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The Fermi surface and conductivity of calcium

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Abstract. A comparison is proposed between a Fermi surface for calcium calculated by the cellular method and de Haas–van Alphen periods recently measured by Condon and Marcus. The calculations predict calcium metal to be a semiconductor at high pressure and this agrees semiquantitatively with the recent results of Stager and Drickamer.

For many years the only band calculation on calcium was that of Manning and Krutter (1937). We have now performed a complete calculation of this metal and we wish to report on the comparison of our results with recent measurements of two properties of calcium metal that are directly related to its band structure. These are the de Haas–van Alphen periods measured by Condon and Marcus (1961, 1964) and the determination of the resistance at very high pressure by Stager and Drickamer (1963). Our calculations show calcium to be much less of a free-electron metal than the model proposed by Harrison (1960, 1963) and it appears that this fits the experimental results more satisfactorily.

The calculations were carried out by means of the cellular method as modified by Altmann (1958). Their general outline is the same as that given by Altmann and Bradley (1962, 1964) for the hexagonal close-packed metals.

We used a self-consistent potential field with exchange for Ca^{2+}, kindly computed for us by Dr. D. F. Mayers, to which the uniform charge distribution of one electron was added in the unit cell. In a further approximation we determined a **k**-dependent potential, properly self-consistent in the Hartree sense, but this showed no important differences in the eigenvalues.

We find that the first band is nearly full, with small kidney-shaped pockets of holes at the points K and U. A rough idea of their disposition is given in figure 1. The pockets at K are concave towards the inside of the zone and those at U towards the outside of it. Otherwise they are identical. In Harrison's model the pockets of holes at K and U are connected via holes at W, forming a torus-like monster. Our surface results from the dismembering of Harrison's monster into separate pieces.

Our second band is nearly empty and consists of saucer-shaped pockets of electrons centred at L, very much like in Harrison's model.

The experimental results of Condon and Marcus that we require appear in figures 2 and 3. Unfortunately, the samples of metal that they used turned out to be microcrystalline aggregates and their other results do not show cubic symmetry. For the same reason, the crystal directions as determined from external faces cannot be relied upon entirely. Condon and Marcus find three basic periods, which we call l ($3{\cdot}05\times10^{-7}$ G^{-1}), m ($0{\cdot}77\times10^{-7}$ G^{-1}) and s ($0{\cdot}57\times10^{-7}$ G^{-1}). On analysing all their results, Condon and Marcus show that l and s are correlated and l and m anti-correlated, as indeed appears in figure 2. Condon and Marcus interpreted their results

by reference to Harrison's Fermi surface. Harrison predicted some seven orbits, many of which do not appear experimentally. We show in figure 2 the correlation with Harrison's orbits (identified with Greek letters) given by Condon and Marcus. It is

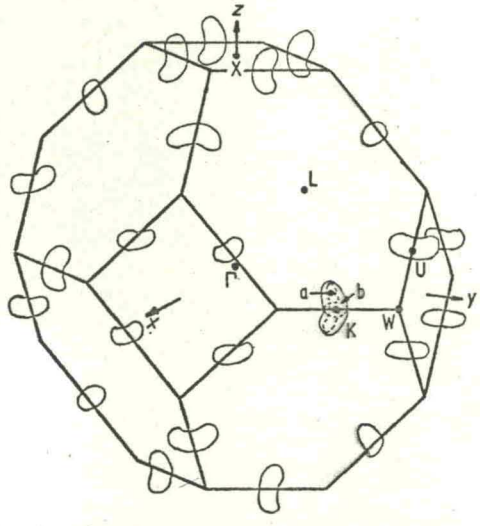

Figure 1. The Fermi surface for the first band of Ca. Sections a and b belong to the planes ΓKL (110) and ΓKW (001) respectively.

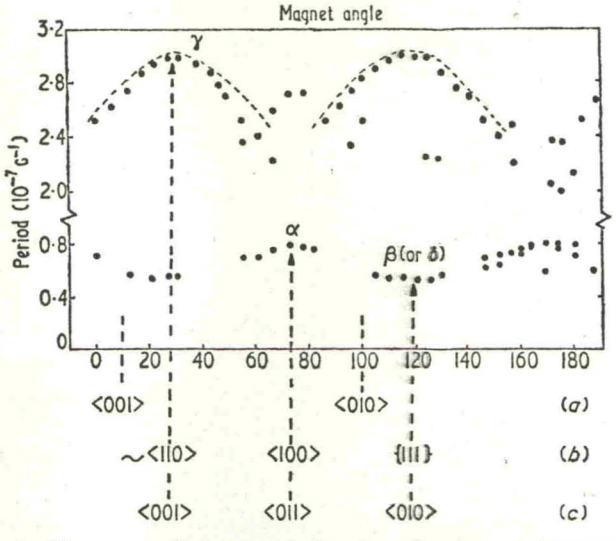

Figure 2. de Hans–van Alphen periods after Condon and Marcus. Magnetic field rotated in the (100) plane. (*a*) Orientations with respect to external face; (*b*) Condon and Marcus re-assignment to fit Harrison's Fermi surface; (*c*) our re-assignment.

apparent that this interpretation entails almost no correlation between the crystal directions given by external faces and the true directions of the magnetic field with respect to the microcrystallites.

The periods that we have calculated and our assignments appear in the table.

