errors of convergence in the cellular method, which are not present when a muffin tin potential is used. However, we computed all the energy eigenvalues for the first half dozen bands at all points of symmetry with the muffin tin potential and we did not find any difference as regards the convergence of the expansions. In fact, when the lowest level at Γ is taken as the zero of energy we found that, with two or three exceptions, all the levels for MT coincided with those for Ti4 within 0.03 ryd, and that there is no serious difference in the Fermi surface obtained for those two fields. Since the difference for MT and Ti4 is not significant, the results for MT are not presented in this paper.

All the self-consistent fields of the ions were kindly computed for us by Dr. D. F. Mayers.

3. The bands

The bands computed are shown in figures 3 to 8. For Sc, Ti4, Y and Zr five points (including the ends) were computed along all the lines of symmetry shown, except KM for which three points were computed. Broken lines indicate interpolated bands. For Ti2 and Ti3 only points of symmetry were computed. In every case, the notation is that of Altmann and Bradley (1965 a).

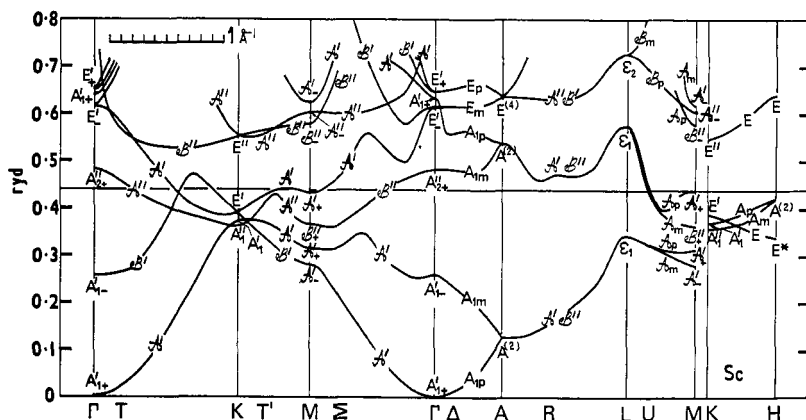


Figure 3. Bands for Sc; the value of ΓA_{1+} is -0.607 ryd.

Mattheiss (1964) computed only the ΓK direction for Ti. His bands agree very well qualitatively with those for Ti3, except that the levels $\Gamma E_{-}'$ and $\Gamma A_{2+}''$ are interchanged. The quantitative agreement is also quite good as comparison with his bands will show. The only other set of bands published for these metals is that for Zr computed by Loucks (1967). The agreement both qualitatively and quantitatively is reasonable for the first three or four bands along the ΓK and ΓM directions but the dip of the $T\mathcal{B}''$ curve does

not appear in Loucks's calculation. We must admit, however, that this line was the very first that we computed in 1962, and the standard of accuracy then achieved was not quite as good as in later calculations. Indeed, for all later calculations along the line ΓK we used more terms in the wave function and obtained better convergence. On the other hand, there is a crossing in Loucks's bands that appears most unlikely to be genuine. This is the one between the band that joins the lowest level at Γ and the doubly degenerate level at K

