Fermi Surface in Aluminum

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The band structure of aluminum is reconsidered in a combined experimental and theoretical approach very similar to that originally used by Heine. A more careful analysis of the de Haas-van Alphen data of Gunnersen has indicated a considerable flexibility in models consistent with it and has allowed the proposal of a Fermi surface which is much closer to that expected on theoretical grounds than the model suggested by Heine. It is found here that the first Brillouin zone is completely filled; that the second zone contains a single closed surface surrounding a region of holes; and that the third zone contains a multiply-connected surface which gives rise to all of the observed de Haas-van Alphen oscillations.

I. INTRODUCTION

HEINE[1] has proposed a model for the shape of the Fermi surface in aluminum. His work was based largely upon studies of the de Haas-van Alphen effect in aluminum by Gunnersen[2] and upon experimental studies of the anomalous skin effect[3] and low-temperature specific heat.[4] This experimental information was supplemented by band calculations which he performed.[5] Since the determination of the Fermi surface from such information is not a unique, straightforward procedure, it appeared desirable to re-examine this problem.

The approach here differs from that of Heine only in emphasis; the same experimental and theoretical information is used, but a very much different conclusion is reached. Heine has suggested that pockets of holes exist at the corners of first Brillouin zone; pockets of electrons (centered on each zone face) exist in the second zone, and very small pockets of electrons exist along the edges of the third zone. Here it is proposed that the first zone is completely full, that the second zone contains a single closed surface enclosing about one hole per atom, and that a multiply connected region exists in the third zone again lying along the edges of the zone but connected at the zone corners.

The procedure followed here involves first the construction of the Fermi surface in detail using a free-electron model. Particular distortions of the surface are then suggested on the basis of Heine's band calculations. The de Haas–van Alphen effect is considered by re-examining the high-frequency data of Gunnersen. It is found that the pockets proposed by Gunnersen are in no sense uniquely given by the data, but that the data are, in fact, completely consistent with the free-electron model as modified slightly in either of two different ways. Consideration of the anomalous skin-effect measurements eliminates one of these possibilities. The resulting model is found to be consistent with specific heat data and still contains sufficient flexibility to accommodate the low-frequency data of Gunnersen.

The resulting picture, then, fits all of the data considered and is very close to the picture originally proposed using the free-electron model. The small deviations from the free-electron model are in all cases in the direction suggested by the band calculations and of a magnitude consistent with them. The proposed model is felt to contain a much higher degree of consistency with the theoretical considerations than that originally proposed by Heine.

II. FREE-ELECTRON MODEL

As a first approximation, the free-electron Fermi surface is constructed. This was done by Heine,[1] but is repeated here for completeness and in order to give a more detailed geometric description.

In this approximation it is assumed that the Fermi surface is a free-electron sphere in wave-number space, large enough to contain three electrons per atom. Portions of this sphere lie in the second, third, and fourth Brillouin zones, the first zone lying completely within the sphere. The portions in the higher zones might be rearranged into the first zone by translating various sections by a reciprocal lattice vector. This then is the reduced zone scheme used by Heine. It, however, leads to many isolated portions which intersect the zone faces. It is much easier to picture the surface if these are again rearranged to obtain closed or multiply-connected regions with as little intersection with the zone face as possible. Here these steps are replaced by a single equivalent construction which is much easier to perform.

The reciprocal lattice is constructed and a free-electron sphere is drawn around *each* reciprocal lattice point. Then any point in wave-number space which lies within one of the spheres corresponds to an occupied electron state with an energy determined by the distance from that point to the center of the corresponding sphere. Points which lie within two spheres are occupied in two zones, etc. Thus several sets of Fermi volumes are obtained, each of which repeats throughout wave-number space with the periodicity of the reciprocal lattice, with points differing by a reciprocal lattice vector being equivalent. Then to find the Fermi surface in the second

[1] V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957).
[2] E. M. Gunnersen, Phil. Trans. Roy. Soc. (London) **A249**, 299 (1957).
[3] T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 336 (1955).
[4] Howling, Mendoza, and Zimmerman, Proc. Roy. Soc. (London) **A229**, 86 (1955).
[5] V. Heine, Proc. Roy. Soc. (London) **A240**, 354 and 361 (1957).

