

'Diffuse Scattering' of the Fermi electrons in monovalent metals in relation to their resistivities

By

Sir K.S. Krishnan, F.R.S., and A. B. Bhatia, D. Phil.

With 4 diagrams

ABSTRACT

The main step in the calculation of the electrical resistivities of monovalent metals, in which the conduction electrons are almost completely degenerate, is the calculation of the relaxation time  $\tau$  of the electrons at the Fermi surface, which in these metals is a sphere, and is well inside the first Brillouin zone. Since the wave-length  $\lambda$  and hence the group velocity  $v$ , of the Fermi electrons is known, the calculation of  $\tau$  means also the calculation of the mean free path  $l = v\tau$  of these electrons. Now the finite <sup>mean</sup> free path of these electrons arises ultimately from the scattering — particularly the large-angle scattering — of these electrons in their passage through the crystal, ~~the scattering being due to~~ <sup>by</sup> the thermal agitation <sup>ed</sup> of <sup>its</sup> the atoms, ~~and the consequent thermodynamic local fluctuations or inhomogeneities in the crystal.~~ Hence a detailed knowledge of the scattering coefficient of the crystal for the Fermi electrons, incident and scattered along different directions in the crystal, would enable us to calculate  $\tau$  or  $l$ .

Now the scattering coefficient  $\beta$  depends on two factors.\*

1. The atom form factor for scattering which in monovalent metals may be taken to be isotropic <sup>(i.e. independent of the direction of incidence, or of scattering separately, but  $\lambda$ -dependent on the angle of scattering  $\phi$  between the two, and on  $\lambda$ .</sup> scattering. (Extensive measurements are available on the scattering of slow electrons by the rare gases, which give us information regarding the atom form factor for the scattering of the Fermi electrons in the corresponding alkali metals and the variation of these factors with  $\phi$ .)
2. The structure factor of the crystal, which, ~~even in~~ besides being a function of ~~the wave-length,~~  $\lambda$ ,

~~cubic crystals like those of the monovalent metals,~~  
 (~~even in a cubic crystal,~~)  
 will vary, with the direction of incidence and of scattering; ~~For a given wave-length the structure factor of a crystal is~~ <sup>but will, however, be</sup> independent of the nature of the waves, i. e. independent of whether they are ~~X~~ X-rays, or electron or neutron waves. (The 'diffuse scattering' of X-rays of long wave-lengths has been studied in great detail, both theoretically and experimentally, ~~and the results hold equally well for the scattering of electron waves of the same wave-length.~~ <sup>(from which one can)</sup> ~~They enable us to~~ calculate the structure factors of the monovalent metals for their respective Fermi wave-lengths, for different directions of incidence <sup>and</sup> of scattering in the crystals.)

Using these data for the atom form factor and for the structure factor of the crystal, the mean free path of the Fermi electrons is calculated <sup>(in the present paper)</sup> in detail ~~for one~~ <sup>(for different directions of incidence, for one)</sup> typical monovalent metal, namely sodium crystal. The free path <sup>l</sup> is given by

$$1/l = \Psi \cdot \nu^2 RT \beta \sigma,$$

where  $\nu$  is the number of atoms per unit volume,  $\sigma$  is the cross-section of the atom for total scattering in all directions,  $\beta$  is the compressibility, and  $\Psi$  is a numerical factor which varies from a maximum of 2.2 for incidence along [110] to a minimum of about 0.9 for incidence along [100], its average value being close to the minimum, and nearly unity. [With  $\Psi$  actually unity the right-hand side of the above expression for  $1/l$  can be seen to be just the Einstein - Smoluchowski expression <sup>(the attenuation coefficient of a)</sup> for ~~scattering by a~~ <sup>(medium for long waves; which)</sup> liquid ~~in~~ shows that in sodium, and presumably also in other monovalent metals, the mean free path of the Fermi electrons may be taken roughly as the reciprocal of the attenuation coefficient of the crystal due to scattering, and the scattering may be regarded as due almost wholly to the local thermal fluctuations in density, and the Fermi wave-length as long enough for the Einstein - Smoluchowski formula for density scattering to be applicable.

New para

1. INTRODUCTION

(in which the conduction electrons are almost completely degenerate)

In an electronic conductor, e.g. a metal crystal, it is only the electrons near the Fermi surface that can make effectively collisions and thus take part in conduction. Hence a detailed knowledge of the coefficient of scattering along different directions in the crystal, of the Fermi electrons, will be helpful in our understanding its electrical properties. In general the wave-lengths of these electrons are of the order of the inter-atomic distance. Now the scattering coefficient of a crystal depends both on the atom form factor, <sup>i.e.</sup> ~~or~~ the <sup>ro</sup> cross-section of the atom for scattering, and on the structure factor of the crystal. For waves much shorter than the interatomic distance, or much longer, both these factors are easily evaluated, but for intermediate wave-lengths, such as are involved in electrical conduction, the <sup>eval</sup> calculation is more ~~complicated~~. <sup>(difficult, but has been done by earlier workers.)</sup> The atom form factor for scattering of electrons of such wave-lengths has been studied theoretically by Faxén and Holtmark (1927), and experimentally by Ramsauer and Kollath (1932), and others. The technique for the calculation of the structure factor of the crystal for scattering of these wave-lengths is also available, since the structure factor for "diffuse scattering" of X-rays has been studied extensively, both theoretically and experimentally, and the structure factor of <sup>a</sup> ~~the~~ crystal for the scattering of electrons — or of any other waves — is the same as for the scattering of X-rays of the same wave-length. (In the usual discussions on diffuse scattering of X-rays, however, attention is directed mainly to the neighbourhood of the Bragg spots, whereas in the scattering of the Fermi waves we shall be concerned mainly with the region between the central spot and the immediately surrounding Bragg spots.) <sup>(i.e. metals of the first group in the Periodic Table.)</sup>