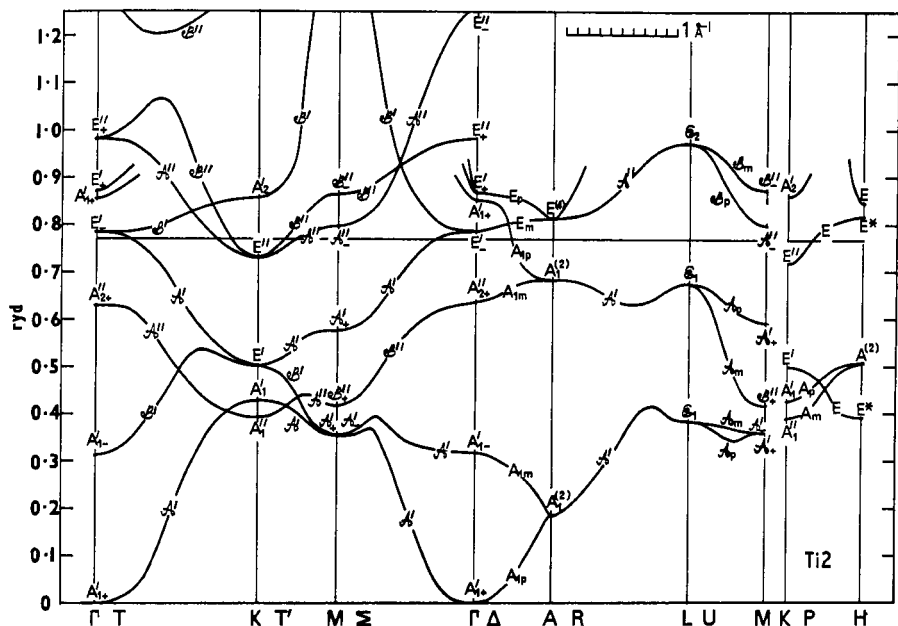


Figure 4. Bands for Ti2; the value of ΓA_{1+} is -0.390 ryd.

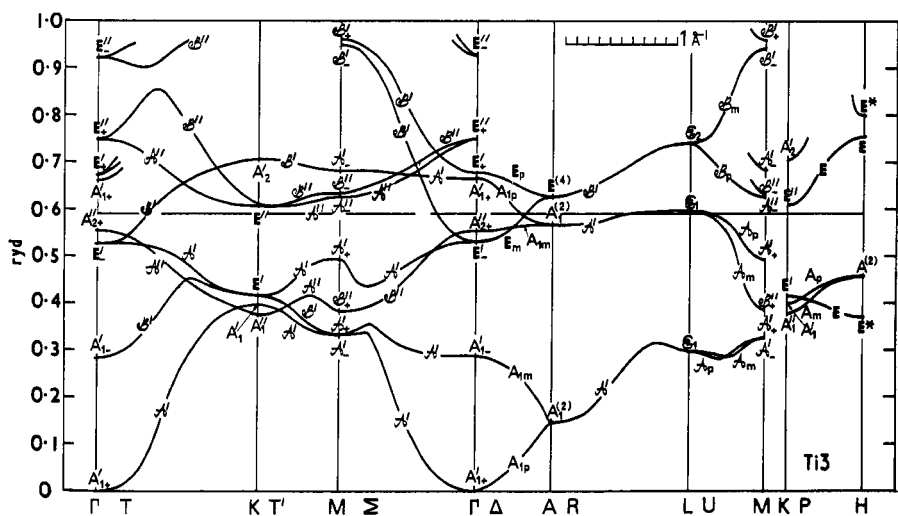


Figure 5. Bands for Ti3; the value of ΓA_{1+} is -0.634 ryd.

(which must be T_{2g}'), and the band that starts from the level immediately below at K. This latter level is most unlikely to be anything else except A_{1g}' so that the band coming from it must be T_{2g}' and cannot cross a T_{2g}' band. Loucks has treated all the values of k as general ones and cannot identify directly the symmetry of his levels, which may explain this difficulty.

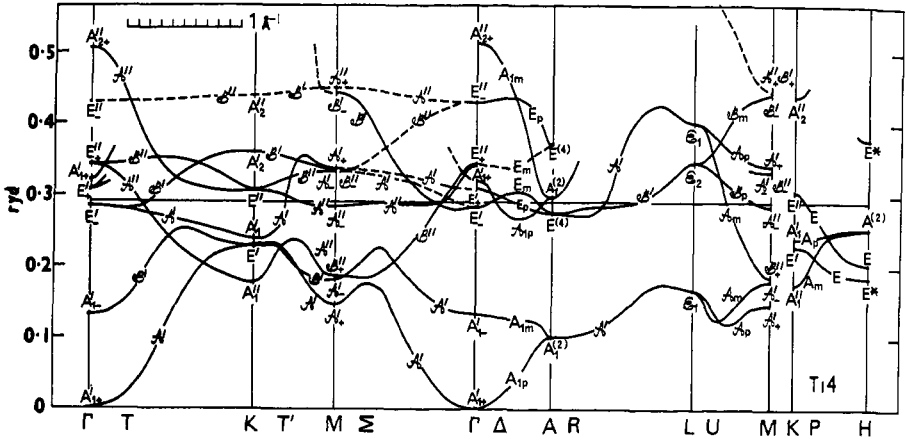


Figure 6. Bands for Ti4; the value of $\Gamma A_{1g} +$ is -0.856 ryd.