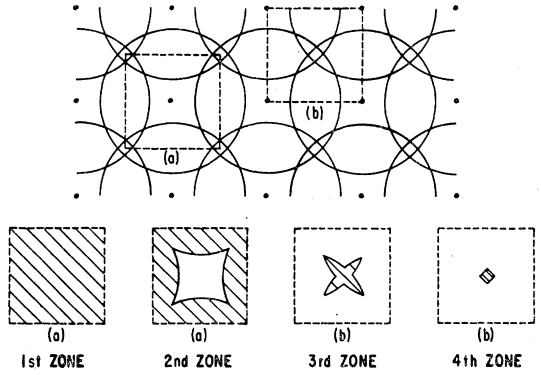

FIG. 1. Schematic determination of the free-electron Fermi "surface" in a two-dimensional square lattice. The diagram above indicates free-electron "spheres" drawn around each reciprocal lattice point; the dashed squares (a) and (b) represent two choices of Brillouin zones used in the drawings below. The cross-hatched areas below correspond to regions occupied by electrons.

zone, for example, a single Brillouin zone is drawn around some convenient point and the surface bounding the doubly-occupied volume in that zone is drawn. Such a procedure is carried out schematically for a two-dimensional square lattice in Fig. 1. The corresponding surfaces obtained for aluminum are shown in Fig. 2. Various symmetry points are indicated. It is noted, of course, that the symmetry of a point is determined by its position in the reciprocal lattice rather than its position with respect to the zone surface. Furthermore, the figure drawn has the same symmetry as the point at the center of the selected zone, which may not be full cubic symmetry. The third zone has been centered on X and the fourth on L.

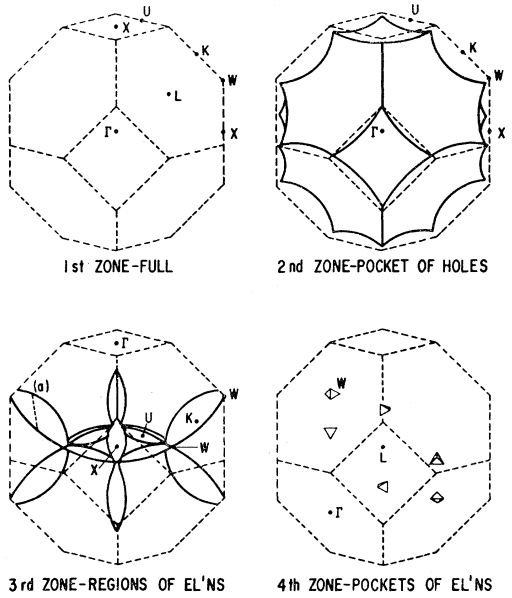

FIG. 2. Free-electron Fermi surface in aluminum, constructed in a manner analogous to that indicated in Fig. 1. Various symmetry points are specified in each zone; points K and U are equivalent. The dotted curve (a) corresponds to an electron orbit in wave-number space corresponding to a particular orientation of magnetic field discussed in the text.

This approximation to the Fermi surface is not as crude as might at first be thought. Heine's band calculations indicate that the free electron energies are quite close to those he obtained except within 0.05 atomic unit of the zone face in the first and second zones. (The distance $\Gamma-X$ is 0.822 for comparison.) This feature can probably be extended to the higher zones, where deviations are expected only near various symmetry planes. However, much of the surface in the third zone, and all of the surface in the fourth zone lies close to such symmetry planes and some distortions may be expected. The nature of the distortions of the surfaces in Fig. 2 may be guessed by considering the results of band calculations performed by Heine.

III. CONSIDERATION OF BAND CALCULATIONS

Heine has calculated the energy of points of high symmetry in the various zones. He has pointed out that such calculations are of limited reliability; thus we will use them only to indicate qualitatively how the free-electron surfaces may be modified. Table I gives the free-electron energies[6] and those obtained from band calculations for the relevant symmetry points. The shift of each state with respect to the Fermi energy is also listed. These will be considered, band by band, to see what modifications of the surfaces shown in Fig. 2 are to be expected.

