

CURRENT PROBLEMS IN RESEARCH

Electrical Resistivity at Low Temperatures

The pressure dependence of the electrical resistance of metals gives some clues about their Fermi surfaces.

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During this century there have been many investigations of the dependence of electrical resistivity of metals on temperature and pressure (1, 2). Broadly speaking, however, most of the temperature measurements have been made at atmospheric pressure, and most of the pressure measurements have been made at temperatures around room temperature. I would like here to describe some experiments which combine the two kinds of measurements and which are designed to find out how resistivity depends on pressure at low temperatures.

Why do we want this information? I shall first try to answer this question by contrasting the changes brought about by variations of temperature with those brought about by variations of pressure. We may think of a solid metal as consisting of a lattice of positive ions agitated by thermal vibrations and of an interpenetrating gas of conduction electrons. For many purposes we may discuss the metal in terms of its energy levels—for example, the energy levels associated with the normal modes of vibration of the lattice or the allowed kinetic energy levels of the conduction electrons. In general, if the volume does not change, these energy levels do not change, and an alteration of the temperature simply alters the *distribution* of the electrons or lattice

vibrations among these levels. But if the volume changes, then the levels themselves also change. Thus, changing the temperature at fixed volume acts as a method (albeit a rather gross one) of exploring how these levels are distributed; altering the volume is a means of changing them. A combination of the two methods therefore enables us both to change the levels and to investigate their properties after the change.

Having emphasized the different roles of temperature and pressure changes, I would now like to show that in certain ways they are closely related. It is a fact of experience that the thermal expansion coefficient of most substances is positive. Consequently, from the thermodynamic identity expressed in the equation:

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \quad (1)$$

it follows that the entropy of such substances falls when they are isothermally compressed. But now it is well-known from thermodynamics that at constant pressure the entropy of a substance also falls when its temperature is lowered. We therefore see that in this respect an increase in pressure is similar to a decrease in temperature. Indeed, so attractive is this idea that G. N. Lewis (3) wished to use it as a basis for extending the third law of thermodynamics. His tentative statement of such an extension was as follows: "At all temperatures the entropy of a pure

crystal is zero at infinite pressure." The proposal was never in fact developed, presumably because the extrapolation to infinite pressure cannot usefully be made; whatever the formal similarity between increasing pressure and decreasing temperature, their actual physical effects are ultimately quite different (4). For more restricted purposes, however, this similarity is quite valid and very useful, as I now hope to show.

The equilibrium lattice properties of many metals can be discussed in terms of a reduced temperature $\tau = T/\theta$, where T is the actual temperature and θ is the characteristic lattice temperature of the metal (for example, the Debye temperature). θ , which ideally is independent of T , is related to the characteristic frequency of the lattice, and if the lattice is compressed its characteristic frequency, and hence θ , increases. Thus the reduced temperature may be decreased either by reducing the actual temperature or by increasing the pressure. This suggests that pressure coefficients and temperature coefficients must be related. Take, as an example, the lattice entropy S , which depends only on T/θ . Thus

$$\begin{aligned} \left(\frac{\partial S}{\partial \tau}\right)_v &= \frac{S'}{\theta} \quad \left(S' \equiv \frac{dS}{d\tau}\right) \\ \left(\frac{\partial S}{\partial V}\right)_T &= -\frac{S'}{\theta} \cdot \frac{T}{V} \cdot \frac{d \ln \theta}{d \ln V} \end{aligned}$$

Therefore

$$\left(\frac{d \ln S}{d \ln V}\right)_T = \gamma \left(\frac{d \ln S}{d \ln T}\right)_v \quad (2)$$

Here I have introduced the parameter γ (which equals $-d \ln \theta / d \ln V$), called the Grüneisen parameter. We thus see that the volume coefficient of entropy is related to the temperature coefficient of entropy by the parameter γ . In fact, a thermodynamic transformation of this equation leads to Grüneisen's law of thermal expansion:

$$\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = \frac{\gamma \beta C_V}{V} \quad (3)$$

where C_V is the specific heat at constant volume, β is the compressibility, and $(1/V)[(\partial V/\partial T)_p]$ is the thermal expansion coefficient. This relationship then affords a means for determining γ (which measures the change of θ with

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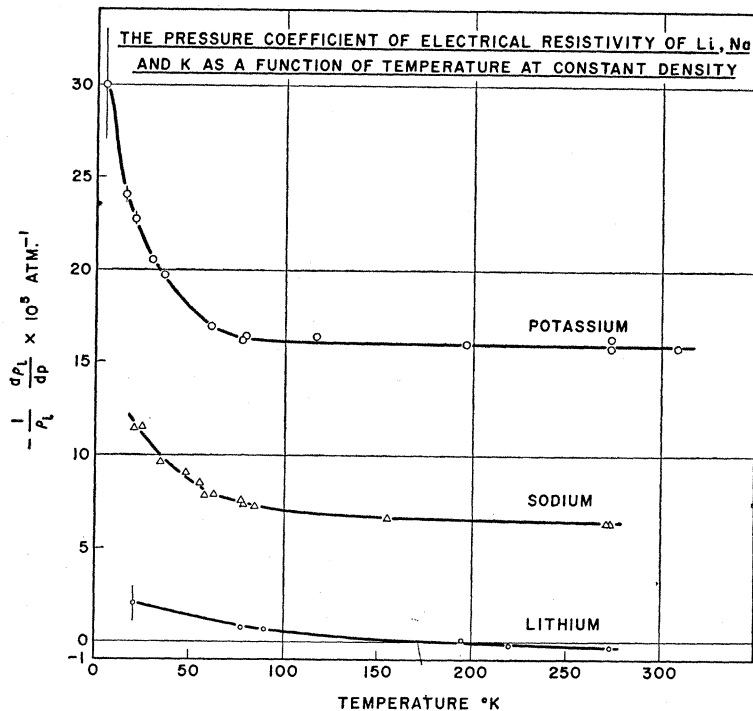
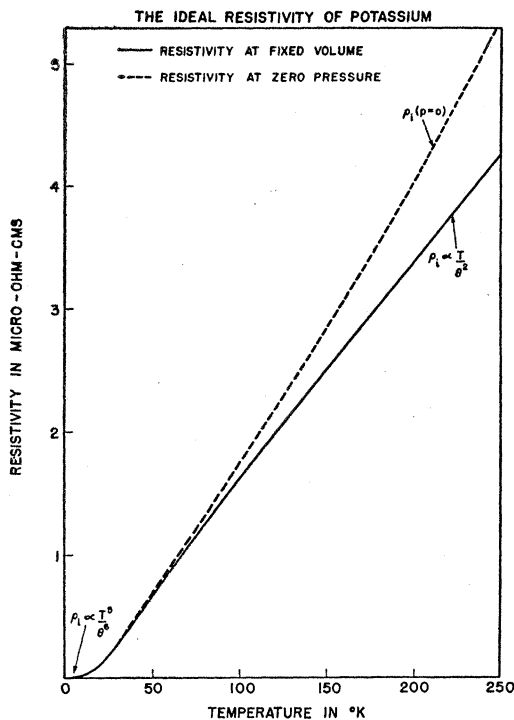


Fig. 1 (left). The electrical resistivity of potassium as a function of temperature. The solid line shows the resistivity at a fixed volume (that at 0°K under zero pressure); this is the quantity which is most convenient for direct comparison with theory. Fig. 2 (right). The pressure coefficient of electrical resistivity of lithium, sodium, and potassium as a function of temperature at constant density (13).

volume) in terms of readily observable quantities.

