de Haas–van Alphen Effect in Calcium*

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The de Haas–van Alphen (dHvA) effect has been studied in single crystals of calcium using the modulation method in magnetic fields up to 55 kOe. Data are presented for (111), (210), and one off-symmetry plane. Four distinct orbits were observed with dHvA frequency minima at [110] or [100] directions. The results do not support calculations predicting a disconnected first-band Fermi surface for calcium. The dHvA data of crystalline calcium are consistent with the topology of the two-orthogonalized-plane-wave model in which the first band is connected and pockets of electrons are about the point L of the second zone.

I. INTRODUCTION

The only experimental measurements of the Fermi surface of calcium have been made by Berlincourt[1] and Condon and Marcus.[2] Both used the de Haas–van Alphen (dHvA) effect to obtain extremal cross-sectional areas of the Fermi surface. Berlincourt, using a pulsed-field technique, found one frequency with a value of $(1.7 \pm 0.15) \times 10^7$ G. Condon and Marcus, using a torsion method and a maximum field of 33 kOe measured dHvA frequencies of three different orbits on the Fermi surface. However, their samples were not single crystals and the assignment of crystal orientation to their data appears inconsistent. This has made their results inconclusive when trying to fit them to calculations of the Fermi surface.

Following these experiments, there have been a series of theoretical calculations of the band structure and Fermi surface of calcium with widely differing results. The main difference between the various calculations is whether the hole surface consists of several pieces, and if so, where they are situated in the Brillouin zone, or if it is a connected hole surface. In the single-orthogonalized-plane-wave (single-OPW) model,[3] the hole surface is multiconnected and the electron surface consists of four pockets each centered at the point L of the Brillouin zone. Electron pockets at L which resemble lenses or ellipsoids are predicted by all calculations. The hole surface of the two-OPW model[4] is also connected but in the [100] direction it is open in the center in contrast with the single-OPW model. In 1971, Altmann *et al.*[5] calculated the band structure of calcium by a cellular method using a Slater-type potential and obtained with a Fermi energy of 0.31 Ry a connected hole surface of similar shape to that of the two-OPW model. Previously, however, Altmann and Cracknell[6] predicted pockets of holes around the symmetry point K that were not connected. Two different results have been given also by Chatterjee and Chakraborti who found disconnected pockets of holes about the symmetry point K by an OPW method[7] and about the point W by a quantum-defect method.[8] Unconnected pockets of holes about W were also obtained by Vasvari[9] using a nonlocal-pseudopotential method and by Dreesen and Pyenson[10] from a first-principles nonrelativistic-Green's-function calculation.

The purpose of this work is to clarify experimental measurements of the Fermi surface of calcium, again using the dHvA effect, by employing the modulation method[11] with a superconducting magnet and computer analysis of the data, and to see which theoretical model is in agreement with experiment.

II. EXPERIMENTAL METHOD

The calcium samples were prepared by McCreary[12] as in previous dHvA experiments. They were typically 2 cm long and up to 1 cm in diameter with numerous growth faces. Since calcium reacts rapidly in air to form a surface layer of oxide or hydroxide which eventually transforms a sample into a white powder, samples were handled with minimum exposure to air. The surface layer made x-ray analysis very difficult. However, some results were obtained using Laue back-reflection and precession techniques which indicated that the samples were not single crystals, but rather a large number of crystals joined together. A small sample, typically $3 \times 2 \times 2$ mm, was cut from a larger piece by the acid-saw technique using a mixture of one part hydrochloric acid and three parts methanol.