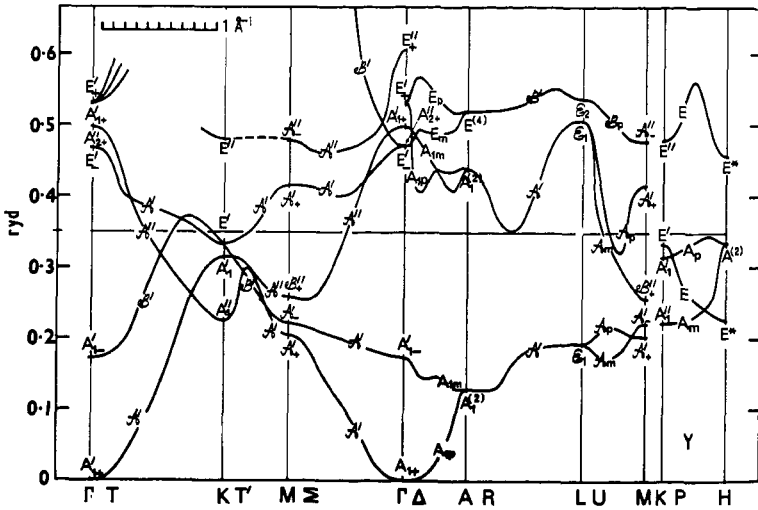


Figure 7. Bands for Y; the value of $\Gamma A_{1g} +$ is -0.411 ryd.

We describe briefly in table 2 the nature of the levels below the Fermi surface at the points of symmetry. It can be seen that the main s contribution appears at Γ and that, as the edge of the Fermi surface is approached, these levels turn into d states. Also, as expected, hybridization is considerable and even the f contribution is not negligible. The fact that the Ti wave functions are more d-like is a consequence of the field Ti4 used. From figure 5 it can be seen that Ti3 is more s-like.

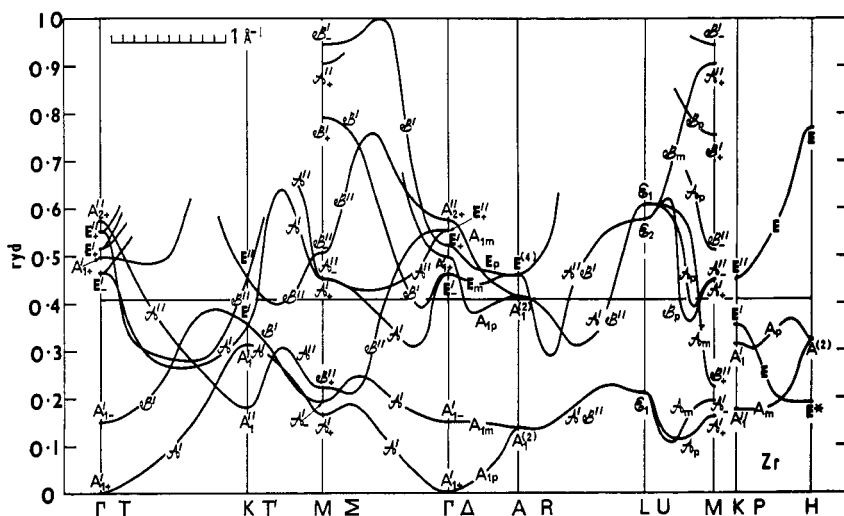


Figure 8. Bands for Zr; the value of $\Gamma A_1 +$ is -0.537 ryd.