TABLE I. Energies of high-symmetry points (Heine). Energies are in rydbergs relative to the band minimum. The values in parentheses represent rougher calculations than the others.

		Free electron	Band calculation	$\Delta(E-E_F)$
Fermi level		1.11	1.09	0.00
First zone	Γ	0.00	0.00	+0.02
	X	0.89	0.81	−0.06
	K, U	0.99	0.93	−0.04
	W	1.09	1.01	−0.06
Second zone	L	0.69	(0.72)	(+0.05)
	X	0.89	0.93	+0.06
	K, U	0.99	0.97	0.00
	W	1.09	1.01	−0.06
Third zone	L	(2.40)	(2.24)	(−0.14)
	K, U	0.99	(1.08)	(+0.11)
	X	(1.74)	(1.74)	(+0.02)
	W	1.09	1.06	−0.01
Fourth zone	W	1.09	1.18	+0.11

For the free-electron model, the first zone was full. The presence of the lattice potential lowers the energy

[6] The free-electron energies were calculated using the Bohm-Pines model [D. Pines, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 408], by Heine. Energies of states above the Fermi energy are out of the range of the expression given by Pines and were determined from $E=(k^2/k_F^2)E_F$.

of the highest-energy state (W) in this zone and substantiates the conclusion that the zone is full.

The band calculations indicate that in the second zone the symmetry points near the edges and corners of the free-electron Fermi surface are lowered, while those near the faces are raised. This tends to smooth off the surface and make it more nearly a sphere. This considerably strengthens the free-electron conclusion that there is no contact between the second-zone Fermi surface and the zone boundary.

In the third zone, the energy of the points W, corresponding to the intersections of the arms of the surface, are slightly lowered, tending to fatten up the surface around these intersections. Points at the centers of the arms, on the other hand, are raised near to the Fermi energy, suggesting that the arms are narrowed down and possibly pinched off.

The energy corresponding to W in the fourth zone is raised considerably above the Fermi energy, and these pockets are expected to be emptied.

Thus the Fermi surface suggested by the band calculations is that of a large, fairly smooth surface in the second zone, and six pockets in the third zone which may or may not have connecting arms.

If such pockets in the third zone were the size and shape of the pillows proposed by Gunnersen on the basis of de Haas–van Alphen data, their total area would be small. Thus the total area of the Fermi surface would be approximately equal to that of the surface in the second zone, which is somewhat less than the area determined from anomalous skin-effect data. This led Heine to propose the distortions of the second-zone surface into the zone faces and consequent distortions of the third-zone surface, as well as pockets of holes, in the first zone. In view of the crucial consequences of Gunnersen's proposed surfaces, it seems advisable to re-examine the de Haas–van Alphen data.

IV. DE HAAS-VAN ALPHEN EFFECT

The de Haas–van Alphen effect gives a measure of the maximum or minimum cross-sectional area of a piece of the Fermi surface, where the cross section is taken perpendicular to the magnetic field. Thus measurements with various field directions give a kind of mapping of the Fermi surface. It is only possible to *deduce* the shape of the Fermi surface, however, if the surface is relatively simple and contains a center of symmetry. Since this would not appear to be the case in the third zone, the best that can be done is to propose a surface and adjust it until it fits all of the data. This is, of course, where the theoretical considerations which have been made are of great value.

Two possibilities are suggested in the previous section for the Fermi surface in the third zone; isolated pockets at points W, or a multiply connected surface, such as that shown in Fig. 2, suitably modified. These two possibilities will be considered in order.

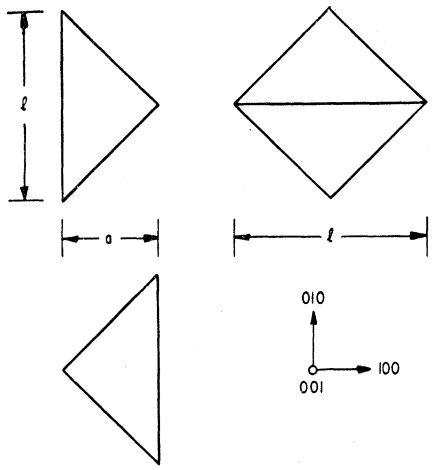

FIG. 3. Tetrahedral pockets having the symmetry of a point W in the reciprocal lattice. The dimensions a and l are adjustable.