In good metals like the alkali <sup>or</sup> ~~and~~ the noble metals, in which the Fermi surface is well within the first Brillouin zone, and is a sphere, the calculation of the scattering

coefficient for the Fermi electrons becomes much simpler, since all the Fermi electrons have the same wave-length, and this wave-length is too long to give any Bragg reflection: in the alkali metals, which are body-centred cubic, this wave-length is 14% <sup>longer</sup> ~~greater~~, and in the noble metals, which are face-centred cubic, 11% <sup>longer,</sup> ~~greater~~, than that necessary to ~~give~~ give the first Bragg reflection in the backward direction.

Detailed calculations are given in the present paper of the structure factor <sup>sodium</sup> of crystal ~~of the alkali and the noble metals~~ for scattering of wave-lengths too long to give any Bragg reflection. Some rough estimates can be made of the atom form factor for scattering of the Fermi electrons by the atoms in these metals. These data are then utilized to calculate the relaxation time of the Fermi electrons in these metals, and thence <sup>its</sup> ~~their~~ electrical resistivities.

In a previous paper (Krishnan and Bhatia, 1944) ~~it was~~ <sup>it was</sup> shown <sup>n</sup> from certain general considerations, that in the alkali and the noble metals the mean free path of the Fermi electrons may be taken roughly to be equal to the reciprocal of the attenuation coefficient of the metal for the passage of these electrons, the attenuation being due to scattering by the thermally agitated atoms in the metals; and that for the Fermi wave-length the scattering may be taken to be due predominantly to the local thermal fluctuations in density, and the attenuation coefficient to be given practically by the Einstein - Smoluchowski formula.)

The detailed calculations made in the present paper (in sodium metal, and presumably in other monovalent metals too) show that these results are good approximations. It is needless to add that they simplify considerably the calculation of electrical resistivities.

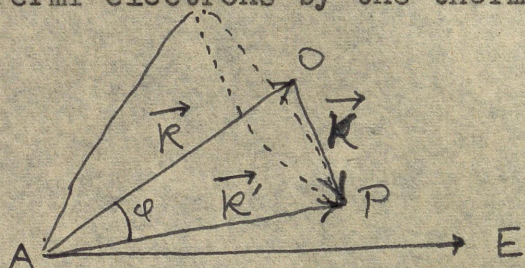
## 2. ELECTRICAL RESISTIVITY IN RELATION TO THE SCATTERING OF THE FERMI ELECTRONS

As is well-known the specific resistance  $\rho$  of a good metal or alloy is given by the expression#

$$\rho = \frac{m}{n v e^2} \cdot \frac{1}{\tau} \quad \dots \quad (1)$$

$$= \frac{h}{n v e^2 \lambda} \cdot \frac{1}{l} \quad \dots \quad (2)$$

where  $\tau$  is the relaxation time of the Fermi electrons, of wave-length  $\lambda = (8\pi/3n\nu)^{1/3}$  and of group velocity  $v = h/m\lambda$ , ~~that~~  $l = v\tau$  is their mean free path,  $\nu$  is the number of atoms per unit volume, and  $n$  is the number of conduction electrons per atom, and the other letters have their usual significance.\* All the quantities in (1) and (2) are known except  $\tau$  (or  $l$ ), and the main problem in calculating the electrical resistivities of good metals or alloys is therefore one of calculating  $\tau$  (or  $l$ ) in terms of the scattering of the Fermi electrons by the thermally agitated atoms.



Let  $\vec{OE}$  (see Fig. 1) be the direction of the applied electric field. Consider electrons at the Fermi surface moving along any given direction  $OP$ , and scattered ~~at an angle~~ <sup>along  $AP$ , the</sup> ~~at an angle~~ <sup>(of scattering being)  $\phi$</sup> . The wave-vectors  $\vec{K}$  and  $\vec{K}'$  ( $K' \approx K$ ) of the incident and the scattered electron-waves respectively, are as marked in the figure.  $\vec{K}$  is the wave-vector of the elastic wave that produces the scattering, where  $K \approx 2K' \sin \frac{\phi}{2}$ . Consider now the quantity  $\Delta p_E / p_E = \Delta k_E / k_E$ , where  $p = \hbar k$  is the momentum of the incident Fermi electron, and  $\Delta p = \hbar \Delta k$  is the change in its momentum due to scattering, and the subscripts  $E$  denote the components along  $\vec{OE}$  of these quantities.  $\Delta \vec{k}$  will evidently be equal to  $\vec{K}$ .