Because of the difficulties encountered using x rays to examine the crystals, instead of the conventional technique of x-ray orientation of the sample prior to mounting or using the morphology of the crystal as used by Condon and Marcus,[2] samples were mounted with no preconceived concept of orientation and the determination of orientation was attempted from the symmetry of the dHvA data. Out of ten samples examined, four appeared to be monocrystals except for small crystallites

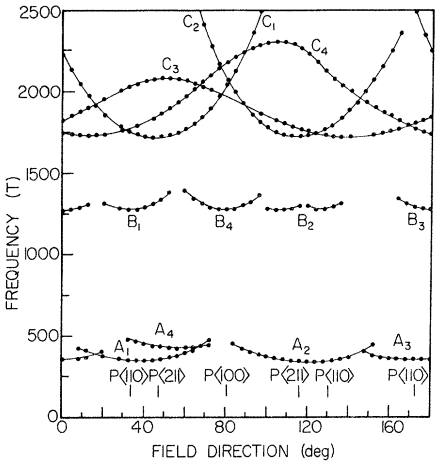

FIG. 1. dHvA frequencies of calcium sample 1 for field directions in an off-symmetry plane with normal 20° from the [110] direction in a (001) plane and 5° from the [010] direction in a (100) plane. Projection of principal crystal directions on to the plane are specified.

and it was possible to orient three, which are called samples 1–3. Samples 1 and 2 showed small signals from crystallites which were easily distinguished and excluded from the single-crystal data while sample 3 appeared to be a single crystal. Many samples were investigated because we wished to find [100] and [110] directions which are important for the measurement of the Fermi surface of calcium. Fortunately, two symmetry planes containing these directions were found.

Experiments were done by the modulation technique[11] with the sample in a 55-kOe superconducting magnet having an electronic field sweep.[13] A modulation frequency of 517 Hz was used with a typical modulation field of 80 Oe. For most of the experiments, the range of magnetic field was from 30 to 50 kOe which resulted in an error in the measured frequency of ±4 T. Samples glued in a sample holder were inserted into a modulation and pick-up coil assembly with a turning mechanism to rotate the crystal through 360° about an axis perpendicular to the field direction. A data acquisition system was used to digitally record the dHvA signal together with magnetic field values on magnetic tape for subsequent computer analysis. Typically, ten pairs of field and signal readings were recorded per dHvA oscillation over approximately 500 oscillations.

All measurements, except the temperature dependence of the signal, were done at 1.2 K with the sample immersed in liquid helium kept at a low-vapor pressure by pumping. For the temperature dependence of the signal, a Texas Instruments precision pressure gauge was used to measure the vapor pressure of the helium gas above the sample. The signal amplitude was measured at fixed magnetic field values in the temperature range 1.2–3 K at approximately 0.2 K intervals.

III. EXPERIMENTAL RESULTS

The dHvA frequencies obtained from sample 1 are shown in Fig. 1. Discussion of the assignment of the crystallographic directions is given in the next section. The spectrum consists of three distinct frequency ranges. The low-frequency range consists of three branches A_1, A_2, and A_3, each with an angular range of approximately 60° and a minimum frequency of 340 T. A fourth branch A_4 extending over 40° has a minimum frequency of 420 T. The mid-frequency range extends from 1270–1400 T. Again there are four branches although B_2 has a much weaker angular dependence than the other three. Finally there are four high-frequency branches, each with a minimum frequency of 1720 T. Two branches C_1 and C_2 are not continuous and can be followed in frequency up to about 2500 T. The dHvA signal decreases in amplitude as the field direction moves away from the minimum-frequency orientation. The other two branches are continuous through 180°, C_3 having a maximum frequency of 2085 T and C_4 a maximum frequency of 2310 T. Second and higher harmonics of most of the dHvA frequencies and sums of $(B_4 + C_1)$ and $(B_4 + C_2)$ were detected but are omitted from Fig. 1.

The results obtained from sample 2 are shown in Fig. 2. There are three low-frequency branches each with minimum frequency of 325 T, the minima each being separated by 60°. The extent of each branch is approximately 70°, so that this low frequency is observed in all field directions. In the mid-frequency range there are four branches although B_3 was not a strong signal and has a smaller angular dependence than the other three.

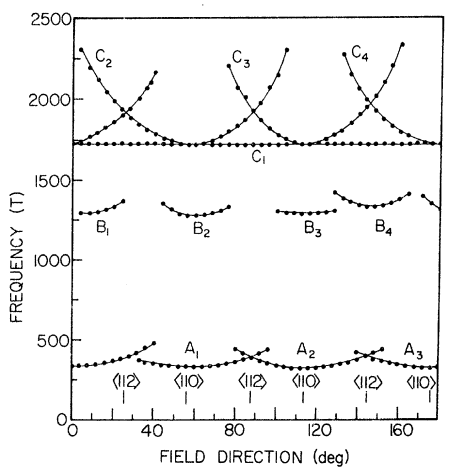

FIG. 2. dHvA frequencies of calcium sample 2 for field directions in a (111) plane.