1. Isolated Pockets

Since the pockets have the symmetry of a tetrahedron, it is appropriate, as a first approximation, to try a tetrahedron having the appropriate symmetry. Such a surface is shown in Fig. 3, with the two adjustable parameters a and l. Six such figures would appear in the third zone, two of which lie at zone corners for the zone centered on X in Fig. 2. They would be located at the position of the fourth-zone pockets for the zone centered on L. The possibility that these surfaces are joined at the corners is neglected for the moment.

Assuming six such surfaces with appropriate orientations, it is possible for any orientation of field to consider cross sections perpendicular to the field and shift these back and forth along the field to obtain a maximum area. This involves a somewhat tedious geometric calculation, but it has been done for all fields perpendicular to a [100] direction or to a [110] direction. This includes enough directions to give a quite complete description of the effect. From these areas, the period of the de Haas–van Alphen oscillations for all such field directions can be calculated in terms of a and l, using the relation

$$\Delta(1/H)=4\pi^2e/hcA,$$

where $\Delta(1/H)$ is the period and A is the area in wave-number space.

It turns out that the smallest area obtained for a field in [110] direction is $al/(2\sqrt{2})$. If this is associated with the small period oscillation found by Gunnersen, it is found that al equals 0.0214 atomic unit. For comparison, note that the area of a square face of the Brillouin zone is 0.338 atomic unit. The ratio a/l is abritrarily set at 0.425 and the results plotted in Figs. 4 and 5 along with Gunnersen's data. The effect of changing the ratio a/l is simply to shift the dashed portions of the curves in proportions to a/l without changing the solid portions. This, of course, also shifts the cusps where the dashed

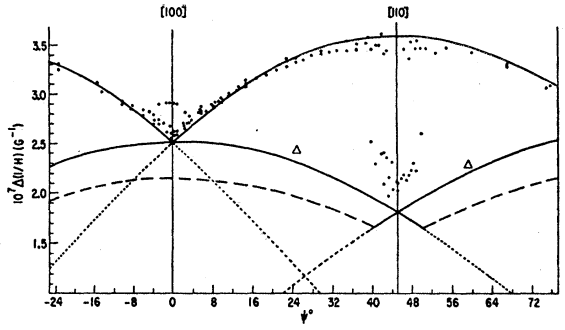

FIG. 4. de Haas-van Alphen periods as measured by Gunnersen,[2] along with theoretical curves. The magnetic field lies in the (001) plane; ψ is the angle the field makes with the [100] direction. The solid and dashed curves combine to give the results deduced from tetrahedra located at symmetry points W. The solid and dotted curves combine to give the results deduced from infinite prisms lying along [110] directions.

portions join the solid ones. All of the curves shown are found to be simple sine curves.

The fit is remarkable and is achieved with only a single adjustable parameter, so long as a/l remains small. Correspondingly, Gunnersen's pillow-shaped pockets (which correspond to symmetrized combinations of the above tetrahedra) may be made arbitrarily large and thin so long as the area looking at them edge-on is fixed. The particular shape he proposed depends directly on his particular extrapolation to low periods, where no data exist (corresponding to the dashed portions of our curves).

One might ask what modifications in the proposed shape would be required to improve the fit to the data at the cusps in the [100] and [110] directions. It is found that in almost all cases the maximum cross-sectional area of a tetrahedron does not include a corner of the tetrahedron. It does, however, include a corner at each cusp and each cross-over point in Figs. 4 and 5 with the exception of that in the [111] direction. In addition, the areas corresponding to the entire solid curves Δ in Fig. 4, include a corner. Rounding off the corners of the tetrahedra would lower the area and increase the period in these regions without affecting the rest of the curves. Thus the required improvement in fit can be obtained by simply rounding off the corners.