\* See for example Mott and Jones, Theory of Properties of Metals and Alloys, Oxf. Univ. Press 1936, or Fröhlich, Theorie der Metalle, Springer 1936.

Let  $S_{kk'}$  be the fraction of the Fermi electrons moving along direction  $\vec{k}$  which is scattered per unit volume of the crystal, per unit solid angle,\* along direction  $\vec{k}'$ . The reciprocal of the mean free path appearing in (2) will then be given by

$$\frac{1}{l} = \frac{1}{v\tau} = \frac{1}{4\pi} \iint S_{kk'} \frac{\Delta k_E}{k_E} d\omega_k d\omega_{k'}, \quad \dots (3)$$

where  $d\omega_k$  and  $d\omega_{k'}$  are elements of solid angles about the directions  $\vec{k}$  and  $\vec{k}'$  respectively, and both the integrations extend over the whole of the  $4\pi$  solid angle. It will be seen from (3) that  $1/l$  may also be regarded as  $4\pi$  times the average value of  $S_{kk'} \frac{\Delta k_E}{k_E}$ , the average being taken over all directions of scattering  $\vec{k}'$ , and all directions of incidence  $\vec{k}$  of the Fermi electrons @

Even in a cubic crystal, because of its elastic anisotropy the scattering coefficient  $S_{kk'}$  will be a function of  $\vec{k}$  and  $\vec{k}'$ . Even so, with a detailed knowledge of  $S_{kk'}$  <sup>as a function</sup> ~~for different~~ directions of  $\vec{k}$  and  $\vec{k}'$ , which as we shall show in the present paper is not difficult to obtain, the integration in (3) can be done numerically.

---

\* The probability that <sup>a Fermi</sup> ~~an~~ electron travelling along  $\vec{k}$  is scattered per unit time per unit solid angle along  $\vec{k}'$  is given by

$$P_{kk'} = S_{kk'} v,$$

where  $v$  is the velocity of the ~~Fermi~~ electron.

@ In the derivation of expression (1) it is implicit that  $1/\tau$  is the same for all the Fermi electrons, i.e. for all directions of incidence since in the metals that we are considering all the Fermi electrons have the same wavelength. When  $1/\tau$  varies with the direction of incidence, one may as an approximation, use the average value of  $1/\tau$  taken over all directions of the Fermi electrons, as we have done in expression (3).

In the usual discussions on the electrical resistivities of these metals, it is assumed for convenience that  $S_{\vec{k}\vec{k}'}$  is a function of the angle of scattering  $\varphi$  between  $\vec{k}$  and  $\vec{k}'$ , and is independent of the directions of  $\vec{k}$  and  $\vec{k}'$  separately. This assumption will hold when the crystal is elastically isotropic, and when further the Fermi wave-length is much longer than is necessary to give any Bragg reflection, i.e.  $\lambda \gg 2d \sin \frac{\varphi}{2}$  where  $d$  is the lattice spacing corresponding to the first Bragg reflection. Neither of these conditions, however, is satisfied in the alkali or the noble metals, since many of them are <sup>elastically</sup> highly anisotropic, and  <sup>$\lambda$ ,</sup> as we have seen,  $\lambda$  is only slightly greater than  $2d$ . Holding for the present to the assumption that  $S_{\vec{k}\vec{k}'}$  is a function of  $\varphi$  alone, which we can denote by  $S_\varphi$ , we may evaluate (3) in a simple manner, since we can now keep one of the directions  $\vec{k}, \vec{k}'$ , say  $\vec{k}$  fixed, and find the average value of  $S_\varphi \cdot \Delta k_E / k_E$  over all directions of the other, namely  $\vec{k}'$ . We can do this averaging in two steps. First we keep  $\varphi$ , and hence  $S_\varphi$ , constant, and average  $\Delta k_E / k_E$  over all azimuths of scattering; which is the same as averaging  $(k \sin \frac{\varphi}{2}) / k_E$  over these azimuths, the average <sup>is just  $k \sin \frac{\varphi}{2} / k_E$ , or</sup> being equal to <sup>just</sup>  $(1 - \cos \varphi)$ , which gives for  $1/l$  the value

$$\frac{1}{l} = \frac{1}{v\tau} = \int_0^\pi S_\varphi (1 - \cos \varphi) 2\pi \sin \varphi d\varphi, \dots (4)$$

which is independent of the direction of incidence  $\vec{k}$  in the crystal.

Though we do not adopt the approximation that  $S_{\vec{k}\vec{k}'}$  is a function of  $\varphi$  alone, and <sup>(of the directions)</sup> independent of  $\vec{k}$  or  $\vec{k}'$  separately, we shall have occasion to use expression (4), since even in <sup>elastically</sup> highly anisotropic crystals like the alkali metals there <sup>in reciprocal space</sup> are regions in which for certain directions of incidence the scattering coefficient is roughly a function of  $\varphi$  alone.