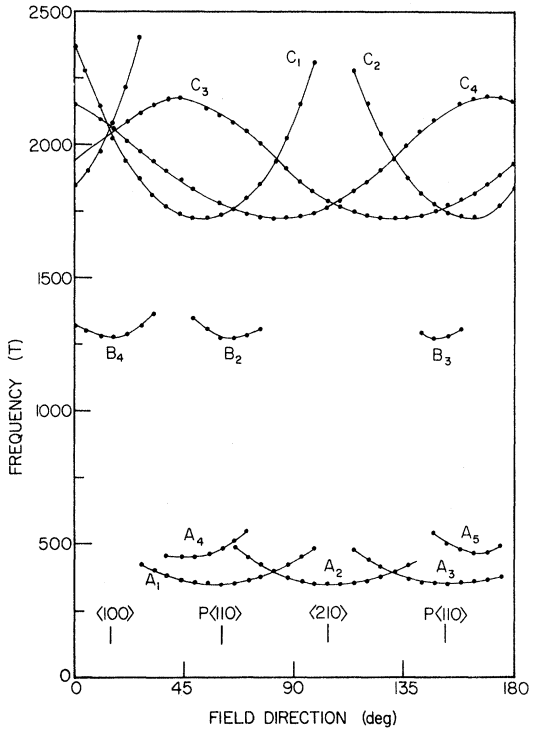

FIG. 3. dHvA frequencies of calcium sample 3 for field directions in a (210) plane.

The high-frequency branches are interesting. C_1 is isotropic with a frequency of 1724 T, while the other three branches have minimum frequencies of 1722 T and show threefold symmetry. The cross-over frequency of these three branches is 1950 ± 20 T.

Figure 3 shows the results obtained from sample 3. There are three main branches in the low-frequency region each with a minimum frequency of 345 T while two branches A_4 and A_5 from weaker signals are present from 40°–70° and 130°–175°, respectively. The minimum frequency of these two branches is 450 T. No low-frequency signal was observed between 5° and 25°. In the mid-frequency range a strong branch B_4 was found between 0°–33° with a minimum frequency of 1278 T. Two much weaker branches B_2 and B_3 are also present in this mid-frequency range with a minimum frequency of 1270 T. In the high-frequency range there are two open branches C_1 and C_2. Again, as the frequency increased, the signal was found to decrease in strength, preventing these branches from being followed to higher frequencies. The other two branches are followed through the 180° rotation. Both have the same maximum frequency of 2180 T while all four have the same minimum frequency of 1720 T. At 15° all four branches have the same frequency of 2060 T; this is also the orientation of the minimum of the strong branch B_4.

The cyclotron mass at the minimum of the branch B_4 from sample 3 was determined from the temperature dependence of the amplitude of the signal; this gave a value of $(0.52 \pm 0.02)m_0$. Using this value of the mass, the Dingle temperature calculated from the field dependence of the signal is (1.1 ± 0.1)K.

The cyclotron mass at the minimum of one of the high frequency branches was measured and found to be $(0.60 \pm 0.03)m_0$.

IV. DISCUSSION OF RESULTS

We shall use the two-OPW Fermi-surface model to interpret the results and at the end of this section compare the fit of this model with the results and with the various other Fermi surfaces proposed for calcium.

