THE TRIVALENT METALS

Family resemblances diminish still further among the trivalent metals, and we consider only the simplest, aluminum.[13]

Aluminum

The Fermi surface of aluminum is very close to the free electron surface for a face-centered cubic monatomic Bravais lattice with three conduction electrons per atom.

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[12] Be and Mg have c/a ratios close to the ideal value, but Zn and Cd have a c/a ratio about 15 percent larger.

[13] Boron is a semiconductor. The crystal structure of gallium (complex orthorhombic) leads to a free electron Fermi surface extending into the ninth zone. Indium has a centered tetragonal lattice that can be regarded as fcc, slightly stretched along one cube axis, and many of its electronic properties are recognizable distortions of those of aluminum. Thallium is the heaviest hcp metal, and therefore the one with strongest spin-orbit coupling. Its Fermi surface appears to resemble the free electron surface of Figure 9.11, in which the splittings on the hexagonal faces are retained (in contrast to beryllium, the lightest hcp metal).

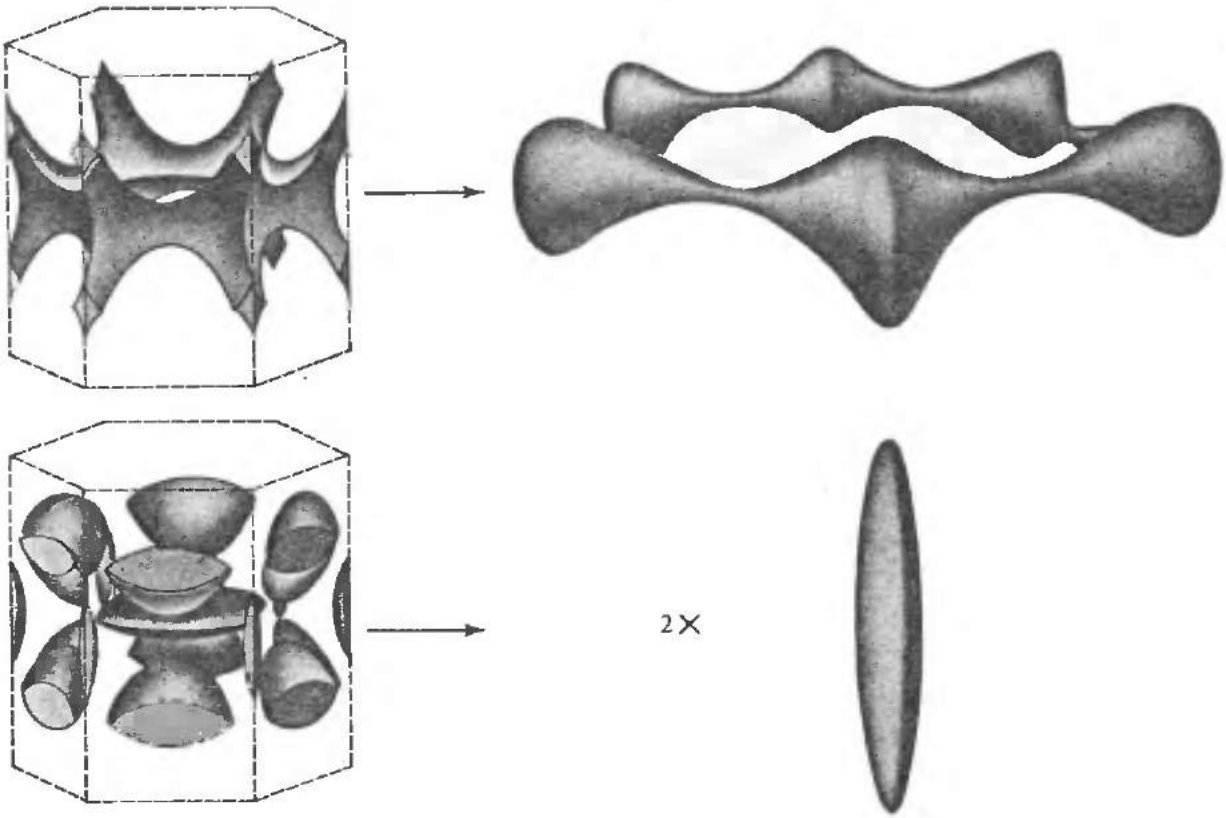

Figure 15.13
The measured Fermi surface of beryllium. (T. L. Loucks and P. H. Cutler, *Phys. Rev.* A **133**, 819 (1964).) The free electron "monster" (upper left) shrinks to a "coronet" (upper right) and all the other free electron pieces (lower left) vanish except for two "cigars" (lower right). The coronet encloses unoccupied levels, and the cigars contain electrons.

pictured in Figure 15.14. One can verify (Problem 4) that the free electron Fermi surface is entirely contained in the second, third, and fourth zones (Figure 15.14c). When displayed in a reduced-zone scheme the second-zone surface (Figure 15.14d) is a closed structure containing unoccupied levels, while the third-zone surface (Figure 15.14e) is a complex structure of narrow tubes. The amount of surface in the fourth zone is very small, enclosing tiny pockets of occupied levels.