### 3. DIFFUSE SCATTERING AS DUE TO THERMAL AGITATION

The influence of <sup>the</sup> thermal agitations of the atoms in a crystal on the intensities of the Bragg reflections, and of the 'diffuse scattering' along other directions, has been discussed among the earlier investigators by Darwin (1914) and by Debye (1914). Let  $R$  be the structure factor of the crystal, defined as usual by

$$R = \frac{S}{v\sigma}, \quad vs$$

where  ~~$v$  is the number of atoms per unit volume and  $\sigma$  is~~  $\Delta$  is the scattering coefficient of an atom in the crystal per unit solid angle, or the atom form factor <sup>for intensity,</sup> all the three quantities  $R$ ,  $S$  and  $\Delta$  referring to the given wave-length and to the same directions of incidence and of observation. In the monatomic metals that we are considering,  $\Delta$  may be regarded as practically isotropic, i.e. a function of only  $\varphi$  and  $\lambda$  in the combination  $\sin \frac{\varphi}{2} / \lambda$ .

The major effect of the thermal spread of the atomic centres about their mean positions will be to make the atom form factor at temperature  $T$ , namely  $\Delta_T$ , fall off more rapidly with increase of  $\sin \frac{\varphi}{2} / \lambda$  than the corresponding form factor  $\Delta_0$  of the non-vibrating atom, according to the well-known expression

$$\left. \begin{aligned} \Delta_T \Delta_0 &= \Delta_0 s_0 e^{-2M} \\ M &= 8\pi^2 \frac{\overline{\xi^2}}{\lambda^2} \left(\sin \frac{\varphi}{2} / \lambda\right)^2 \end{aligned} \right\}, \dots (5)$$

where  $\overline{\xi^2}$  is the mean square of the amplitude of the thermal oscillations, and is given at room temperature, which in these metals is sufficiently high in comparison with the Debye temperature to make the thermal energy proportional to  $T$ , by

$$4\pi^2 \nu_v^2 m \overline{\xi^2} \approx kT,$$

where  $\nu_v$  is the vibration frequency, and  $m$  the mass, of the atom.

then along external vector  $\varphi$  where angle between directions of incidence & scattering

atom. The result is a rapid fall of intensity of the Bragg reflections particularly of higher orders, with rise of temperature. This is observed, and the fall is roughly in accordance with (5).

The question naturally arises as to what happens to the energy represented by the diminution of the intensities of the Bragg reflections consequent on increase of temperature. Obviously it should appear as diffuse scattering along other directions, and besides, if a sufficient number of higher order Bragg reflections is included in the range  $0 < \varphi \leq \pi$ , we should have for any given direction of incidence

$$\nu \int \frac{\Delta_0}{\varphi_0} d\omega - \nu \int \frac{\Delta_T}{\varphi_T} d\omega = \int S d\omega, \quad \dots (6)$$

where the integrations extend over the whole of the  $4\pi$  solid angle of scattering.

If the only effect of the thermal agitations may be regarded as a static swelling up or inflation of the scattering atoms, as is implied in the above treatment, then, in addition to the integrated value of  $S$  over all directions being equal to the difference between the integrated values of  $\nu \frac{\Delta_0}{\varphi_0}$  and of  $\nu \frac{\Delta_T}{\varphi_T}$  over these directions, as given by (6),  $S$  will be equal to  $\nu \left( \frac{\Delta_0}{\varphi_0} - \frac{\Delta_T}{\varphi_T} \right)$  along every direction. Though some extensive measurements by Jauncey and his collaborators apparently lend support to this conclusion, it is now realised, both from theoretical considerations, and from scattering experiments made with a narrow parallel pencil of incident monochromatic X-rays, which verify the theory, that such a detailed balancing between  $\nu \left( \frac{\Delta_0}{\varphi_0} - \frac{\Delta_T}{\varphi_T} \right)$  and  $S$  does not occur.

#### 4. CALCULATION OF DIFFUSE SCATTERING

A detailed calculation of the directional distribution of intensity of the diffuse scattering of X-rays in crystals due to thermal agitation has been made by Faxén (1923) and by Waller (1923, 1925, 1928), and more recently, and from

a different point of view, by Sir C.V.Raman (1941). We may mention immediately that in crystals in which all the normal modes of vibration are of the acoustic type, e.g. those of the alkali and the noble metals, the Faxén-Waller treatment and the treatment by Sir C.V.Raman give identical results.

(The criterion adopted by Sir C.V. Raman for distinguishing between the "acoustic" and the "optical" normal modes of vibration of a crystal, is not the same as the criterion adopted here.)

The Faxén-Waller treatment has been simplified, or made more rigorous, by Zachariassen, Born, Weigel, and Jahn\*, among others. We shall adopt here the results as presented by Jahn (1941) since they are in a form directly applicable to our problem.

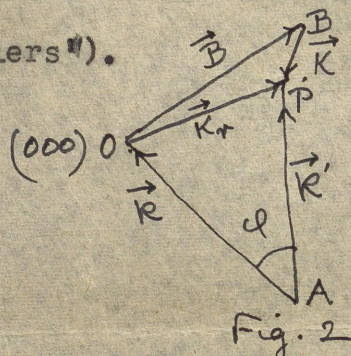
Consider the reciprocal lattice of a given cubic crystal and the first Brillouin zones surrounding each of the points of the reciprocal lattice, including (000). These zones will be filled by a quasi-continuous and uniform distribution of cells, each cell defining a wave-vector  $\vec{K}$  associated with the elastic standing waves that represent the normal modes of vibration of the crystal. Each K-cell will correspond to three normal modes of vibration of the crystal answering respectively to the three directions of vibration or displacement — and the three frequencies — associated with the particular value of  $\vec{K}$ .