Considerations of this kind can also be applied to the discussion of the pressure dependence of the electrical resistivity of metals, but first I must describe briefly how this resistivity depends on the temperature (5). It is convenient to distinguish between two sources of electrical resistivity: (i) a temperature-dependent part ρ_i (the ideal resistivity), due to the thermal vibrations of the lattice, which vanishes as the temperature approaches zero, and (ii) a temperature-independent part ρ_o (the residual resistivity), which is due to chemical and physical imperfections in the lattice.

In a perfectly periodic lattice the conduction electrons can move without hindrance; that is to say, the electrical resistance of the metal is then zero. If physical imperfections or chemical impurities are introduced into the lattice, these will then upset the perfect periodicity and cause electrical resistance by scattering the electrons when they are accelerated by an electric field. If, in addition, the lattice temperature is raised so that thermal vibrations of the ions begin, these vibrations also contribute to the electrical resistance. The part of the resistance caused by the lattice vibrations may be thought of as approximately proportional to the mean square amplitude of vibration of the

ions. If the mass of the ions is M , their characteristic vibrational frequency is ω , and their amplitude of vibration is x , then at a high temperature T

$$M\omega^2 x^2 = kT$$

by the classical theorem of the equipartition of energy. Therefore, by introducing a characteristic temperature θ such that $\hbar\omega = k\theta$,

$$x^2 = \frac{\hbar^2}{k} \frac{T}{M\theta^2}$$

and the resistivity due to thermal vibrations, ρ_i , is proportional to $T/M\theta^2$. At the lowest temperatures ρ_i is no longer proportional to the mean square amplitude of the lattice vibrations because at these temperatures the lattice waves are less efficient in scattering electrons; in fact, $\rho_i \propto T^5/\theta^6$ in this temperature region. In quantum language, it is usual to discuss the scattering of electrons by lattice waves in terms of "phonons." A phonon is a quantum of lattice energy analogous to the photon in electromagnetic radiation. The total number of phonons in the lattice varies as T at high temperatures and as T^3 at low temperatures. The temperature dependence of the number of phonons largely determines the temperature dependence of the ideal resistivity. At low temperatures, however, the "momen-

tum" of the phonons falls off and the resistivity, as indicated above, falls off as T^5 —that is, more rapidly than the number of phonons. Figure 1 illustrates the temperature dependence of the electrical resistivity of a typical monovalent metal, potassium.

If the effect of pressure on the ideal electrical resistivity arises solely from the change produced in θ , we should expect that at high temperatures

$$\frac{d \ln \rho_i}{dp} = - \frac{2d \ln \theta}{dp} \quad (4)$$

and at low temperatures

$$\frac{d \ln \rho_i}{dp} = - \frac{6d \ln \theta}{dp} \quad (5)$$

Since θ increases with pressure, we see at once that as far as the lattice contribution is concerned the effect of pressure is to diminish the electrical resistivity (6). Moreover we see that the pressure coefficient of ideal resistivity at low temperatures should be three times that at high temperatures. Figure 2 shows how the pressure coefficient of resistivity of lithium, sodium, potassium, and copper varies with temperature. The temperature dependence is of the general form to be expected. Note, however, that in lithium the pressure coefficient at high temperatures is anomalous, being positive.

In more general terms, there are theoretical grounds for believing that

$$\rho_i = \frac{K}{T} f(T/\theta_R)$$

where K measures the interaction between the conduction electrons and the lattice vibrations and θ_R is a temperature characteristic of the resistive properties of the lattice (1). (The results I have already quoted are simply special cases of this, indicating that at high temperatures $f(T/\theta_R)$ approaches T^2/θ_R^2 , and at low temperatures, T^6/θ_R^6 .) This relationship means that the product $\rho_i T$ is a function of a reduced temperature τ equal to T/θ_R , and we may expect, by analogy with the behavior of the thermodynamic properties of the lattice, to relate the pressure coefficient of electrical resistivity at a given temperature with the temperature coefficient of electrical resistivity at that temperature. In theoretical considerations it is more logical to work in terms of volume coefficients; in these terms the relationship is as follows (6):

$$\frac{d \ln \rho_i}{d \ln V} = \frac{d \ln K}{d \ln V} - \frac{d \ln \theta_R}{d \ln V} \left(1 + \frac{d \ln \rho_i}{d \ln T} \right) \quad (6)$$

The term $d \ln K / d \ln V$, which depends on the properties of the conduction electrons and on the static lattice, should be effectively independent of temperature at normal and low temperatures, as is also the term $d \ln \theta_R / d \ln V$. This relationship, therefore, tells us that the volume coefficient and the temperature coefficient of the ideal resistivity are linearly related; this in turn means that $d \ln \rho_i / d \ln V$ will change with temperature only at temperatures at which $d \ln \rho_i / d \ln T$ itself changes. This conclusion explains why we must make measurements at low temperatures if we wish to find any temperature variation of the pressure dependence of electrical resistivity, since a glance at Fig. 1 shows that only at low temperatures does the temperature coefficient of resistance change significantly.

Equation 6 means that if we measure the pressure and temperature coefficients over a suitable temperature range we can determine $d \ln \theta_R / d \ln V$ and $d \ln K / d \ln V$ separately, in this way distinguishing the lattice contribution to the pressure coefficient from the contribution of the electron properties. Before comparing the experimental results with these theoretical predictions I should like to say something about the experimental methods.

Hydrostatic Pressure at Low Temperatures

The application of hydrostatic pressure at low temperatures (7) presents a problem because all substances become solid under pressure at these temperatures; at pressures above about 30 atmospheres there are no true fluids at the lowest temperatures. The substance which retains its fluid properties at a given pressure to the lowest temperature is helium (the He^3 isotope is very slightly, though for our purposes not significantly, better than the He^4 isotope in this respect). For that reason, and also because solid helium can be used to produce an effectively hydrostatic pressure, we have used this substance as our pressure transmitting medium (8, 9). Other solids can of course be used for this purpose [Hatton (10) used solid hydrogen], and for some purposes the solid to be studied can act as its own pressure medium; that is to say, the metal is directly compressed in a cylinder by a piston without any intervening substance (see 11).

In Fig. 3 is shown part of the melting curve of He^4 (12). Points to the right of and below this curve correspond to the fluid phase, and as long as we are using this phase the application of pressure is quite straightforward. To understand how pressures and temperatures corresponding to the solid phase are

produced, we must know something of the equation of state of the solid. This information is also indicated in Fig. 3, in which it is shown how the pressure in the solid varies with temperature at various fixed volumes (12). It may be seen that at constant volume the pressure in the solid is not very dependent on the temperature; this is because in solid helium most of the pressure arises from the vigorous zero-point motion of the helium atoms and is thus independent of the temperature (incidentally, it is this strong zero-point motion which makes liquid helium the stable phase at 0°K at normal pressures).