It should be noted that the only solid curves of Figs. 4 and 5 which fail to appear in the data are the curves Δ. This could be associated with the fact that these are the only curves for which the maximum cross-sectional areas run into the corners and therefore have a lower density of states (that is, the area changes more rapidly with displacement parallel to the field for these curves). Since the dashed curves are not found experimentally, though they correspond to areas which do not traverse the corners, it is concluded that these portions of the data lie below the threshold of observable periods. This implies that a/l must be less than about 0.35; thus l would be greater than 0.25 atomic unit while a would be less than 0.087 atomic unit.

It is seen that these tetrahedra give a very natural explanation of the de Haas–van Alphen data.

2. Multiply Connected Region

If the Fermi surface in the third zone resembles that shown in Fig. 2, it is reasonable to expect de Haas–van Alphen oscillations associated with the arms. The band calculations have indicated that these arms may be reduced in size at the centers and expanded at the intersections, thus reducing the taper. A reasonable starting model, then, consists of untapered arms of cross-sectional area A_0. If A_0 is associated with the largest observed period in the [110] direction, the solid and dotted curves of Figs. 4 and 5 are obtained. Again all curves are sinusoidal.

Improvement of the agreement with experiment at lower periods can be obtained by introducing a taper in the arms such that the cross-sectional area is smaller at the intersections. The curves beyond the [100] cusp correspond to areas such as that indicated by (a) in Fig. 2. Such contributions would disappear if the arms were distorted slightly so that the maximum cross sections ran into the intersections of the arms. Thus if the arms were bent [the arm (a) being bent in the plane of the paper], such highly inclined orbits would tend to increase monotonically from one end of the arm to the other, and no maximum would occur. This would tend also to eliminate the curves Δ of Fig. 4.

A fit to the data has been obtained without specifying the shape of the cross section of the arms A_0. The data require that the magnitude of the area be about 0.0075 atomic unit, while the free-electron model gives 0.015 atomic unit, thus a modification in the linear dimensions of the arms of only 30% is required.

This model also gives a quite natural explanation of the data but requires some patching to explain the disappearance of the data in some regions of orientation.

3. Comparison of Models

The fact that the multiply connected surface lies very close to that of the free-electron model (modified in the

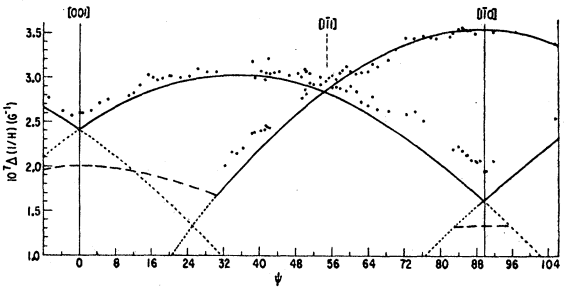

FIG. 5. de Haas-van Alphen periods as measured by Gunnersen,[2] along with theoretical curves. The magnetic field lies in a (110) plane; ψ is measured from the [001] direction. The solid and dashed curves combine to give the results deduced from tetrahedra located at symmetry points W. The solid and dotted curves combine to give the results deduced from infinite prisms lying along [110] directions.

direction indicated by the band calculations) gives strong support for this model. The pocket model would require rather large deviations from the free-electron model; on the other hand, though these also could be in the direction suggested by the band calculations. When the anomalous skin effect is considered in the following section, it will be seen that the pocket model becomes untenable.

V. OTHER INFORMATION

Heine has pointed out that the anomalous skin effect data indicates that the total area of Fermi surface is very close to the free-electron value. In the free-electron model, some 80% of the Fermi surface lies in the second zone, 20% in the third, and less than 1% in the fourth. The major modification of second zone Fermi surface suggested by the band calculations is the suppression of the points near symmetry points W. This tends to reduce the area in the second zone, but not drastically since most of that surface is quite far removed from the zone faces. The disappearance of the pockets in the fourth zone has negligible effect, so the surface in the third zone must certainly hold its own and probably increase in area.