In the alkali metals, which are body-centred cubic, the first Brillouin zone surrounding each point of the reciprocal lattice is the rhombic dodecahedron bounded by faces of the type  $\{110\}$ . The distance from the reciprocal point forming the centre of the dodecahedron to the faces of the dodecahedron will be  $1/2d_{110}$ , where  $d_{110}$  is the grating spacing of the (110) planes in the crystal.

---

\* For a good account of the subject see symposia of papers on the subject in Proc. Ind. Acad. Sc. Vol. 14, 1941, and in Proc. Roy. Soc. Vol. 179, 1942, and the reports by Mrs. Lonsdale and by Max Born in Reports on Progress in Physics, Phys. Soc. London, 1942-43.

In the noble metals, which are face-centred cubic, the first Brillouin zone is the orthotetrakaidekahedron, or the 14-hedron, bounded by  $\{111\}$  and  $\{200\}$  faces, i.e. the octahedron  $\{111\}$  truncated by the cubic faces  $\{200\}$ . In both the alkali and the noble metals these first zones can accommodate one K-cell per atom, i.e. all the normal modes of vibration will be of the acoustic type, and further the first zones surrounding the various reciprocal lattice points will be similar and similarly oriented, and these zones will fill up the whole of the reciprocal space without overlapping. (As is well-known, both the rhombic dodecahedron and the orthotetrakaidekahedron described above are "space-fillers").



Consider now a narrow pencil of monochromatic electron waves of wave-number  $k = 1/\lambda$  incident along AO (See Fig.2), where O is the origin (000) of the reciprocal lattice, and consider the radiations scattered along AP, where  $AP = |R'| \approx |R|$ , and  $\varphi$  is the angle between AO and AP or the angle of scattering as before. Let P—which, following Laval, we may call the "pole of diffusion"<sub>K</sub> lie in the zone associated with the reciprocal lattice point B. Let  $\vec{B}$  denote the vector OB, and  $\vec{K}$  the elastic wave-vector from B to P. The vector  $\vec{K}_r$  defined by

$$\vec{K}_r = \vec{B} + \vec{K}$$

will bisect externally the angle between the direction of incidence  $\vec{R}$  (AO) and the direction of observation  $\vec{R}'$  (AP). The structure factor R of the crystal for the given direction of incidence and of scattering will be given, according to Jahn, by

according to Jahn, by\*

$$R = e^{-2M} \frac{\nu K T}{\rho} \left\{ \left( \frac{\vec{K}_r \cdot \vec{e}_1}{N_1} \right)^2 + \left( \frac{\vec{K}_r \cdot \vec{e}_2}{N_2} \right)^2 + \left( \frac{\vec{K}_r \cdot \vec{e}_3}{N_3} \right)^2 \right\} \dots \quad (7)$$

where  $\rho$  is the density of the medium,  $N_1, N_2, N_3$  are the three frequencies, and  $\vec{e}_1, \vec{e}_2, \vec{e}_3$  the three unit polarization vectors, i.e. unit vectors along the directions of displacement of the atoms, associated with the particular elastic wave-vector  $\vec{K}$ .

Following again Jahn, we may rewrite (7) in the form

$$R = e^{-2M} \cdot \frac{\nu K T}{\rho} \left[ B^2 \sum_{i=1}^3 \frac{(LA_i + MB_i + NC_i)^2}{N_i^2} + 2BK \sum_{i=1}^3 \frac{(LA_i + MB_i + NC_i)(lA_i + mB_i + nC_i)}{N_i^2} + K^2 \sum_{i=1}^3 \frac{(lA_i + mB_i + nC_i)^2}{N_i^2} \right], \dots \quad (8)$$

where  $L, M, N$  are the direction cosines of  $\vec{B}$ ,  $l, m, n$  those of  $\vec{K}$ , and  $A_i, B_i, C_i$  those of the polarization vectors  $\vec{e}_i$ ,  $i = 1, 2, 3$ .

In the special case when the pole of diffusion  $P$  lies in the central Brillouin zone, i.e. in the zone associated with (000), the first two terms in (8) vanish, since for this zone  $B = 0$  (and  $\vec{K}_r \equiv \vec{K}$ ), and we are left with the third term alone. The expression for  $R$  then reduces to

$$R = e^{-2M} \frac{\nu K T}{\rho} \sum_{i=1}^3 \frac{(lA_i + mB_i + nC_i)^2}{V_i^2} \dots \quad (9)$$

where  $V_i = N_i/K$  is the phase velocity of the elastic wave.

---

\* Except for a constant of proportionality which is left undetermined in Jahn's expression, but is easily evaluated when we regard scattering as reflection from the appropriate thermal elastic waves in the crystal (Krishnan and Bhatia, 1947), and is included in (7).