Our technique of applying high pressures in the solid state can be described as a constant-volume method. The pressure is first applied at such a temperature that the helium is still just fluid—that is, at a temperature close to, but to the right of, the melting curve shown in Fig. 3. The high-pressure bomb is then closed off so that the helium is kept effectively at constant volume, and it is then cooled to the required low temperature. In this process, in which the helium becomes solid, about one-quarter of the applied pressure is lost. However, the pressure existing in the bomb in the final state can be deduced from a knowledge of the initial density (which is also of course the final density) and the final temperature. Our measurements have

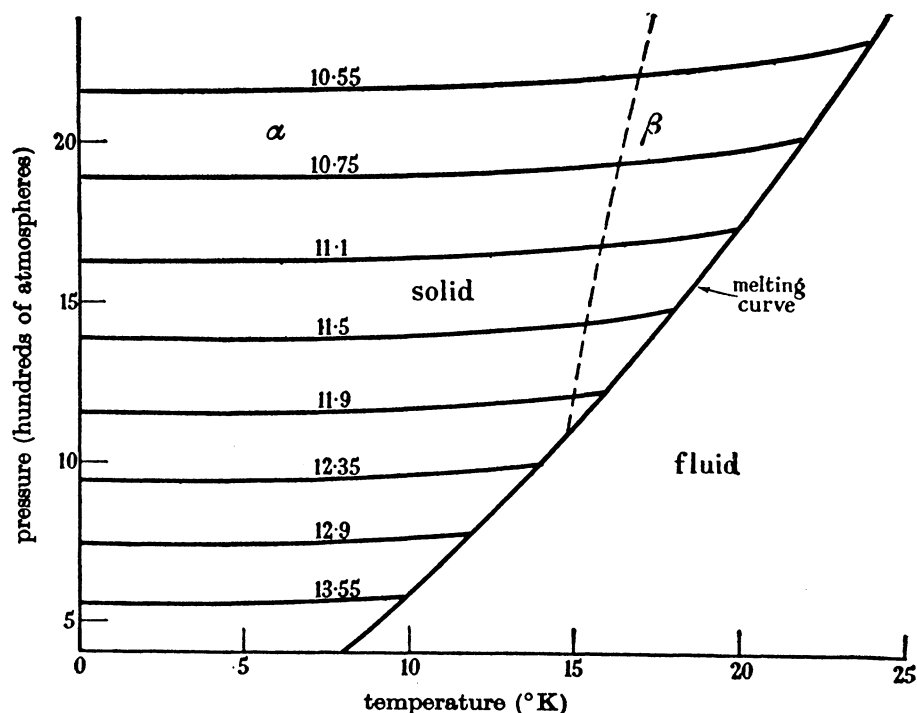


Fig. 3. Part of the melting curve of He^4 and the lines of constant volume in the solid. The figures give the corresponding molar volume in cubic centimeters. [After Dugdale and Simon (12)]

shown that this technique of applying pressure by means of solid helium does in fact produce a very close approximation to hydrostatic pressure (9).

Our measurements so far have been confined to the monovalent metals—in particular to copper and the alkali metals, except cesium (9, 13). Alkali-metal specimens used in the measurements of resistance at low temperatures have usually been enclosed in glass capillaries because the metals are chemically very reactive and mechanically very soft. For the measurement of pressure effects such specimens are not satisfactory, and we have used extruded bare wires mounted loosely on insulated formers; a photograph of such a speci-

men is shown in Fig. 4. The photograph shows the specimen mounted in position and ready to be enclosed by the high-pressure bomb, which is made of beryllium copper; the high-pressure seal is made by means of a steel lens ring.

Expectations and Findings

As already mentioned, we expect a linear relation between the logarithmic volume coefficient of ideal resistivity and the logarithmic temperature coefficient of ideal resistivity. Figure 5 shows that such a linear relationship does in fact exist (9, 13) for those

metals (lithium, sodium, potassium, and copper) for which the necessary data are available. In these graphs I am referring to the high-temperature modifications of sodium and lithium—that is to say, the body-centered cubic phases. At low temperatures both these metals partially transform to a close-packed phase; in lithium this transformation affects the pressure coefficient of resistivity so greatly that no reliable results have been obtained below about 75°K on this metal.

From the curves in Fig. 5 we can deduce for each metal the two quantities $d \ln \theta_R / d \ln V$ and $d \ln K / d \ln V$. These values are given in Table 1. For comparison, the Grüneisen parameter γ [or $-d \ln \theta_D / d \ln V$ (14)], which, as I showed earlier, can be evaluated from readily available thermodynamic data, is also included; it is evident that the change of θ_R with volume is quite similar to that of θ_D , as one might expect. Although accurate pressure measurements over a sufficiently wide temperature range have so far been made on only the four metals mentioned, the quantity $d \ln K / d \ln V$, which can be derived from high-temperature measurements only, by assuming that $-d \ln \theta_R / d \ln V$ equals γ (the Grüneisen parameter), has been derived for all the monovalent metals. The results are presented in Table 2 (columns 2, 3, and 4); the data for cesium are rather uncertain.

In order to understand why some of these values of $d \ln K / d \ln V$ are positive and why some are negative, it is necessary to digress and to explain something more of the behavior of the conduction electrons (5). Although it often gives a good approximation to imagine the conduction electrons moving through the ionic lattice as though they were free electrons (apart from the scattering processes which I have mentioned), it is in general necessary to take account of the fact that their motion is in fact modified by the periodic potential inside the static crystal. This can often be done by assigning an "effective" mass to the electron which differs from its true mass but takes account of interaction with the lattice potential. Another important feature of the electron motion arises from the fact that electrons obey the Pauli exclusion principle. At the absolute zero of temperature the electrons take up a configuration of minimum energy which, classically, would be one of zero kinetic energy—that is, with all the electrons at rest. Because of the