Table 2. Nature of the wave functions

| | Sc | Ti4 | Y | Zr |
|------------------------|-----|-----|-----|-----|
| $\Gamma A_1 +$ | S | S | S | S |
| $\Gamma A_1 -$ | ds | ds | ds | ds |
| $\Gamma E -$ | D | D | D | D |
| $\Gamma A_2 +$ | P | P | Pf | Pf |
| $K A_1''$ | D | D | Df | D |
| $K A_1'$ | dp | Dp | dp | dp |
| $K E'$ | dsp | Dps | dsp | sdp |
| $M_1 \mathcal{A}' +'$ | dps | D | Ds | Ds |
| $M_1 \mathcal{A}' -'$ | sdp | dsp | dsp | sdp |
| $M_1 \mathcal{B}'' +'$ | Dp | Dp | dp | dp |
| $M_1 \mathcal{A}' +'$ | pds | dps | pds | pds |
| $A A_1^{(2)}$ | sp | sdp | sdp | sdp |
| $A A_1^{(2)}$ | dp | dps | dp | dp |
| $L \mathcal{C}_1$ | dps | Ds | ds | ds |

The contributions are listed in order of magnitude and where contributions are greater than 80% the appropriate letter is written in capitals. Contributions are listed only if they are greater than 5%.

4. The Fermi surfaces

In order to display the sticking together of the n and $n+1$ bands on the AHL plane we represent all the Fermi surfaces in the double Brillouin zone discussed by Altmann and Bradley (1964).

4.1. Scandium

The sections of the Fermi surface are shown in figure 9 and a perspective in figure 10. The basic feature of the surface is a sinuous tube of holes along ΓA and a pillar of electrons along KH multiply connected *ad infinitum*, from which extensions protrude towards the central axis of the cell as well as towards M .

Since there is no experimental evidence on this metal as yet, it is premature to discuss orbits in detail. Estimates for them are not difficult to obtain from the figures.

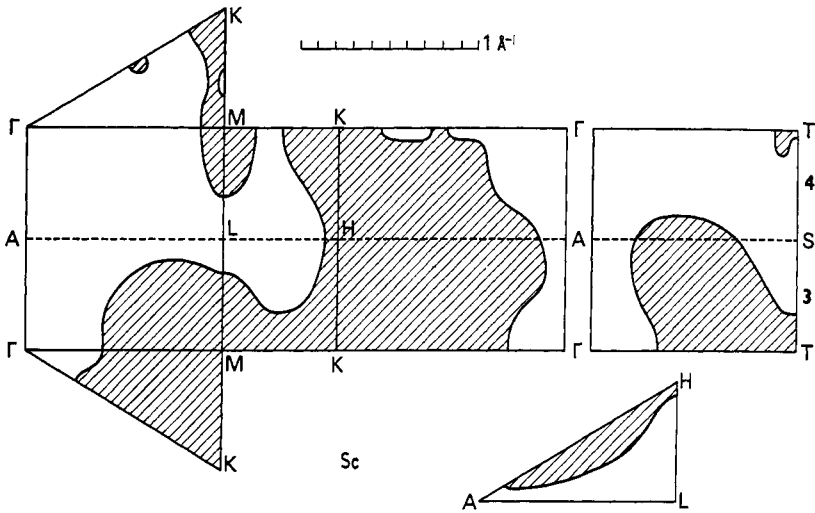


Figure 9. Sections of the Fermi surface of Sc. S is the midpoint of LH. The hatched areas contain electrons.

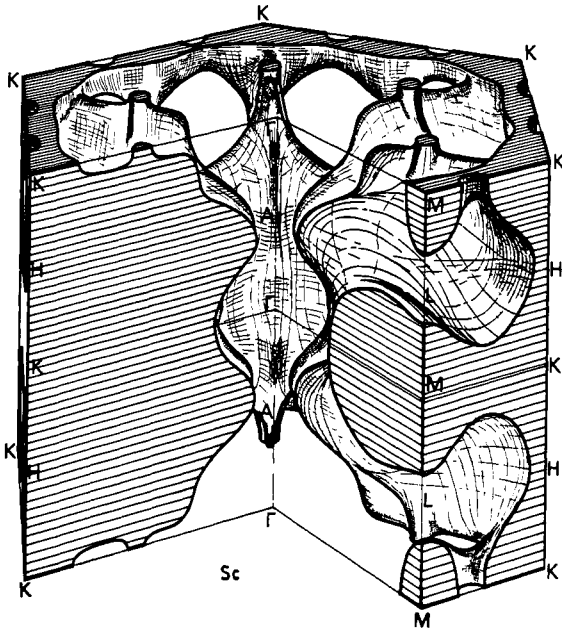


Figure 10. The Fermi surface of Sc (third and fourth bands). The object shown contains electrons.