A two-OPW calculation was carried out using Harrison's[4] effective potential for calcium. The resulting Fermi surface is shown in Fig. 4. The principal orbits likely to be detected according to this model are the following: (α) an orbit around the intersection of the four first-zone arms, seen when the magnetic field is along a [100] crystal axis. It has a predicted minimum frequency of 1316 T. (β) is an orbit around the second-band lens. The minimum area is seen with the magnetic field along a [110] direction and has a frequency of 2000 T. (δ) is another orbit around the junction of the

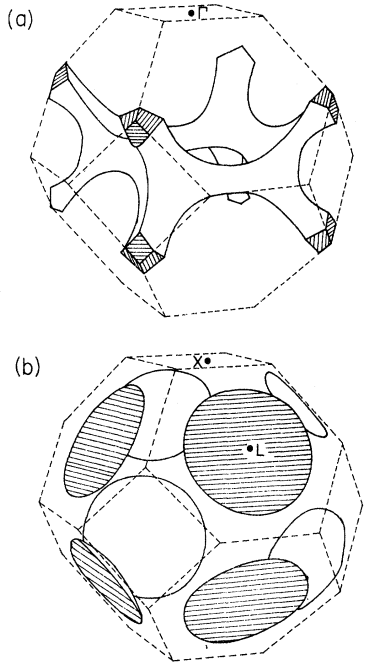

FIG. 4. Two-OPW model of the Fermi surface of calcium. (a) First-zone hole surface with the zone centered at X; (b) second-zone electron surface with the zone centered at Γ.

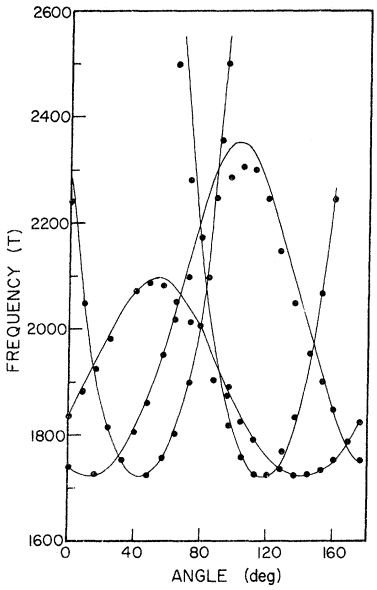

FIG. 5. Comparison of calculated electron frequencies with the high frequencies of sample 1.

four first-band arms but with the field in a [110] direction. The predicted minimum frequency is 1410 T. (γ) is the minimum section of a first-band arm corresponding to orbits with the field in a [110] direction with a predicted minimum frequency of 233 T. (ζ) is a nearly circular orbit around the inside of the four arms. It should be seen with the field in a [100] direction with a predicted minimum frequency of 3300 T. (η) is an approximately square orbit around the outside of the four arms; its predicted minimum frequency is 11 760 T with the magnetic field in a [100] direction.

In all four samples four high-frequency branches were observed each branch having a minimum frequency of 1720 T. In all cases these branches were either continuous throughout the 180° rotation or gradually decreased in strength as the frequency increased, until the signal was undetectable. These results indicate that these frequencies come from four separate closed pieces of the Fermi surface. Thus, it is concluded these branches originate from the four lenses of the electron surface in the second Brillouin zone; the two-OPW calculation predicts a minimum frequency of 2000 T which is in reasonable agreement with the experimental value.

The sample orientation was found by using the symmetry of the data together with a computer simulation of the electron Fermi surface. The computer model consisted of four ellipsoids of revolution about ⟨111⟩ directions, centered at the points L of the Brillouin zone. The dimensions of the lenses were obtained from the experimentally observed minimum frequency of 1720 T and a maximum frequency of 12 000 T obtained from the two-OPW calculation.

Figure 5 shows the high-frequency branches together with the computed high-frequency branches for sample 1 with an orientation that is 20° from the [110] direction in a (001) plane and 5° from the [010] direction in a (100) plane. It is seen there is good agreement and by calculating the frequency spectrum for planes close to the one plotted it was determined that the plane of rotation of the sample is that specified above to within ±2% in each direction. Using this, the orientations are marked on Fig. 1 where the letter P indicates a principal crystal direction projected on to the plane of rotation.