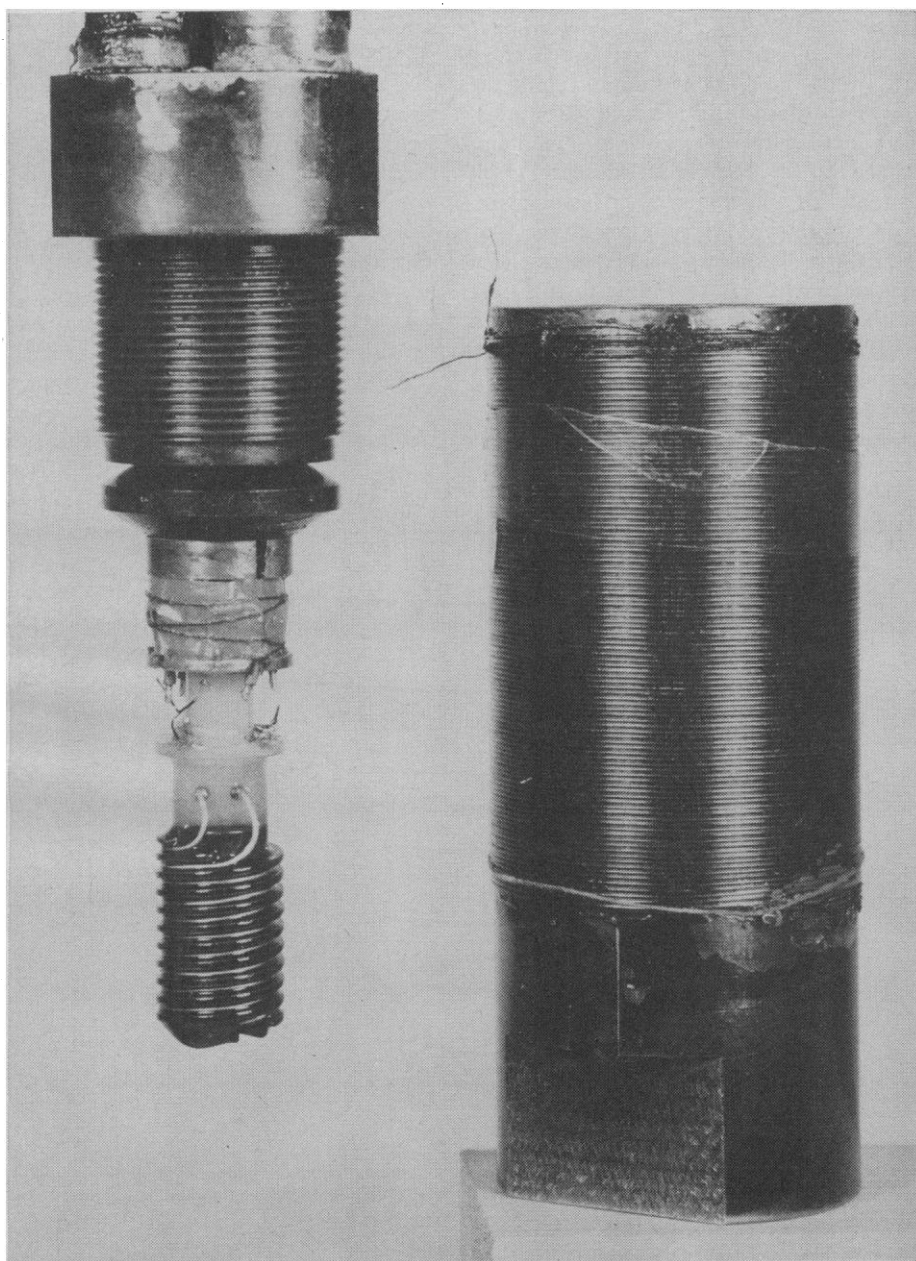


Fig. 4. A photograph of a typical alkali metal specimen wound on an insulated former. At right is the beryllium-copper bomb which encloses the specimen.

Table 1. Data on resistivity for lithium, sodium, potassium, and copper.

Metal	$-\frac{d \ln \theta_R}{d \ln V}$	Grüneisen parameter γ	$\frac{d \ln K}{d \ln V}$
Li	1.0	0.9	-3
Na	1.3	1.3	+1.8
K	1.4	1.3	+2.9
Cu	2.3	2.0	-1.8

exclusion principle, however, this is not possible, since each state of kinetic energy can be occupied by only two electrons (of opposite spin). Consequently the electrons "fill up" all the lowest kinetic-energy levels available to them until all the electrons are accommodated. Therefore, at the absolute zero of temperature all the lower kinetic-energy levels are filled up to a certain value E_0 , and above this the levels are all empty. The value of E_0 in a typical monovalent metal, if expressed as an equivalent temperature, is around 50,000°K—in other words, this is the temperature to which a classical electron gas would have to be heated to have a similar kinetic energy. It is evident from this that even at room temperature the additional kinetic energy of the electrons that is due to thermal motion is tiny as compared to their zero-point energy, so that for some purposes we can treat the electrons as being effectively at 0°K. The maximum energy E_0 of the electrons at 0°K (or more generally, their chemical potential) is referred to as the Fermi energy of the electrons, E_F , and this quantity varies with volume; in the simplest approximation of quasi-free electrons, $E_0 \propto V^{-2/3}$.

How are the electron velocities distributed over the various directions in space? In an ideal gas the distribution would be isotropic—that is, the average velocity would be the same in all directions. In discussing electrons in metals it is more convenient to work, not directly with the electron velocity or momentum, but (since the properties of electrons are governed by wave mechanics) with the electron's wave number k , which in the case of completely free electrons would be related to the momentum by the De Broglie relationship $hk = p$. The energy of such electrons (of mass m) is given by $E = h^2 k^2 / 2m$, so if we plot the components of k , k_x , k_y , and k_z along cartesian axes (k -space), the surfaces of constant energy would therefore be spheres (corresponding to an isotropic distribution of velocities). The surface

corresponding to the Fermi energy of the electrons is called the Fermi surface. If the electrons are not free but are influenced by the potential field of the lattice, then the Fermi surface will no longer be a sphere but will be more or less distorted, depending on the influence of the lattice potential; the symmetry of the Fermi surface taken as a whole is closely related to that of the crystal. The importance of the Fermi surface arises from the fact that only electrons close to the Fermi surface have unoccupied electronic levels in their neighborhood—in other words, these are the only electrons which can be thermally excited (at normal temperatures) or scattered by lattice waves or impurities.

The wavelike properties of electrons imply that, like x-rays, electrons in a crystal may suffer Bragg reflections. Thus, if an electron propagating in a certain direction in the crystal has just the right wavelength to satisfy the Bragg condition, it will be reflected by the appropriate lattice planes. Suppose that we choose some particular direction in the crystal and then find the minimum value of k which an electron propagating in that direction must have to satisfy the Bragg relation; suppose, further, that we do this for all possible directions. Then if we draw these k -vectors from the origin in k -space, it turns out that their ends lie on a polyhedron about the origin, this polyhedron having the symmetry of the lattice. This polyhedron is referred to as the first Brillouin zone of that lattice, and it is relevant to any kind of wave that can propagate through the lattice (in particular lattice waves and electrons). If for the electrons we draw surfaces of constant energy in k -space, all those surfaces lying within the Brillouin zone are continuous, whereas those surfaces which intersect the zone boundary will, in general, suffer a dis-

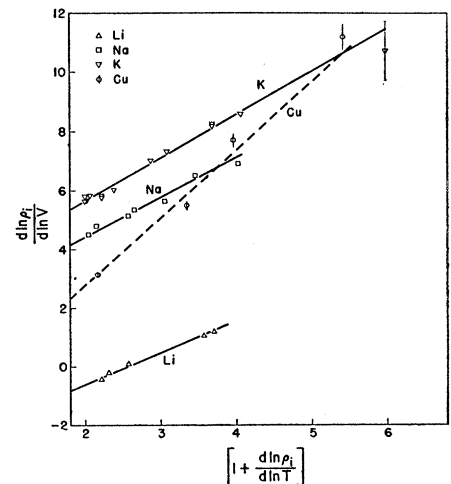


Fig. 5. The logarithmic volume coefficient of the ideal resistivity of lithium, sodium, potassium, and copper, shown as a function of the logarithmic temperature coefficient.

continuity; there is in fact a forbidden energy region at the zone boundaries such that electrons with energies lying within this range cannot propagate in the lattice.

The volume of the zone in k -space is such that if the crystal has N atoms per unit volume (15), then the zone can accommodate N electrons of a given spin, uniformly distributed throughout the zone. Since electrons can exist in two independent spin states of the same wave vector, the zone can contain just $2N$ electron states.

This latter conclusion has the following important consequence. In a monovalent metal, which has just one conduction electron per atom, the Fermi surface which encloses all the electron states in k -space must therefore comprise a volume equal to half that of the Brillouin zone. This in turn means that if in cubic monovalent metals the Fermi surface is nearly spherical it can be entirely contained within the first zone without anywhere touching it. This

Table 2. Data on resistivity for the monovalent metals.

Metal	$\frac{d \ln \rho_i}{d \ln V}$ at 0°C	2γ	$\frac{d \ln K}{d \ln V}$	$\left(\frac{d \ln \rho}{d \ln E}\right)_V \equiv x$	$\frac{d \ln K}{d \ln V} / x$	θ_0	θ_R^*	θ_R / θ_0	$\frac{M \theta_0^2 V^2 \rho_i}{T}$
Li	-0.49	1.8	-2.3	6.7	-0.3	369†	385†	1.04	7.2
Na	4.6	2.6	2.0	-2.7	-0.7	152‡	205‡	1.35	2.0
K	5.7	2.6	3.1	-3.8	-0.8	90	116	1.29	2.0
Rb	3.7	3.0	0.7	-2.3	-0.3	55	58	1.06	3.1
Cs	(4)	3.2		-0.2		40	45	1.13	4.4
Cu	3.0	4.0	-1.0	+1.6	-0.6	344	333	0.97	8.4
Ag	3.9	4.8	-0.9	+1.1	-0.8	225	223	0.99	6.3
Au	5.5	6.2	-0.7	+1.5	-0.5	165	175	1.06	13.5

* The value for cesium was taken from MacDonald (1). The other values of θ_R were taken from (13) and (9) for the alkali metals and from (27) for the noble metals. † Two-phase mixture. ‡ Estimated value for the body-centered cubic phase.