Computed periods			Experimental assignments		
Name of orbit	Field axis	Period	Name of period	Field axis	Period
a	⟨011⟩	3·8			
a′	⟨001⟩	~3·8	*s*	⟨001⟩	0·57
b	⟨001⟩	8·3	*l*	⟨001⟩	3·0
c	⟨011⟩	1·2	*m*	⟨011⟩	0·77

All periods in 10^{-7} G^{-1}.

It should be noticed that the field axis under 'experimental assignment' is our interpretation of the one that corresponds to the true orientation of the microcrystallite. It can be seen from figure 2 that this interpretation can be simply derived from an assumed rigid rotation of the microcrystallite with respect to the external face. Orbits a and b can be identified from figure 1. Orbit a′ is derived from a by rotation so as to make the section perpendicular to the *y* axis. This does not alter much the area of the

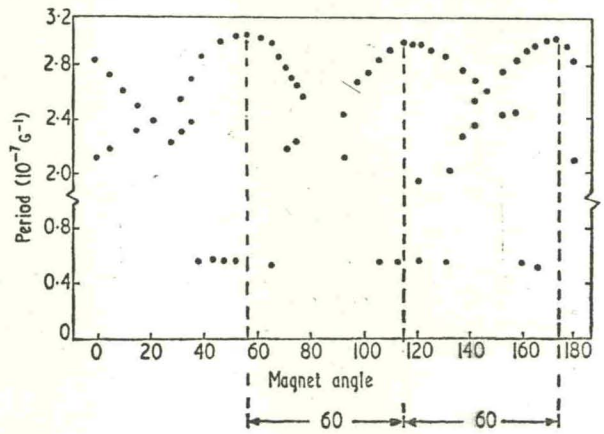

Figure 3. de Haas–van Alphen periods after Condon and Marcus. Magnetic field rotated in the (111) plane.

section, as indicated in the table. The orientation that we assign to the period *s*, which we correlate with a′, agrees in fact with that given by Berlincourt (1960). (However, his sample was also microcrystalline so that his orientations are open to suspicion).

The orbit b is assigned to *l* on the following grounds. (i) It should appear together with *a′*, as is the case for *l* and *s*. (ii) It has the right angular dependence shown in figure 2 for *l*. In fact, Condon and Marcus postulate a hyperboloidal shape for the part of the Fermi surface from which this orbit originates, since the period decreases more rapidly than the one computed from a cylindrical shape (which is given in broken lines in figure 2). The same result appears for our kidney-shaped objects (see figure 4). (iii) When the magnetic field is rotated in the (111) plane it cuts each of the six kidneys that lie around a hexagonal face through the same section. (This is not exactly b but it is rotated about 35° from it.) The distance between the maxima should then be 60°, exactly as appears from figure 3. However, the magnitude of the peaks should have been some 30% lower than *l* but, since the crystal directions are not quite exact, we did not consider this discrepancy a crucial one.

The orbit c is not displayed in our drawings. It is the section of the saucer-shaped pocket of holes around L in the second band with a plane perpendicular to the hexagonal face through L.

It should be noticed, in favour of our interpretation, that we obtain exactly the right number of orbits and that we do not require such a drastic re-assignment of the crystal directions as the one necessitated by Harrison's model. On the other hand, a drawback of our interpretation is that it does not explain why *m* and *s* do not seem to appear together. Also, of course, the size of the pockets is too small. Clearly, their linear dimensions must be about twice as large as those computed. This means that our results should be made a little more free-electron-like, going some way towards Harrison's model. Of course, errors of this magnitude must be expected when one is dealing with such small overlaps between the bands (a few hundredths of a rydberg), especially since we made no attempt to introduce *ad-hoc* modifications of the field to improve the agreement.

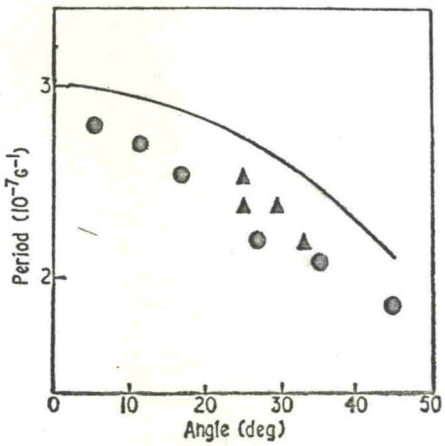

Figure 4. Angular dependence of the b orbit; our periods scaled so that maximum value coincides with *l*. Full line, cylindrical surface; circles, our theoretical prediction; triangles, experimental values.

As regards the resistance of calcium at high pressure, Stager and Drickamer (1963) have found that calcium becomes an intrinsic semiconductor at about 140 kilobars. We have estimated, by means of the experimental values of the compressibility of Ca and its pressure dependence, that at 140 kilobars the lattice constant of Ca is about 10% smaller than its equilibrium value. Clearly, in order to explain the onset of semiconductivity, one must find that the overlap between the first and second band is reduced and eventually vanishes when the lattice constant is diminished. We have computed this overlap, that is the difference between the levels K_1 in the first band and L_2' in the second, as a function of the lattice constant and we find that it vanishes when the latter is diminished by 5%. This corresponds to a pressure of about 35 kilobars. Of course, such estimates of the pressure are of necessity very rough but it is very probable from this result that our original overlap should have been somewhat larger, that is, that our bands should have been rather more free-electron-like. This is in agreement with the trend of our de Haas–van Alphen periods but, on the other hand, we believe that it would not be at all easy to explain the semiconductivity of calcium metal by means of a nearly free-electron picture.

A full account of the calculations and results will be published shortly.

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