In order for tetrahedral pockets to give the required area, a/l would have to be reduced to about 0.06 so that $l=0.6$ atomic unit. But this extends the Fermi surface deep into regions where the free-electron approximation should be good and where the free-electron energy is much higher than the Fermi energy. Also, Heine's calculations for points near W in the third zone do not indicate such flat energy surfaces. Thus the pocket model must be discarded.

In order to fit the de Haas–van Alphen data with the multiply-connected Fermi surface, it was necessary to reduce the cross-sectional area of the arms below the free-electron value by 50%. This, of course, tends to reduce the area of Fermi surface, but it was pointed out that the shape of the cross section is not determined by the de Haas–van Alphen data. If the cross section is elongated as it is reduced in area, the total Fermi-surface area may be kept the same or increased. Such an elongation only requires shifts in the energies of states which lie close to a symmetry plane, where such corrections to the free-electron model are to be expected.

The proposed model can be seen to be consistent with specific heat measurements at low temperatures. Heine has used these measurements to make a rough calculation of the length of line along which the Fermi surface cuts zone boundaries, which he found to be 92 atomic units. Such a calculation is quite crude, as he has indicated. Furthermore, similar effects might be expected whenever the surface intersects any other symmetry plane (except those including Γ). In the model proposed here the length of intersection with the zone boundary (using the reduced zone scheme as done by Heine) is about twice the total length of the zone edges or 40 atomic units; this being entirely in the third zone. There is an equal length of intersection with symmetry planes in the second zone, corresponding to "edges" of the Fermi surface, which brings the total to 80 atomic units. These numbers are not to be taken very seriously; it is simply noted that a high electronic specific heat is expected to arise from the large amount of Fermi surface which lies close to symmetry planes in wave-number space.

Finally, the low-frequency de Haas–van Alphen oscillations, which Gunnersen observed in aluminum, will be considered. These correspond to a cross-sectional area of about 0.0008 atomic unit and are fairly isotropic. Alloying data indicate that they arise from electrons rather than holes. The only place where these fit conveniently into the proposed structure is at the intersections of the arms. Reasonably isotropic oscillations would result from minimum cross-sectional areas of the arms, since there are arms lying along each of the [110] directions. The cross-sectional area of the arms at the intersections is about 0.0008 according to the free-electron model. Thus in this instance, no modification is required. This is consistent with the high-frequency oscillations which indicated that the arms are tapered toward the ends. It is interesting to find that, though the intersections and the ends of the arms are tiny, the arms are not pinched off.

VI. FINAL PICTURE AND DISCUSSION

The structure of the Fermi surface which is consistent with the data considered and with Heine's band calculations is actually very close to that deduced from the free-electron model and illustrated in Fig. 2. The first zone, as before, is full. The second zone contains a closed surface, filled with holes, which resembles that of Fig. 2, but with the corners rounded off. The fourth zone is empty. The third-zone surface is similar to the free-electron figure, but the arms are to be flattened slightly and their cross-sectional area reduced by 50%. The cross-sectional areas of the arms near the intersections are essentially unchanged. The bowing of the arms suggested by the disappearance of de Haas–van Alphen oscillations associated with the most elongated orbits should probably not be taken seriously; the amount required, in any case, would depend upon the variation of the cross section along the arm. Neglecting this last aspect of the distortion, the third-zone Fermi surface is redrawn in Fig. 6.* The shapes of the arms are somewhat schematic, but their positions are fixed by symmetry and their maximum and minimum areas are fixed experimentally.

Certainly the most striking aspect of these results is how closely they are predicted by the free-electron

* *Note added in proof.*—Further band calculations by the author (to be published) indicate that the arms are probably not flattened as indicated here, but resemble the free-electron shape more closely. Thus it seems preferable to abandon agreement with the somewhat meager anomalous skin effect data.