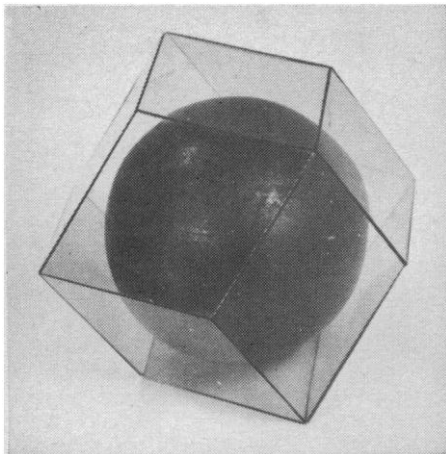


Fig. 6. A model of the first Brillouin zone of a body-centered cubic lattice. The sphere occupies half the volume of the zone.

situation is illustrated in Fig. 6, which shows a model of the first Brillouin zone of a body-centered cubic lattice containing a sphere whose volume is just half that of the zone. Figure 7 shows a two-dimensional square lattice, its two-dimensional Brillouin zone and the Fermi "circle" having an area of just half that of the zone. In Fig. 7 (a, b, c, and d) I have shown, purely schematically, the progressive distortion of the Fermi surface; in d this surface is in marked contact with the Brillouin zone. In general, distortion of the Fermi surface causes those regions which are nearest the zone boundaries to become even closer.

A great deal is now known about the Fermi surfaces of the noble metals from

a variety of techniques which give direct information about the shape and other features of the Fermi surface (16). These methods agree in showing that the Fermi surfaces in copper, silver, and gold all touch the zone boundary. About the alkali metals we have as yet no direct evidence, but indirect evidence suggests that the Fermi surfaces of sodium and potassium are nearly spherical, that the Fermi surface of rubidium is somewhat distorted, and that the Fermi surfaces of lithium and cesium are much more distorted, perhaps touching the Brillouin zone boundary (17, 18). The effects of such distortion on electrical resistivity are discussed later.

When an electric field is applied to a metal the conduction electrons are accelerated and the whole Fermi surface begins to move in the direction of the field (see Fig. 8). The electrons, however, are prevented from continuous acceleration in the field by collisions with phonons (we are considering only the ideal resistivity), and the Fermi-surface movement is almost vanishingly small. The effect of the distortion of the Fermi surface on the scattering of electrons by phonons is a difficult theoretical problem, and detailed studies have only recently been made (19). One of the most important effects arises from a type of scattering process called an "Umklapp" process, which gives rise to large angle scattering of the electrons.

First consider a typical *normal* scattering process in which an electron of

wave vector k is scattered by a phonon of wave vector q into a new state of wave vector k' ; k , k' , and q are related by the vector condition that $k - k' = q$. Moreover, the phonon energy at all normal and low temperatures is very small compared with the Fermi energy of the electrons. Since only those electrons near the Fermi level have neighboring unoccupied states into which they may be scattered, the scattered electron must both start and end effectively at the Fermi surface. Figure 9 shows the geometry of a normal scattering process. As mentioned earlier, the Brillouin zone governs the behavior of all kinds of waves that can propagate through the metal, including lattice waves; the biggest wave vector that a phonon can have is one which reaches from the center of the zone to the zone boundary. This therefore limits the angle through which an electron may be scattered in a normal process, even at the highest temperatures. At low temperatures, where only low-energy phonons (having therefore small wave vectors) are excited, the angle of scattering is even further limited in such processes.

An Umklapp process may be interpreted as one in which the electron is scattered by a phonon and also undergoes a Bragg reflection. In vector terms, the well-known Bragg condition is represented by the equation $k' - k = R$, where R is a reciprocal lattice vector. In Fig. 7 the vectors R' and R'' are two reciprocal lattice vectors for the simple square lattice. Thus, in an Umklapp process the vector condition

$$k' - k = q \quad (7)$$

is replaced by

$$k' - k = q + R \quad (8)$$

where R is a reciprocal lattice vector. Such a process is illustrated in Fig. 10. Its importance lies in the fact that, because the large vector R enters into the process, it makes possible scattering at wider angles than can occur in a normal process. This can also be seen by a geometrical construction. Equation 8 may be rewritten as

$$k + R = k' - q$$

and we begin by representing graphically all the possible vectors $k + R$. Since the k vectors of all electrons which can be scattered must lie on the Fermi surface, the vectors $k + R'$, for example, must lie on the same surface displaced by the vector R' ; the same is

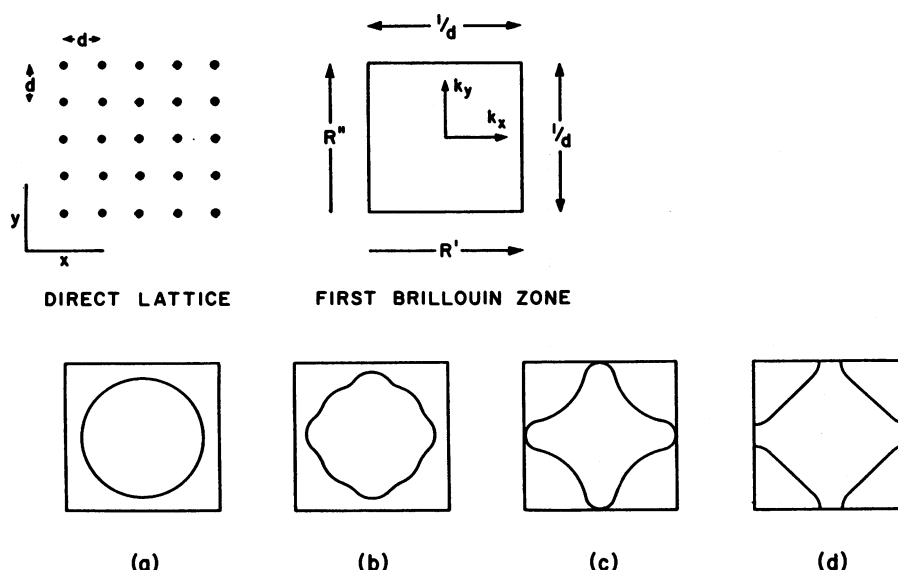


Fig. 7. A two-dimensional square lattice and the corresponding first Brillouin zone. (a) The Fermi "circle" corresponding to one electron per atom; (b), (c), and (d), progressive distortions of the Fermi surface (schematic).