5 SCATTERING REGARDED AS REFLECTION FROM  
APPROPRIATE THERMAL ELASTIC WAVES

In a previous paper, on the scattering of light-waves, i.e. of very long waves, in homogenous media (Krishnan and Bhatia 1947), we showed that the scattering coefficient  $S$  may also be regarded as equal to the maximum value of the ~~see~~ coefficient of reflection from the two sets of progressive elastic waves (the two progressing in opposite directions) whose wave-normals and wave-lengths satisfy the Bragg condition for reflection, either set consisting of three *(corresponding to the three directions of displacement,)* progressive waves, the energy of each of the waves, filling the whole of the medium, being that of a Planck oscillator of the same frequency, or  $kT$  under the present assumptions. The expression for  $R$  comes out on this basis as (Krishnan and Bhatia, 1947)

$$R = \frac{\nu kT}{\rho} \sum_{i=1}^3 \frac{\cos^2 \omega_i}{V_i^2}, \dots \quad (10)$$

where  $\omega_i$  is the angle between  $\vec{K}$  and  $\vec{e}_i$ .

Expression (10), deduced here for long waves, can be seen to be identical with the Faxén-Waller expression (9), except for the factor  $e^{-2M}$ , which for long waves is practically unity.

For shorter waves <sup>-lengths</sup> also, i.e. for  $P$  outside the central Brillouin zone,  $R$  can be calculated in terms of reflections from the elastic waves, and the expression thus obtained is found to be equivalent to the corresponding expression (7) of Faxén-Waller. We demonstrate this equivalence below.

Consider any one set of atomic reflecting planes  $(hkl)$  in the crystal, which, under suitable conditions, can give rise to a Bragg reflection, and let the spacing of these layers be  $d_{hkl}$ . This regular layered structure may be regarded as the limiting case of a plane condensational acoustic wave with its wave-normal perpendicular to the planes, its wave-length equal to  $d_{hkl}$ , and its velocity of propagation zero. Actually since the

distribution of matter in these layers is not sinusoidal, but is concentrated near the plane of the atomic centres, we shall have to take into account the upper partials also, corresponding to the spacings  $1/2$ ,  $1/3$ , etc. times  $d_{hkl}$ . These shorter grating spacings may be regarded as giving rise to Bragg reflections of the second, third and higher orders, corresponding to the reciprocal points  $2(hkl)$ ,  $3(hkl)$ , etc., and since these reciprocal lattice points are considered separately, we shall confine ourselves here to the fundamental spacing  $d_{hkl}$  corresponding to the point  $(hkl)$  of the reciprocal lattice.

Consider now one of the elastic waves representing a normal mode of vibration of the crystal, whose wave-vector is  $\vec{K}$ , and consider also a regular stratification of the crystal of spacing  $d_{hkl}$ . Because of this stratification the above wave may also be regarded as an elastic wave whose wave vector  $\vec{K}_r$  is given by

$$\vec{K}_r = \frac{\vec{1}}{d_{hkl}} + \vec{K}.$$

We shall refer to such waves obtained by the superposition of elastic waves on the stratified layers of the scattering medium, as resultant elastic waves, as distinguished from the primary elastic waves. Whereas the wave numbers of the latter, namely  $\vec{K}$ , are restricted to the limits of the first Brillouin zone, the wave numbers  $\vec{K}_r$  of the resultant elastic waves may have very large values,  $K_r \approx n/d_{hkl}$ .

The frequency of the resultant elastic wave, the displacement of the atoms under it, and the energy per unit volume associated with it, will all be the same as for the primary elastic wave producing it, but the velocity of the resultant wave will naturally be smaller than that of the primary wave in the ratio

$$v_r/v = K/K_r.$$

When the primary wave is a long one, such that  $K \ll K_T$ , the velocity of the resultant wave can become quite small.

These resultant waves can reflect the incident X-rays in the same manner as the primary elastic waves, and thus account for scattering along directions corresponding to <sup>positions of</sup> P outside the central Brillouin zone, i.e. along directions for which there can be no direct reflection from any of the primary waves.

It will be seen from relation (10) that when the total energy in the medium associated with the elastic wave remains fixed, namely at  $K_T$ , the intensity of reflection from the elastic wave, which determines the scattering along the direction concerned, is inversely proportional to the square of its velocity, and hence the intensity of reflection from the resultant wave, because of its low velocity will be larger than that of the reflection from the primary wave by a factor  $(K_T/K)^2$ , which, as K becomes small, or as P approaches the reciprocal point corresponding to the Bragg reflection from the particular set of reflecting planes considered, will become very large.

The intensity of scattering along these directions will also be conditioned by the following.

(1) Just as in reflection by a primary elastic wave, i.e. when P lies in the central Brillouin zone, it is the components of the three displacements along the wave-normal  $\vec{K}$  of the <sup>reflecting</sup> elastic wave that determine the intensity of scattering, so also in the case of reflection by the secondary elastic wave referred to above, i.e. when P lies outside the central Brillouin zone, it is the components of the displacements along  $\vec{K}_T$  that determine the intensity, but the absolute directions of these displacements in the crystal will be determined by the direction of propagation (l, m, n) of the primary wave alone, according to relation (12) to be given in next section.

(2) For the short wave-lengths  $\lambda$  that we are considering now, the temperature factor  $e^{-2M}$  will deviate considerably from unity, and will have to be retained.