The effect of a weak periodic potential is to eliminate the fourth-zone pockets of electrons, and reduce the third-zone surface to a set of disconnected "rings" (Figure 15.15). This is consistent with the de Haas–van Alphen data, which reveal no fourth-zone electron pockets and give the dimensions of the second- and third-zone surfaces quite precisely.

Aluminum provides a striking illustration of the semiclassical theory of Hall coefficients. The high-field Hall coefficient should be $R_H = -1/(n_e - n_h)ec$, where n_e and n_h are the number of levels per unit volume enclosed by the particle-like and hole-like branches of the Fermi surface. Since the first zone of aluminum is completely filled and accommodates two electrons per atom, one of the three valence electrons per atom remains to occupy second- and third-zone levels. Thus

$$n_e^{\mathrm{II}} + n_e^{\mathrm{III}} = \frac{n}{3}, \tag{15.7}$$

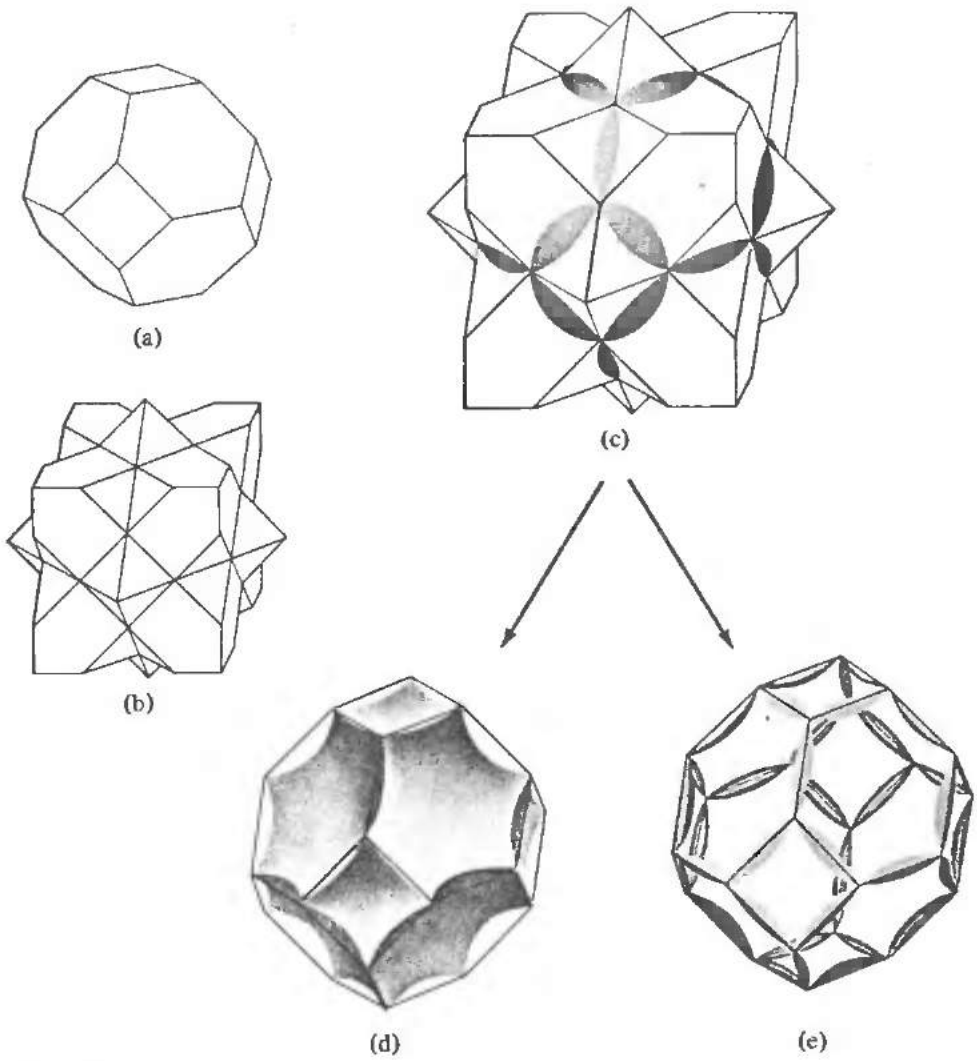

Figure 15.14
(a) First Brillouin zone for an fcc crystal. (b) Second Brillouin zone for an fcc crystal. (c) The free electron sphere for a trivalent monatomic fcc Bravais lattice. It completely encloses the first zone, passing through and beyond the second zone into the third and (at the corners) ever so slightly into the fourth. (d) Portion of the free electron sphere in the second zone when translated back into the first zone. The convex surface encloses holes. (e) Portion of the free electron sphere in the third zone when translated back into the first zone. The surface encloses particles. (The fourth-zone surface translates into microscopic pockets of electrons at all corner points.) (From R. Lück, doctoral dissertation, Technische Hochschule, Stuttgart, 1965.)

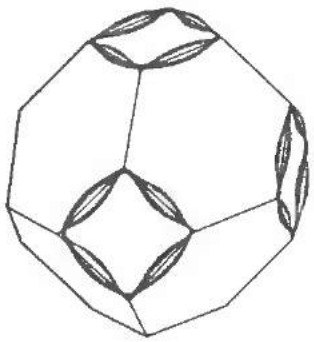

Figure 15.15
The third-zone surface of aluminum, in a reduced-zone scheme. (From N. W. Ashcroft, *Phil. Mag.* 8, 2055 (1963).)

where n is the free electron carrier density appropriate to valence 3. On the other hand, since the total number of levels in any zone is enough to hold two electrons per atom, we also have

$$n_e^{II} + n_h^{II} = 2\left(\frac{n}{3}\right). \tag{15.8}$$

Subtracting (15.8) from (15.7) gives

$$n_e^{III} - n_h^{II} = -\frac{n}{3}. \tag{15.9}$$

Thus the high-field Hall coefficient should have a positive sign and yield an effective density of carriers a third of the free electron value. This is precisely what is observed (see Figure 1.4). From the point of view of the high-field Hall effect aluminum has one hole per atom (the net result of slightly more than one hole per atom in the second zone, and a small fraction of an electron per atom in the third) rather than three electrons.