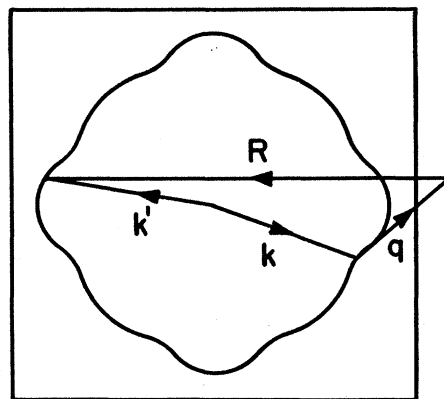
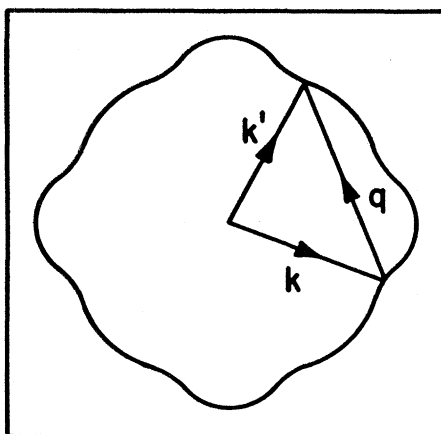
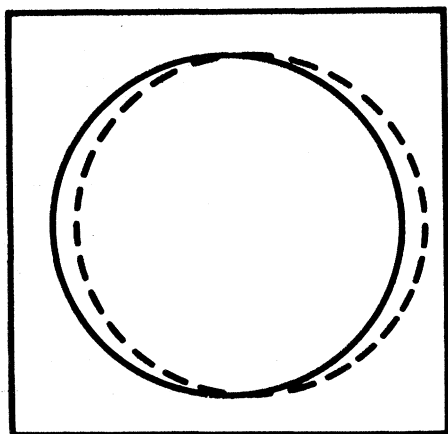


Fig. 8 (left). Displacement of the Fermi surface under the influence of an electrical field. Fig. 9 (middle). A "normal" scattering process. Fig. 10 (right). An Umklapp process.

true for the other reciprocal lattice vectors. Thus, the possible $k + R$ vectors lie on a set of surfaces consisting of the original Fermi surface suitably displaced, as in Fig. 11. In order to satisfy the requirement of conservation of energy, all the vectors k' of the electrons after scattering must lie on the original Fermi surface; so, to satisfy Eq. 8, we must look for vectors $-q$ which go from one of the repeated Fermi surfaces back to the original Fermi surface. Such phonon vectors, illustrated in Fig. 11, give rise to Umklapp processes.

If the Fermi surface does not touch the zone boundary, then q must exceed a certain minimum value or else Umklapp processes are impossible. This minimum value is equal to the distance of closest approach of two adjacent Fermi surfaces—for example, the vector CD in Fig. 11. An Umklapp process with this minimum vector scatters the electron through the maximum angle of 180° (Fig. 12). q vectors which are larger than the minimum usually produce rather smaller scattering angles; nevertheless all Umklapp processes in a monovalent metal cause comparatively large angle scattering.

The existence of a minimum value of q for Umklapp processes means that at low temperatures the number of such processes must begin to fall off because the number of phonons with a large enough wave vector begins to fall off. Thus, the shape of the Fermi surface can influence the temperature dependence of electrical resistivity at low temperatures. It also affects the magnitude of the resistivity, since at all temperatures the more closely the Fermi surface approaches the zone boundary the

greater is the number of phonons that can take part in Umklapp processes. Since, as has been emphasized, these are wide-angle scattering processes, this implies that the nearer the Fermi surface is to the zone boundary the higher is the electrical resistivity, other things being equal. (By "other things" I mean in particular the number of phonons available for scattering the electrons;

this point is discussed in more detail in the next paragraph.) Distortion of the Fermi surface changes not only the number of possible Umklapp processes but also, for example, the velocity of the electrons at the Fermi level, and this too can alter the resistivity. In general, however, it seems that, if the resistivities of the monovalent metals are compared under conditions such as

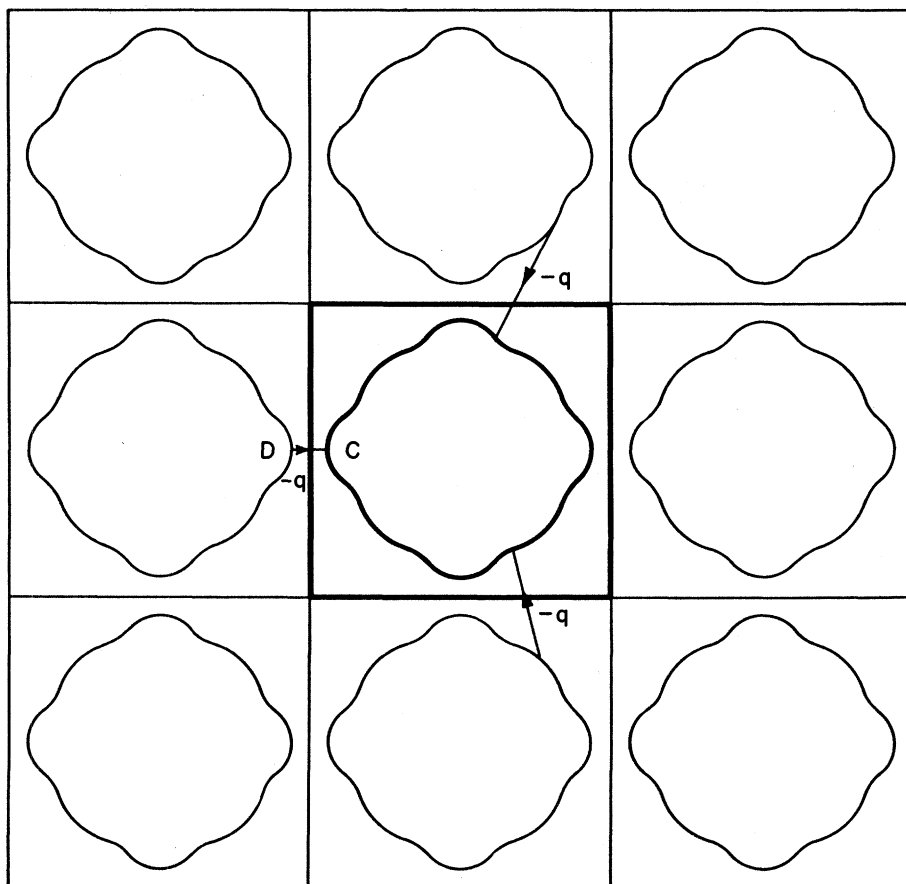


Fig. 11. Repeated zone scheme to illustrate the possible wave vectors which can give rise to Umklapp processes.

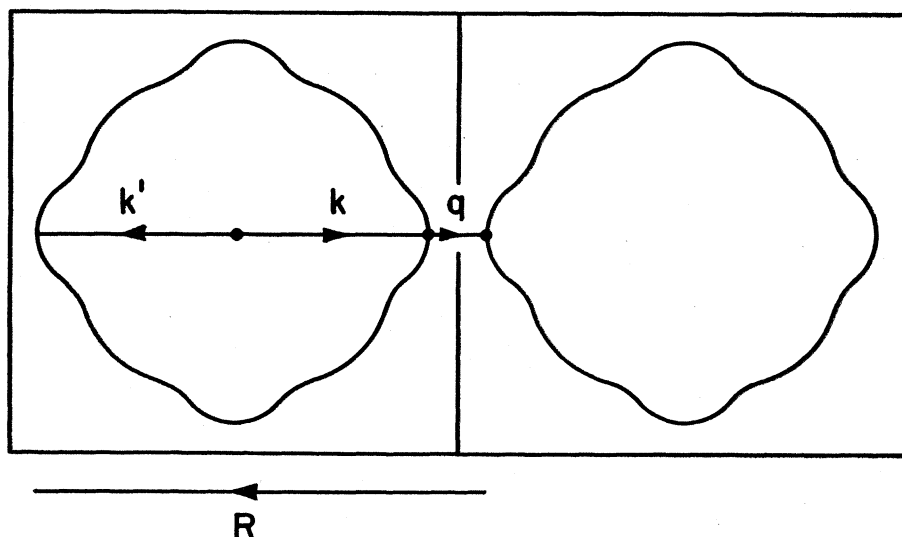


Fig. 12. Electron scattering through 180° by a phonon having the minimum wave number which can cause an Umklapp process.

to eliminate the effects of their different lattice properties, the more distorted the Fermi surface the higher the resistivity. With these ideas in mind let us now look at the magnitude of the resistivities of the monovalent metals.