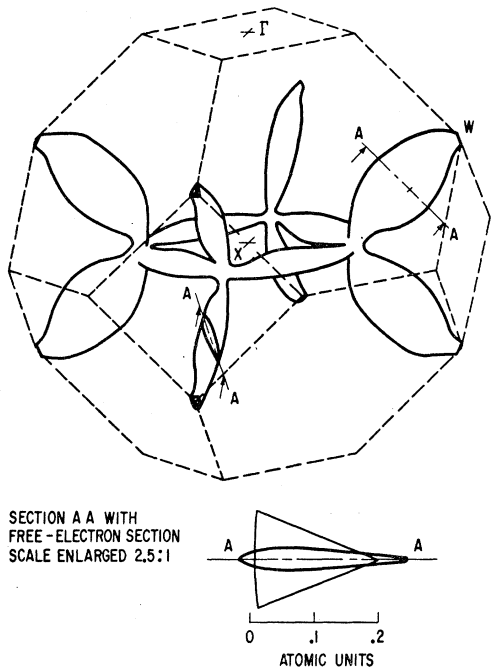

FIG. 6. The proposed Fermi surface in the third Brillouin zone for aluminum. A cross section of one of the arms is given and compared with the free-electron cross section; the detailed shape is somewhat schematic. Some further bowing of the arms is possible and suggested by the data.

model. They are, in fact, even more closely predicted than might be guessed by looking at the results of Heine's calculations. Because of this validity of the free-electron model, the anomalous skin-effect result that the total area of the Fermi surface is equal to the free-electron area need no longer be regarded as accidental.

Another striking point is that a wide variety of models give the same sinusoidal variation of the de Haas–van Alphen period. Thus, only if measurements are made to smaller periods, where deviations occur for some models, can reliable conclusions about the shape of the Fermi surface be made. On the other hand, once a particular surface has been proposed, these measurements are extremely valuable in giving particular dimensions of the surface. The experience with aluminum here would suggest that the free-electron model is sometimes sufficient for proposing a surface without the use of band calculations, though such calculations are certainly of help.

The rather marked resemblance of the proposed Fermi surface for aluminum and that proposed by Gold[7] for lead is also interesting, and, of course, not coincidental. Lead also is face-centered cubic, but has four rather than three conduction electrons per atom. This increases the free-electron Fermi-surface radius by 10%. Thus it tends to shrink the second zone Fermi surface somewhat, fatten up the arms in the third zone, and enlarge the pockets in the fourth. Gold, in fact, finds that the pockets in the fourth zone in lead are not emptied as they presumably are in aluminum.

It should be pointed out that Heine's model, as well as the model proposed here and the alternative model discussed involving pockets at W in the third zone, fits all of the data. The major support for the one proposed here is its extremely close agreement with the free-electrons picture as modified by the results of the band calculations.

One point in support of the alternative model discussed here is its natural explanation of failure of the curves Δ and the dotted curves to appear in the de Haas–van Alphen data. Also, this model, as well as the other two, can accommodate the existence of low-frequency de Haas–van Alphen oscillations, which could be associated with small members connecting the tetrahedra at the corners. These features have not been considered sufficient to outweigh the very large deviations from the expected picture which would be required. It would seem unwarranted to put a great deal of weight upon the failure of certain periods to appear in the de Haas–van Alphen data.

Finally possible ways of definitely deciding between models should be considered. Certainly more extensive de Haas–van Alphen data or band calculations near the points K and U in the third zone would be a help. However, since considerable flexibility is allowed in the detailed shapes for any of these models, these would still leave ambiguity. Knowledge as to whether the de Haas–van Alphen data were coming from electrons or holes would be definitive, but Gunnersen was unable to determine this by alloying; in any case, the interpretation of such an experiment rests on the theory of alloys and is open to some question.

A decision might be made as to whether the de Haas–van Alphen data come from pockets of holes in the first zone or pockets of electrons in the third if it were known whether the second-zone surface intersects the zone boundary. If this surface does not intersect the zone boundary, then the states at W are certainly occupied in the second zone and must also be occupied in the first zone. This would eliminate the possibility of the pockets proposed by Heine. If, on the other hand, the surface does intersect the zone boundary, then the states at W are certainly unoccupied in the second zone and must be also unoccupied in the third and fourth zone. This would eliminate the pocket model discussed here and would require that the arms be pinched off in the model which was proposed. Then in order to explain the low-frequency oscillations, holes would again need to be postulated in the first zone. This leads again to Heine's model, only with the holes in the first zone and the electrons in the third zone changing their roles.[8]

[7] A. V. Gold, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1957), p. 454.