The three low-frequency branches A_1, A_2, and A_3 of sample 1 all have their lowest frequencies on projected [110] directions. These correspond to orbits of type γ around one arm of the hole surface. The fourth low-frequency branch is also from an orbit of type γ, the higher frequency indicating that the orientation for its minimum area to be observed is well off the plane of rotation. No low-frequency dHvA signal occurs in the vicinity of the projection of the [100] direction on the plane of rotation as expected for the γ orbit. The branch B_4 has its minimum frequency of 1280 T on the projection of the [100] direction and is assigned to be from an orbit of type α. The other mid-frequency branches B_1, B_2, and B_3 are all close to projections of [110] directions and are due to orbits of type δ. The two open-ended high-frequency branches C_1 and C_2 both have their minimum frequency at projections of [111] on the plane of measurement and are degenerate at the projection of [100] as expected from two of the electron lenses.

The results of sample 2 shown in Fig. 2 have threefold symmetry which immediately indicates that the plane of rotation is a (111) plane. With this orientation one of the lenses has its smallest area perpendicular to the magnetic field direction for all directions in this plane; this results in the branch C_1 which has a constant frequency of 1724 ±4 T. The other three branches C_2, C_3, and C_4 have their minima in [110] directions and cross each other in the [112] direction. The mid-frequency branches B_1, B_2 and B_3 are due to orbits of type δ. The origin of B_4 is not obvious but it is probably from an orbit of type α since the plane of rotation is about 40° from the [100] direction at the orientation of B_4. The three low-frequency branches, due to orbits of type γ, have their minima in a [110] direction and are degenerate in the ⟨112⟩ directions.

Figure 6 shows the high-frequency branches obtained from sample 3 together with the computer simulation of a [210] axis of rotation. There is good agreement between the two; the presence of

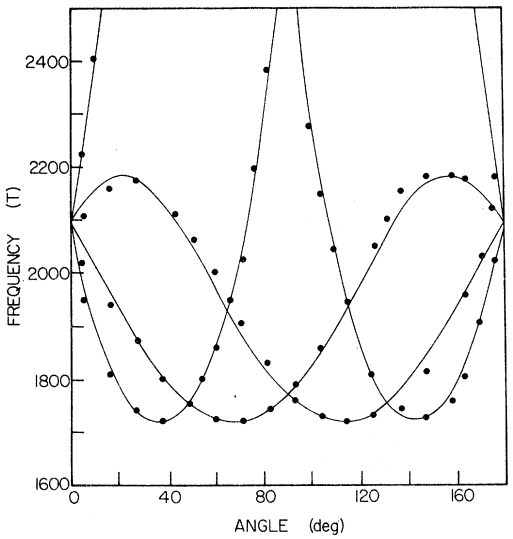

FIG. 6. Comparison of calculated electron frequencies with the high frequencies of sample 3.

a mirror plane in the data and the fourfold degeneracy of the high-frequency branches at 15° verifies that the axis of rotation of the crystal is a [210] direction. The four high-frequency branches are degenerate with a frequency of 2060 T with the field in the [100] direction. The minimum of branch B_4 is also in this orientation, and thus B_4 is due to an orbit of type α. The weaker branches B_2 and B_3 are on projected [110] directions and are due to orbits of type δ. The low-frequency branches A_1, A_2, and A_3 also have their minima in the vicinity of the projection of [110] directions onto the plane of rotation and are due to the orbits of type γ. Branches A_4 and A_5 are also due to the same type of orbit but the orientation for their minimum area to be observed is well off the axis of rotation hence their higher frequencies. Again, no low-frequency signals were observed near the [100] direction as expected from the two-OPW model. An attempt was made to detect higher frequencies in the region around the [100] direction but with no success.

Thus, using a two-OPW model of the Fermi surface we have been able to explain the origin of all the frequency branches measured experimentally. Four distinct orbits have been detected as summarized in Table I. We were unable to measure the masses corresponding to orbits δ or γ because neither frequency dominated the dHvA signal in any orientation.

Although the simple two-OPW model is in good agreement with the experimental results for all the frequencies measured, the model predicts two higher frequencies in the [100] direction which were not observed. When the nature of these orbits is considered this is not really surprising. Orbit ζ, the nearly circular orbit around the inside of the four arms, should have a frequency of approximately 3000 T but with a very limited angular range. The curvature factor $|\partial A_H/\partial k_H|^{-1/2}$ in the expression for the dHvA amplitude will be dominant for this orbit, making the orbit difficult to detect experimentally. The other orbit η, around the outside of the four arms, has a predicted frequency of about 12 000 T; the sample was probably not pure enough for this orbit to be observed.