In comparing the resistivity of different metals it is important to compare not the resistance ρ of a cube of side 1 centimeter but rather that of a cube containing, for example, 1 gram atom of material—that is, the atomic resistivity $\rho/V^{1/3}$ where V is the gram-atomic volume. Moreover, in order to bring out the dependence of the resistivity on the properties of the electrons (for example, the shape of the Fermi surface), the resistivities must be compared at temperatures at which the lattices are in similar states—that is, at temperatures at which the amplitude of the lattice vibrations is some certain fraction of the interatomic distance. This means that, in the high-temperature “classical” region, one should compare not the atomic resistivities but rather the “reduced” atomic resistivities $\rho(M\theta^2V^{1/3}/T)$. (The derivation of this result is rather similar to that of the Lindemann melting formula; here M is the mass of the ions and θ , the characteristic lattice temperature.) The actual temperature T is immaterial since at high temperatures ρ/T tends to reach a constant value and it is this limiting value, at constant density, which we take. A comparison of the reduced resistivities is made in Table 2 (column 10), in which θ_0 is taken from specific heat measurements (20). These Debye θ_0 values, which can be taken as a measure of the temperature dependence

of the phonons, are now quite well established, although in sodium and lithium the low-temperature crystallographic transformations introduce some uncertainty. I should also point out that, since the noble metals have a face-centered cubic structure while the alkali metals have a body-centered cubic structure (except for sodium and lithium at low temperatures), the comparison between the two sets of metals cannot be taken too literally, although the general features should be correct.

It may be seen that of all the monovalent metals, potassium and sodium are outstandingly good conductors, rubidium and cesium are successively poorer, and lithium and the noble metals are worse still. Among the noble metals, silver has the lowest reduced resistivity. This classification corresponds broadly with what is at present known about the Fermi surfaces of the monovalent metals.

Having considered the magnitudes let us now consider the temperature dependence of the resistivity. This is largely governed by the temperature dependence of the number of phonons in the lattice—that is, by the Debye θ_0 . But as we saw in discussing Umklapp processes, the low-temperature resistivity does not depend only on the behavior of the phonons; it also depends on the Fermi surface. If the metal has a distorted Fermi surface, the electrical resistivity tends to remain higher (because of the increased number of Umklapp processes) at low temperatures than that of a metal with a spherical Fermi surface at the same reduced temperature (that is, with the

same number of phonons excited). Roughly speaking, θ_R (which is a measure of the temperature dependence of ρ_i) is proportional to the lowest temperature at which ρ_i behaves classically—that is, the temperature at which ρ_i departs from linearity with T . This temperature should therefore be lower for metals in which Umklapp processes can persist to lower temperatures. Thus, we should expect θ_R/θ_0 to vary with the degree of distortion of the Fermi surface; for a metal with a distorted Fermi surface the ratio should be lower than for a metal with an undistorted Fermi surface. The values of this ratio are given in Table 2 (column 9), and they show roughly the sort of variation we should expect: sodium and potassium have exceptionally large values for the ratio, the other metals have lower values. Interestingly enough, these lower values are all close to unity; why the values of θ_0 and θ_R should be about equal for these metals is not, I think, altogether understood.

These comparisons suggest that the pressure coefficients might likewise be understood, at least qualitatively, in terms of distortion of the Fermi surface. Table 2 (column 4) shows that the values of $d \ln K/d \ln V$, which measure the change of interaction constant with volume, do fit into the pattern. For example, all the noble metals have negative values and so does lithium. These are the monovalent metals with the most distorted Fermi surfaces. Sodium and potassium, the two metals with nearly spherical Fermi surfaces, have values of $d \ln K/d \ln V$ which are decidedly positive; rubidium has an intermediate value. For cesium the data needed here are not reliable, but as we shall see below, cesium too fits into the general picture.

Although there is a clear correlation between the pressure coefficients of resistivity and distortion of the Fermi surface, we still have to understand why in a metal with a spherical Fermi surface $d \ln K/d \ln V$ is positive whereas in a metal whose Fermi surface touches the zone boundary it is negative. This is a theoretical problem which has not yet been fully solved. Nevertheless, let us consider first the example of a spherical Fermi surface which, for simplicity, we shall assume does not distort under pressure (21). A positive value for $d \ln K/d \ln V$ means that a decrease in volume causes the electrons to interact less with the lattice waves. Decreasing the volume increases the Fermi

energy of the electrons, and we may interpret this result as meaning that as the electron energy is increased the electrons are less scattered by the lattice waves. This conforms with the classical idea that a body with greater kinetic energy is scattered less by a given obstacle than one with lower energy.

We have here assumed that on compression of the lattice the Fermi-surface distortion remains unchanged. While this may be true of sodium for small volume changes, theoretical calculations show that this is not generally true (18). In general, in all the monovalent metals, increasing the pressure on the metal increases the distortion of the Fermi surface; if the surface is already touching the zone boundary, pressure will increase the area of contact. Such an increase in the distortion of the Fermi surface under pressure, with the consequent enhancement of Umklapp processes, tends to increase the resistivity. This was originally proposed as an explanation of the anomalous positive pressure coefficient of resistance in lithium (17), and it seems probable that the same basic mechanism occurs in all the monovalent metals.

There are thus two opposing tendencies when a metal is compressed—on the one hand an increasing distortion of the Fermi surface, which increases the interaction constant K , and on the other hand an increase in the Fermi energy, which, as suggested above, tends to decrease K . The trend of the values for $d \ln K / d \ln V$ leads us to suppose that the more distorted the Fermi surface is, the more prominent the first effect becomes. This is perhaps plausible, but without a careful theoretical analysis it is not possible to say more. Unfortunately such an analysis has not yet been made. Nonetheless, quite empirically, it does seem that in the monovalent metals, negative values of $d \ln K / d \ln V$ are associated with a Fermi surface already in contact with the zone boundary, and the large positive values, with a nearly spherical Fermi surface. We might therefore guess that if this parameter is about zero this indicates that the Fermi surface is just about to touch the zone boundary.