The reflectivity of aluminum (Figure 15.16a) has a very sharp minimum, which is neatly accounted for as an interband transition in a nearly free electron model.[14] Figure 15.16b shows the energy bands in a nearly free electron calculation plotted along the line ΓX (passing through the center of the square face of the zone). The bands are plotted as a function of $\mathbf{k}$ within the square face in Figure 15.16c. In a nearly free electron model the bands in Figure 15.16c are easily shown (see Eq. (9.27)) to be displaced by a constant amount $2|U|$, independent of $\mathbf{k}$. Because of the position of the Fermi level it is clear from Figure 15.16c that there is a range of values of $\mathbf{k}$ within the square face for which transitions are possible from occupied to unoccupied levels, all of which differ in energy by $2|U|$. This results in a resonant absorption at $\hbar\omega = 2|U|$, and a pronounced dip in the reflectivity.

The value of $|U|$ deduced from the position of the dip in Figure 15.16a is in good agreement with the value deduced from de Haas–van Alphen data.[15]

THE TETRAVALENT METALS

The only tetravalent metals are tin and lead, and we again consider only the simplest, lead.[16]

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[14] The interband thresholds in the alkali metals were explained in terms of an essentially free electron model; i.e., it was unnecessary to take into account any of the distortions in the free electron bands produced by the lattice potential. The example discussed here is at the next level of complexity: the pertinent transition takes place between levels whose wave vectors lie in a Bragg plane, and the splitting between them is therefore entirely due to the first-order perturbation of the periodic potential, in a nearly free electron model.

[15] In the nearly free electron model the cross-sectional areas at a Bragg plane (which are extremal, and therefore directly accessible from the de Haas–van Alphen data) are entirely determined by the matrix element of the periodic potential $|U|$ associated with that plane. See Eq. (9.39).

[16] Carbon is an insulator or a semimetal (see below), depending on crystal structure. Silicon and germanium are semiconductors (Chapter 28). Tin has both a metallic (white tin) and a semiconducting (grey tin) phase. Grey tin has the diamond structure, but white tin is body-centered tetragonal with a two-atom basis. The Fermi surface has been measured and calculated and is again a recognizable distortion of the free electron surface.