4.2. Titanium

Figure 11 illustrates the drastic changes in the Fermi surface brought about by changes in the field. As discussed in § 2, the most reliable field is Ti3 (see also § 6). Thus we expect the Fermi surface to consist essentially of a globular pocket of holes in the third and fourth bands around L and a globular pocket of electrons around Γ in the fifth and sixth bands. These are exactly the major features of our Fermi surface for Zr (Altmann and Bradley 1964), although in this metal the pocket of electrons around Γ has a narrow hollow tube at Γ itself along ΓA .

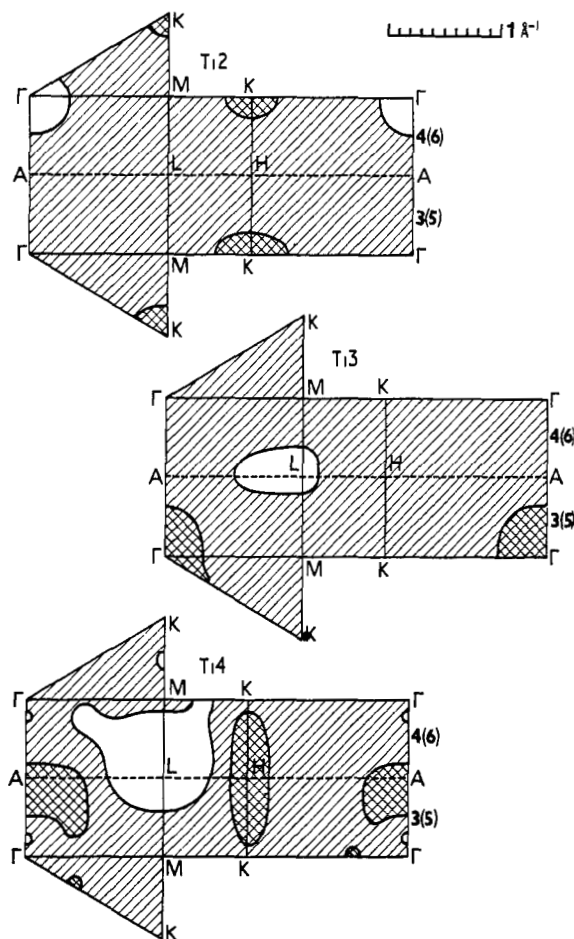


Figure 11. The Fermi surface of Ti. The empty areas contain holes and the hatched areas electrons. Areas with double hatching indicate pockets of electrons in the fifth and sixth bands.

4.3. Yttrium

Figures 12 and 13 give the Fermi surface for Y. As for Ti and Zr, the basic features are repeated in Sc and Y: a hollow column going all along the ΓA axis and a solid one going along KH and extending from it towards M and Γ . In fact, the Sc and Y surfaces appear remarkably similar.

Our results reproduce the same general features obtained by Loucks (1966), as can be seen from figure 12. The only major difference is that in Loucks's results the fourth band is occupied at M, which means that the level $M\mathcal{A}_+'$ in figure 7 must lie below the Fermi energy in his bands. This could easily be produced by small changes in the field. On comparing figures 6 and 7 it can be seen that, from Ti4 to Ti3, $M\mathcal{A}_+'$ moves from above to below the Fermi energy. On the other hand, the level KE' in Y is now very near the Fermi surface (see figure 8), so that if the difficulty about the crossing of levels mentioned for Zr were repeated here it might affect Loucks's Fermi surface.