These considerations obviously lead to an expression for  $R$  identical with expression (7) give above, of Faxén and Waller.

For these short waves we should remember that the atom form factor  $f_0$  will vary markedly with  $\varphi$  unlike for long waves.

#### 6. REMARKS ON THE CALCULATION OF $\bar{\tau}$ FOR SOME SPECIAL DIRECTIONS OF ELECTRON WAVES

Consider the locus of the pole of diffraction  $P$  in reciprocal space when the direction of incidence is kept fixed and the direction of scattering is varied over the whole of the  $4\pi$  solid angle. The locus will evidently be a sphere passing through the origin, of diameter  $2R$ , the diameter through the origin being along the direction of incidence. Following the usual practice we shall call this the "sphere of propagation". Since equal areas on the sphere correspond to equal solid angles of scattering, the calculation of  $1/\bar{l}$  for the given direction of incidence is equivalent to integrating

$$\frac{1}{R^2} S_{KK'} \frac{\Delta R_E}{R_E}$$

over the whole of the surface of the sphere of propagation.

We saw in Section 2 that when  $S$  is a function of  $\varphi$  alone, the average value of  $S_{\varphi} \frac{\Delta R_E}{R_E}$  over all azimuths of scattering correspond to a given angle of scattering  $\varphi$ , is just equal to  $S_{\varphi} (1 - \cos \varphi)$ . *(when the crystal is like ours)* Even in a cubic crystal,

$S_{KK'}$  is not a function of  $\varphi$  alone. If however the incidence is along  $[100]$ ,  $[110]$  or  $[111]$ , which are axes of tetragonal, digonal and trigonal symmetry respectively, and we consider all the crystallographically equivalent directions  $\varphi_i$  corresponding to the same angle of scattering  $\varphi$  and to equivalent azimuthal angles  $\theta_i$ ,

then  $S_{kk'}$  =  $S_{\varphi\theta}$  will be the same for all these direction of scattering, and the average value of  $\Delta R_E / R_E$  over these directions will again be  $(1 - \cos\varphi)$ . Hence for the above directions of incidence in a cubic crystal, the expression for  $1/l$  may be written in the form

$$\frac{1}{l} = \int_{\varphi=0}^{\pi} \int_{\theta=0}^{2\pi} S_{kk'} (1 - \cos\varphi) \sin\varphi \, d\varphi \, d\theta \dots \quad (11)$$

In other words the weightage factor that takes into account the relatively large contribution to  $1/l$  from large angle scattering is equal to  $(1 - \cos\varphi)$ , and hence the same as when  $S_{kk'}$  is a function of  $\varphi$  alone.

## 7. SPHERE OF PROPAGATION WHOLLY INSIDE THE FIRST BRILLOUIN ZONE

Before proceeding to calculate  $1/l$  for the alkali and the noble metals, for their respective Fermi wave-lengths, for which the sphere of propagation extends into the second Brillouin zone also, it will be useful to calculate its value for the special case when  $\lambda$  is large, <sup>i.e. when</sup> and the sphere of propagation is well within the first Brillouin zone. This case is simple since then for every point P on the sphere the velocity of propagation, and the directions of the displacements, are independent of the wave-number K of the elastic wave, though of course they will vary with the direction of  $\vec{K}$ ; and  $V_1$  and  $A_1, B_1, C_1$  occurring in (19) can be expressed in terms of the static elastic constants  $c_{11}, c_{12}, c_{44}$

of the cubic crystal, by the relations

$$\left. \begin{aligned} \{c_{11}l^2 + c_{44}(m^2 + n^2) - \rho V_i^2\} A_i + (c_{12} + c_{44})(lm B_i + nl C_i) &= 0 \\ \{c_{11}m^2 + c_{44}(l^2 + n^2) - \rho V_i^2\} B_i + (c_{12} + c_{44})(lm A_i + mn C_i) &= 0 \\ \{c_{11}n^2 + c_{44}(l^2 + m^2) - \rho V_i^2\} C_i + (c_{12} + c_{44})(ln A_i + mn B_i) &= 0 \end{aligned} \right\} \dots (12)$$

In view of these relations, expression (9) reduces, as Jahn has shown, to

$$R = e^{-2M} \cdot \nu k T \cdot \frac{c_{44}^2 + 2c_{44} \epsilon (l^2 m^2 + m^2 n^2 + n^2 l^2) + 3\epsilon^2 l^2 m^2 n^2}{c_{11} c_{44}^2 + c_{44} (c_{11} + c_{12}) \epsilon (l^2 m^2 + m^2 n^2 + n^2 l^2) + (c_{11} + 2c_{12} + c_{44}) \epsilon^2 l^2 m^2 n^2} \quad \dots (13)$$

$$= e^{-2M} \cdot \nu k T \cdot F_{lmn}, \text{ say,} \quad \dots (14)$$

where  $\epsilon$  is the elastic anisotropy of the crystal, given by

$$\epsilon = c_{11} - c_{12} - 2c_{44}$$

Moreover in this region  $e^{-2M}$  is practically unity, and  $\Delta_\varphi$  practically independent of  $\varphi$ , and equal to  $\sigma/4\pi$ , where  $\sigma$  is the cross-section of the atom for total scattering ~~scat~~ in all directions, and is given by

$$\sigma = \int_0^\pi \Delta_\varphi \cdot 2\pi \sin\varphi \, d\varphi. \quad \dots (15)$$