In no case was there any indication of any of the low-frequency branches being connected to each other. Similarly, the mid-frequency branches were completely isolated from each other. In both frequency ranges there was often a sharp cutoff of the dHvA signal as the crystal was rotated through a few degrees. Thus it appears extremely unlikely that these frequency branches originate from closed pieces of the Fermi surface. Very few of the theoretical papers quote expected extremal areas; the results of Vasvari, whose model seems typical of the unconnected-hole-surface type, do not agree with out measured frequencies.

Altmann, in his third Fermi-surface model for calcium, obtained a first-band surface similar to the two-OPW model. His minimum frequency for orbits of type γ is 263 T compared with 325 T obtained experimentally, and for the orbit β, 1470 T compared with the experimental value of 1720 T. He has ignored the orbits α and δ although they exist in his model and has calculated frequencies of some rather obscure orbits on his Fermi surface none of which match the present data.

In the Condon and Marcus experiment[2] the polycrystalline nature of the sample made any interpretation of the crystallographic directions at which frequencies were observed doubtful. However, three distinct orbits on the Fermi surface were observed with minimum frequencies of 328, 1300, and 1750 T. The lowest frequency is in excellent

TABLE I. dHvA frequencies and cyclotron masses of orbits in calcium.

Orbit	Field direction	Expt. frequency (T)	Two-OPW frequency (T)	m_c/m_0
α	[100]	1275	1310	0.52
β	[110]	1720	2000	0.60
δ	[110]	1270	1408	
γ	[110]	325	233	

agreement with our value of 325 T and their assignment to the γ orbit around the minimum section of the first band arm is correct. We also agree with Condon and Marcus on the assignment of the frequency of 1300 T for which we obtain 1310 T to the α orbit around the intersection of the four first-zone arms. However, the interpretation of their highest frequency of 1750 T was uncertain and was given in terms of either the β or the δ orbit. It is now clear that it was due to the β orbit around the second-band lens. Thus, their interpretation was quite satisfactory. However, because of the uncertainty in their crystal orientation their measurements have been subject to differing interpretations and it has been possible to make them an argument in support of each of the various calculations.[5–9] With this uncertainty removed in the present results, reliable measurements for comparison with calculations are now available.

V. CONCLUSIONS

Orientations of single crystals of calcium have been determined using symmetry of dHvA data. Four distinct orbits have been detected with minimum areas at [110] or [100] directions. The results do not support calculations predicting a disconnected first-band surface for calcium. The dHvA data of crystalline calcium is consistent with the topology of a two-OPW model of the Fermi surface in which the first-band surface is connected and there are pockets of electrons about L in the second zone.

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[1]T. Berlincourt, in *Proceedings of the Seventh International Conference on Low-Temperature Physics* (University of Toronto Press, Toronto, 1960), p. 231.

[2]J. H. Condon and J. A. Marcus, Phys. Rev. 134, A446 (1964).

[3]W. A. Harrison, Phys. Rev. **118,** 1190 (1960).

[4]W. A. Harrison, Phys. Rev. **131,** 2433 (1963).

[5]S. L. Altmann, A. R. Harford, and R. G. Blake, J. Phys. F **1,** 791 (1971).

[6]S. L. Altmann and A. P. Cracknell, Proc. Phys. Soc. Lond. **84,** 761 (1964).

[7]S. Chatterjee and D. K. Chakraborti, J. Phys. C **2,** 120 (1970).

[8]S. Chatterjee and D. K. Chakraborti, J. Phys. F **1,** 638 (1971).

[9]B. Vasvari, Rev. Mod. Phys. **40,** 776 (1968).

[10]J. A. Dreesen and L. Pyenson, Phys. Rev. B **2,** 4852 (1970).

[11]R. W. Stark, L. R. Windmiller, and J. B. Ketterson, Cryogenics **8,** 272 (1968).

[12]W. J. McCreary, J. Met. **10,** 615 (1958).

[13]J. Vanderkooy, J. S. Moss, and W. R. Datars, J. Sci. Instrum. **44,** 949 (1967).