4.4. Zirconium

The results for Zr will not be displayed here, since they have been published before (Altmann and Bradley 1964). The bands of figure 8 are an improved version of those from

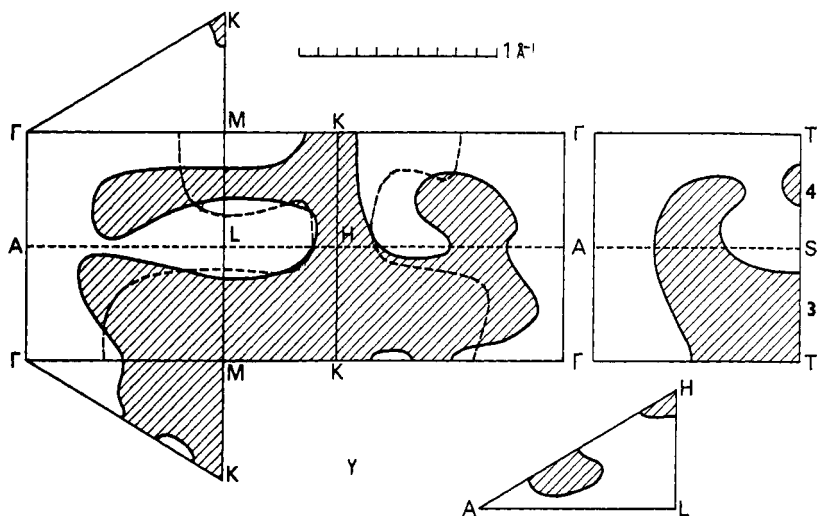


Figure 12. Sections of the Fermi surface of Y. S is the midpoint of LH. The hatched areas contain electrons. The broken lines are the contours obtained by Loucks.

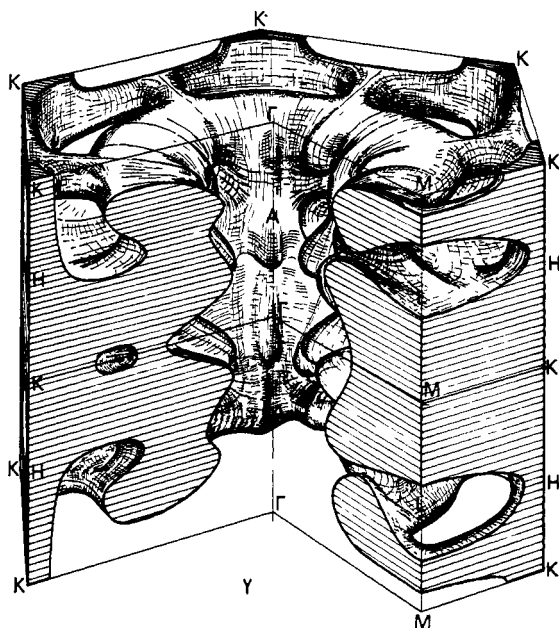


Figure 13. The Fermi surface for Y (third and fourth bands). The object shown contains electrons.

which our previous Fermi surface was constructed and a change must be noticed: the fifth band now just fails to cross the Fermi energy along ΓM . This means that the narrow waist of the pockets of electrons along ΓM now vanishes. This does not affect our conclusions (except for the disappearance of the l period, not observed).

As pointed out by Loucks, a comparatively small number of changes in the relative position of the eigenvalues brings about a substantial difference between the two calculated Fermi surfaces. Nothing very constructive can be said until better experimental results

are available when judicious modification of either of the computed surfaces will be required. In fact, such agreement as Loucks has obtained has already necessitated some modification of his computed results.

Loucks mentions an apparent ambiguity of our results. The α and β periods of Thorsen and Joseph (1963) have their minimum separation (about 10%) for the field along the c axis. As the field is tilted, α (the largest) goes slightly up and β slightly down. In accordance with Loucks, our orbit assignment is such that our periods α and β (see figure 8 of Altmann and Bradley 1964) should come together rather than separating further. This objection does not appear to affect our interpretation at all. In fact, what actually happens is this. When the field is tilted our α and β periods vary very little for an angle of tilt of 0° to 20° . Then the two periods merge over an angle of 3° or so and then β disappears, exactly as found by Thorsen and Joseph. The transition region of 3° or so is too narrow for them to have observed it. Whether this interpretation is right or wrong has to await further experiment, but so far there is no ambiguity in our interpretation of Thorsen and Joseph's results.