Bridgman (22) has measured the pressure dependence of the electrical resistance of the alkali metals at room

temperature up to very high pressures. It is interesting to consider these curves in terms of the distortion of the Fermi surface which we have just been discussing. Bridgman's results are shown in Fig. 13, in which relative resistance is shown as a function of the relative volume. As I have already emphasized, an important part of the change in ideal resistivity with volume arises from the change produced in θ . It is possible, from a knowledge of the compressibility of the lattice as a function of volume, to estimate how θ changes with volume. Using this information and that in Fig. 13, I have estimated how the interaction constant K changes with volume over the full range of pressures; these results are shown in Fig. 14. Lithium is remarkable in that, for it, K always increases under compression; this has already been discussed. The curve for cesium shows a pronounced minimum when its volume has been reduced by about 5 percent. We can now interpret this to mean that at this volume (approximately), contact of the Fermi surface with the Brillouin zone boundary occurs. The behavior of rubidium is rather similar, although for it the

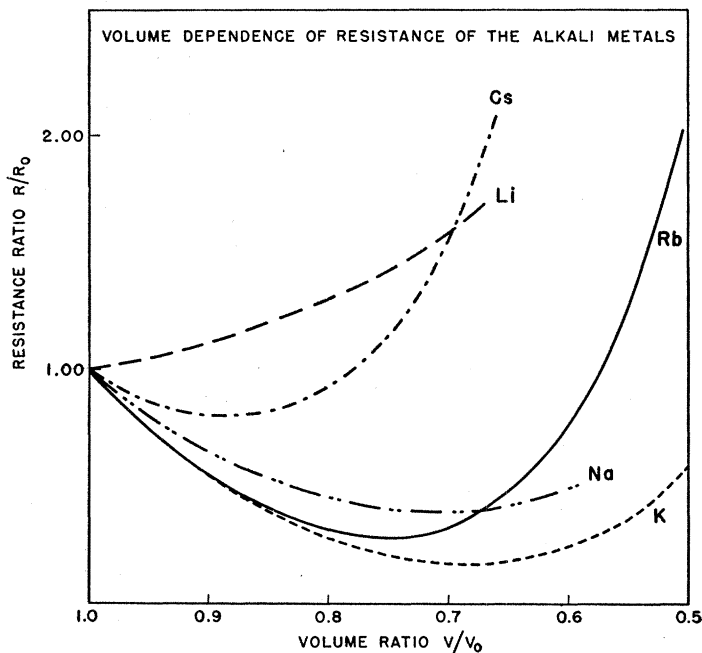
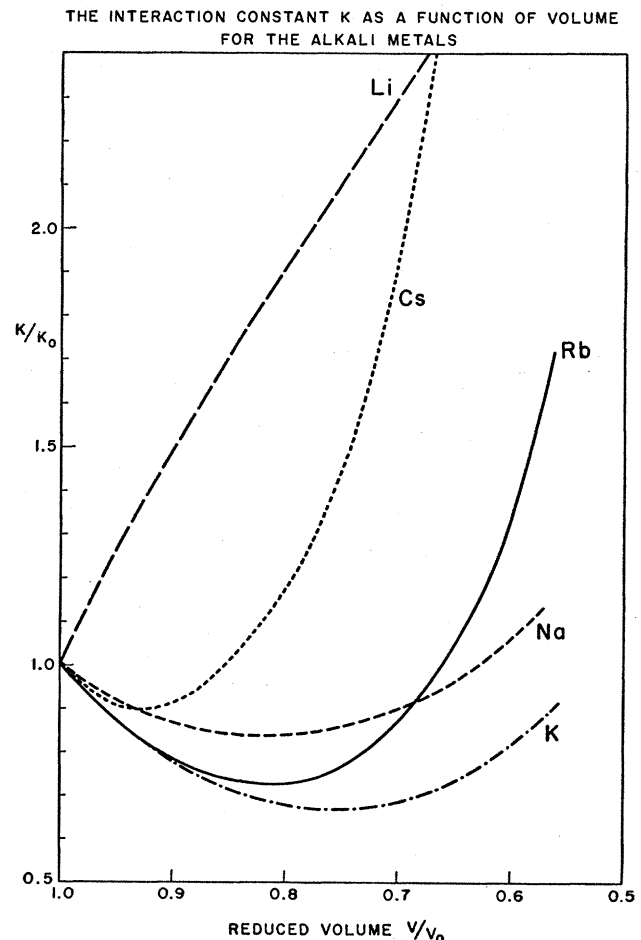


Fig. 13 (above). The change in electrical resistance with volume of the alkali metals at 0°C. [From Bridgman (22)] Fig. 14 (right). The change in interaction constant K with volume for the alkali metals. [Derived from Fig. 13]



minimum is reached at a rather higher pressure. Sodium and potassium behave rather differently from the others: for these two metals K increases rather slowly after the minimum has been reached. Nevertheless it seems that in all these metals we are seeing the effect on K of progressive distortion of the Fermi surface.

Pressure Coefficients and Thermoelectric Power

At high temperatures (temperatures which are large as compared to the characteristic temperature of the lattice) the absolute thermoelectric power of a metal S is related to its resistivity by the following relationship (23):

$$S = -\frac{\pi^2 k^2 T}{3eE_F} \left(\frac{d \ln \rho(E)}{d \ln E} \right)_{E=E_F} \quad (9)$$

(k is Boltzmann's constant and e is the electronic charge). This relationship (24) expresses the fact that the thermoelectric power of a metal depends on how the resistivity of the metal varies with its Fermi energy, and from the measured values of the thermoelectric power of a metal at high temperature it is thus possible to obtain a measure of this variation through the quantity

$$x = \left(\frac{d \ln \rho(E)}{d \ln E} \right)_{E=E_F}$$

One way of altering the Fermi energy of a metal is to compress it. Thus there should be some relationship between the volume coefficient of resistivity and the value of x for that metal. It is not to be expected that x will be related to the total change of resistance due to the volume change because this involves the change in the amplitude of the lattice vibrations, which has no counterpart in x . If, however, we eliminate the part due to changes in the lattice vibrations and consider $d \ln K / d \ln V$, we might expect that this would be related to x . In Table 2 a comparison of these quantities is made for the monovalent metals, and the ratios are listed (column 6). If the change in K with volume were due entirely to the

change in the Fermi energy E_F with volume and if the Fermi surface did not distort under pressure, this ratio would be simply $d \ln E_F / d \ln V$. For a spherical Fermi surface this has the value $-2/3$, since E_F is proportional to $V^{-2/3}$. It may be seen that for all the metals the value lies between -0.3 and -0.8 ; in particular for sodium and potassium, the two metals whose Fermi surfaces are most nearly spherical, the value of the ratio is quite close to $-2/3$.

If the interpretation given above of the minimum in the resistance-versus-pressure curve of cesium is correct, and if the thermoelectric power is intimately related to the quantity $d \ln K / d \ln V$, the thermoelectric power of cesium should be very sensitive to pressure and should in fact change sign at quite modest pressures (pressures similar to that required to reduce the resistance to its minimum value). Recent measurements on the thermoelectric power of cesium at 0°C (25) show that this change of sign does indeed occur and that the thermoelectric power of cesium is extremely sensitive to pressure; it changes by nearly 1/2 percent per atmosphere.

To sum up, we may say that the pressure coefficient of the ideal resistivity of a metal changes appreciably only at low temperatures ($T < \theta/3$); moreover, experiments show that this change is related to the change in the temperature coefficient of resistivity in the way that theory predicts. There appears to be a close connection between the electronic contribution to the pressure coefficient of resistance on the one hand and the thermoelectric power of the metal on the other. When one comes to consider the magnitude of the pressure coefficient it is clear that in some metals, notably lithium, cesium, and the noble metals, this can only be understood in terms of the distortion of the Fermi surface of the metal. This distortion is also reflected in the temperature dependence and the magnitude of the resistivity. All this emphasizes how desirable it would be to obtain direct information about the shape of the Fermi surfaces in alkali metals (26).

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26. It is a pleasure to acknowledge the collaboration of Dr. D. Guban in much of the experimental work described here. I am very grateful to Dr. D. K. C. MacDonald for his encouragement and interest at all times and wish to thank him and Dr. A. V. Gold for many valuable discussions and for reading the manuscript.
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