[8] Still another model exists which will explain all of the data. It consists of very flat surfaces at the square zone faces in the second

Ultrasonic attenuation measurements in the presence of a magnetic field should provide the answer to this question. Geometric resonances in these experiments give a measure of maximum and minimum diameters of the Fermi surface[9] and tend to see the grosser aspects of the Fermi surface rather than small pockets. Thus resonances associated with the second-zone surface should be seen. If this surface intersects the zone boundary, then the resonances should become profoundly modified when the field orientation is such that the diameter in question leads to the region of intersection. Such modifications have been seen by Morse and Gavenda[10] in the resonances in copper. If the surface does not intersect the zone, the simple resonance should be seen for all orientations. Very possibly the results of such a measurement would not be simple and some interpretation would be necessary, but they should shed light on the question. Attempts are being made at this laboratory to observe the geometric resonances in aluminum.

zone which contain electrons and which give rise to the high-frequency de Haas–van Alphen oscillations. Remaining portions of surface could be distorted to explain the remaining data. Heine discarded this possibility on the basis that theoretically one would expect these surfaces to be flatter than the de Haas–van Alphen data allow. It was seen in Sec. IV, however, that this is not true, so they cannot be discarded on such grounds. This possibility is not considered here because it requires rather major deviations from what is expected theoretically (deviations comparable with those required by Heine's model). If it were to turn out that the second-zone Fermi surface does intersect the zone face, and that major deviations are, in fact, required this possibility should be reconsidered.

[9] Such effects were originally proposed by A. B. Pippard [Phil. Mag. **2**, 1147 (1957)] and have been observed in copper by R. W. Morse and J. D. Gavenda [Phys. Rev. Letters **2**, 250 (1959)]. They have been treated for a free-electron gas by T. Kjeldaas and T. Holstein [Phys. Rev. Letters **2**, 340 (1959)] and somewhat more extensively by Cohen, Harrison, and Harrison (to be published).

[10] R. W. Morse and J. D. Gavenda, Phys. Rev. Letters **2**, 250 (1959).

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Paramagnetic Resonance Spectra of Chromium and Manganese in the Spinel Structure*

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The paramagnetic resonance spectrum of Cr^{3+} was measured on the single crystal of ruby spinel $MgAl_2O_4$ at the wavelengths of 3 cm, 1.2 cm, and 8.6 mm. The spectrum confirms that Cr^{3+} is at a B site and can be described with an axial spin Hamiltonian $S=\frac{3}{2}$, $2D=0.990\pm0.005$ cm^{-1}, $g_{\parallel}=1.986\pm0.001$, $g_{\perp}=1.989\pm0.002$.

The paramagnetic resonance spectrum of Mn^{2+} was measured on the single crystal of $ZnAl_2O_4$ at 3 cm. The spectrum consists of six nearly isotropic lines with $A=74.9\pm0.5\times10^{-4}$ cm^{-1}, $g=2.000_2\pm0.001$. The cubic or axial splitting was less than 8×10^{-4} cm^{-1}. The spectrum is indicative that Mn^{2+} is located at an A site.

I. INTRODUCTION

THE mineral spinel, $MgAl_2O_4$, and other crystals isomorphous with it, are of the general composition MR_2O_4 in which M and R are divalent and trivalent ions, respectively. The system forms a close-packed structure. The lattice can be considered to consist of two sublattices. One type of cation is surrounded by six oxygen ions arranged approximately at the corners of an octahedron and this is in general referred to as the B site. In the A site the cation is surrounded by four tetrahedrally situated nearest-oxygen neighbors.[1]

Spinel-type compounds containing ions belonging to the first transition group have become recently important. They are nonconducting and antiferromagnetic or ferrimagnetic. The magnetic properties of these materials are determined to a large extent by their relative distribution of the ions M and R at the octahedral or tetrahedral sites.[2–6]

The distribution of the various ions among A and B sites has been investigated by x-ray and neutron diffraction.[7–10] Recently a simple theoretical explanation of the cation distribution has been given by McClure[11] and by Dunitz and Orgel[12] using crystal-field and symmetry considerations.

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