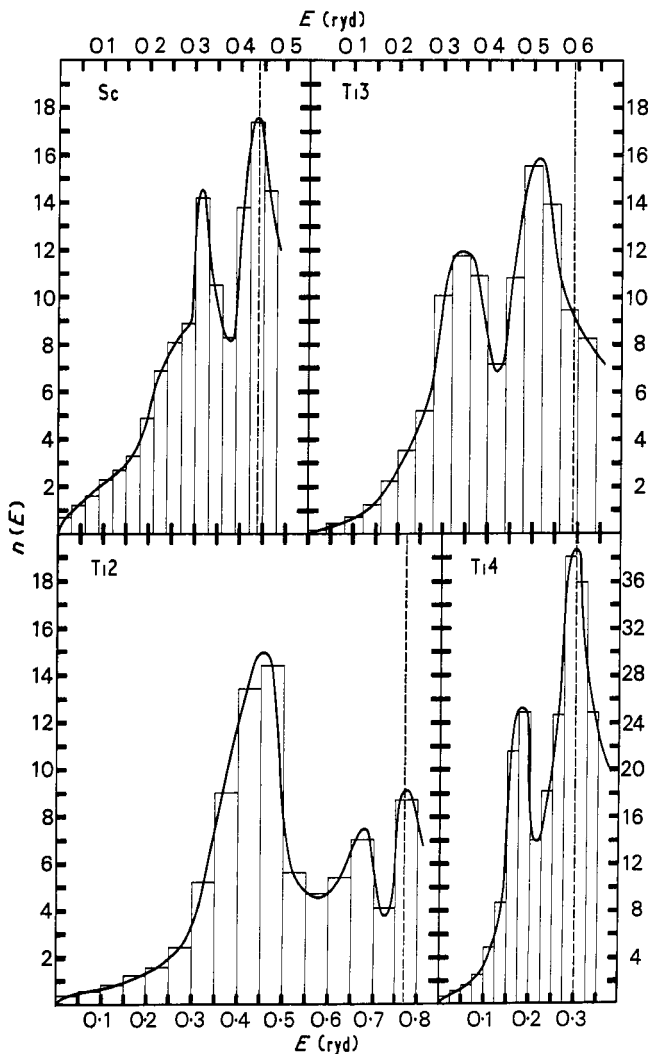


Figure 14. The density of states $n(E)$ for Sc and Ti. $n(E)$ is given in electron states of both spins per rydberg per atom. The histograms are calculated and the curves are plausible interpolations that have the same area as the histogram. The broken lines indicate the Fermi energies. The change of scale for Ti4 should be noticed.

5. The density of states

Figures 14 and 15 display the density of states for the various fields used. It will be noticed that the curves for the pairs Sc, Ti3 and Y, Zr show a reasonable degree of rigidity.

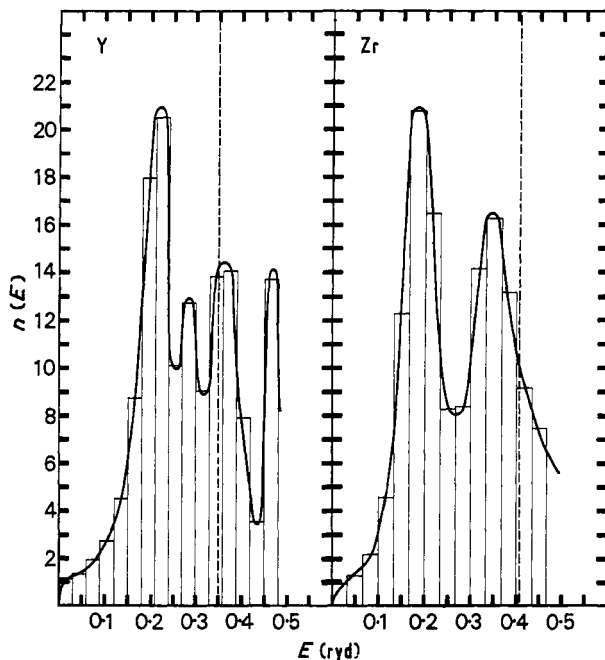


Figure 15. The density of states $n(E)$ for Y and Zr (see legend to figure 14).

The curve for Zr differs from that given in a preliminary communication (Altmann and Bradley 1962)[†] which explains another apparent discrepancy pointed out by Loucks. It can be seen that, as expected by this author, the Fermi energy cuts the curve near the sharp minimum.

6. Heat capacities and bandwidths

Table 3 collects our main results on heat capacities and bandwidths. It can be seen that, after phonon enhancement is allowed for, the agreement is quite fair for Ti3 and Zr. In fact, the values of $n(E_F)$ 'exp.' are probably fairly good estimates although (Jensen, private communication) they are likely to be overestimated by 30% or so. This would make the agreement even better for these metals.

On the other hand, when the Fermi surface hits a peak of the density-of-states curve, as in Sc and Y the agreement is poor (although the agreement for Loucks's Y is very good). However, the values of $n(E_F)$ 'exp.' for these metals are not as reliable as those for Ti and Zr and they must be considered as no more than rough guesses (Jensen, private communication). It appears, nevertheless, unlikely that they could go down to our value unless some new effect such as a spin fluctuation enhancement could be operative (Jensen, private communication).

It must be appreciated, on the other hand, that we are dealing here with narrow peaks and that quite small changes in the bands could raise the peaks very considerably.

[†] However, the new curve was shown at the Bristol Solid State Conference of January 1964 and was widely circulated.

Table 3. Heat capacities and bandwidths

| | $n(E_F)$ | | γ (10^{-4} cal mol $^{-1}$ degK $^{-2}$) | | E_F (ryd) | δ_s (ryd) | Bandwidth | | Exp. (ev) |
|-------------|----------|--------|--|------|----------------|---------------------|-------------------|------|------------------|
| | Calc. | 'Exp.' | Calc | Exp. | | | Estimate (ryd) | (ev) | |
| Sc | 17.6 | 33.6 | 7.4 | 25.8 | 0.44 | 0.11 | 0.33 | 4.5 | |
| Ti2 | 9.1 | 14.4 | 3.8 | 8.15 | 0.77 | 0.11 | 0.66 | 8.9 | 6.0 ^a |
| Ti3 | 9.2 | | 3.9 | | 0.59 | 0.11 | 0.48 | 6.5 | |
| Ti4 | 38.6 | | 16.2 | | 0.30 | 0.10 | 0.20 | 2.7 | |
| Y | 14.3 | 31 | 6.0 | 24.1 | 0.35 | 0.11 | 0.24 | 3.3 | |
| Y (Loucks) | 26.8 | | 11.2 | | 0.337 | | | | |
| Zr | 10.3 | 12.7 | 4.3 | 6.95 | 0.40 | 0.12 | 0.29 | 3.9 | 4.0 ^b |
| Zr (Loucks) | 9.1 | | 3.8 | | 0.387 | | | | |

a, Skinner, Bullen and Johnston 1954; b, Shaw and Jossem 1959.

$n(E_F)$, the density of states at the Fermi energy, is given in electron states of both spins per rydberg per atom. The calculated value is that obtained directly from the density-of-states curves. The value headed 'Exp.' is a rough estimate of the value of $n(E_F)$ which, after allowing for phonon enhancement, would reproduce the experimental value of γ . These values come from Jensen and Maita (1966) except the one for Y (Jensen, private communication).

All the values of γ come from Gschneider (1964).

The calculated values of γ are not corrected for phonon enhancement. They are obtained from the calculated values of $n(E_F)$ of the first column.

δ_s is an estimate of the width of the s band, obtained by working out the width of that part of the first band in the ΓM direction for which the wave function contains an s contribution of 80% or more. The values for Ti2 and Ti3 are guesses since the wave functions were not computed for these fields.

The agreement between our Fermi energies and those of Loucks for Y and Zr is as good as it could be. We have estimated the bandwidths by subtracting the correction δ_s defined in the table, and the agreements shown for Ti3 and Zr are very good.

It is clear from the table that Ti3 is the only one of the titanium fields that gives reasonable density of states and bandwidth.

Acknowledgments

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