Consider incidence of long electron waves along one of the principal directions  $[100]$ ,  $[110]$  or  $[111]$  of the cubic crystal. Expression (11) for  $1/l$  reduces under the above conditions to the simple form

$$1/l = \nu^2 k T (\sigma/4\pi) J \quad \dots (16)$$

where

$$J = \int_{\varphi=0}^\pi \int_{\theta=0}^{2\pi} F_{lmn} (1 - \cos\varphi) \sin\varphi \, d\varphi \, d\theta. \quad \dots (17)$$

When the crystal is elastically isotropic, i.e. when  $\epsilon = 0$ ,  $F$  becomes independent of  $l m n$ , and equal to  $1/c_{11}$ . In that case expression (17) holds whatever may be the ~~direc~~ direction of incidence, and the factor  $(1 - \cos\varphi)$  appearing in (17) intended to give the proper weightage for scattering at large angles, over scattering at small angles, becomes now quite ineffective <sup>ultimately,</sup> and the expression for  $1/l$  merely reduces to

$$1/l = \mu = \nu^2 k T \sigma / c_{11}, \quad \dots (18)$$

where  $\mu$  is the total scattering in all directions, per unit volume of the crystal, or the attenuation coefficient of the crystal for the passage of electron waves along the direction considered, the attenuation being due to scattering, and the coefficient  $\mu$  being defined by

-: 18 :-

$$I_d = I_0 e^{-\mu d},$$

where  $I_d$  is the intensity after traversing a distance  $d$  in the crystal.

If further  $c_{44} = 0$ ,  $C_{11}$  becomes equal to  $c_{12}$  and to  $1/\beta$ , where  $\beta$  is the compressibility of the crystal, and the expression for the attenuation coefficient due to scattering then reduces to the Einstein-Smoluchowski value for a liquid (Krishnan and Bhatia, 1947), namely

$$1/\lambda = \mu = v^2 k T \beta \cdot \sigma \quad (19)$$

as it should.

Coming back to the elastically anisotropic cubic crystal, and considering first incidence of long electron waves along  $[\bar{1}00]$ , we may express  $F_{lmn}$  defined by (13) and (14), in the form\*

$$F_{lmn} = \frac{a + b(l^2 m^2 + m^2 n^2 + n^2 l^2) + c l^2 m^2 n^2}{a' + b'(l^2 m^2 + m^2 n^2 + n^2 l^2) + c' l^2 m^2 n^2} = \frac{A + B \sin^2 2\theta}{A' + B' \sin^2 2\theta}, \quad \dots (20)$$

where

$$A = a + \frac{1}{4} b \sin^2 \varphi$$

$$B = \frac{1}{4} \cos^2 \frac{\varphi}{2} \left( b + c \sin^2 \frac{\varphi}{2} \right)$$

and  $A'$  and  $B'$  have similar values in terms of  $a'$  and  $b'$ , we obtain

\* We should remember here that  $l m n$  are the direction cosines of the elastic wave-vector  $\vec{K}$  which bisects externally the angle between  $\vec{k}$  and  $\vec{k}'$ , and when  $\vec{k}$  is along  $[\bar{1}00]$ , is related to the angle  $\varphi$ , and the azimuth  $\theta$ , of scattering by the relations

$$\begin{aligned} l &= \sin \frac{\varphi}{2} \\ m &= \cos \frac{\varphi}{2} \cos \theta \\ n &= -\cos \frac{\varphi}{2} \sin \theta. \end{aligned}$$

In view of expression (20) for F in which A, B, A', B' are all independent of  $\theta$ , the integration in (17) with reference to  $\theta$  can be done readily. Doing so we obtain

$$J = \int_0^\pi Y (1 - \cos \varphi) \sin \varphi \, d\varphi, \quad \dots (21)$$

where

$$Y = \int_0^{2\pi} F \, d\theta = 2\pi \left\{ \frac{B}{B'} + \frac{AB' - A'B}{B'(A'+B')} \sqrt{\frac{A'+B'}{A'}} \right\}. \quad \dots (22)$$

Changing the variable in (21) by putting  $f = 1 - \cos \varphi$ , we obtain

$$J = \int_0^2 Y f \, df$$

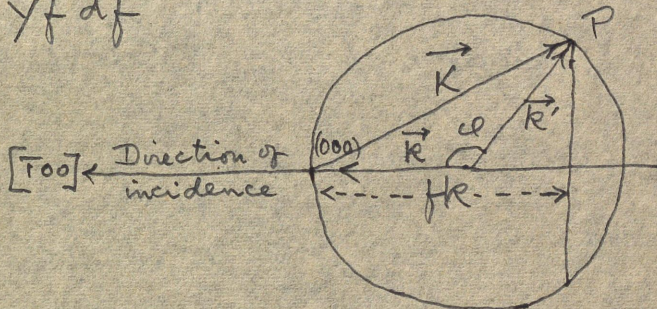


Fig. 3

Obviously  $fR$  represents the perpendicular distance from (000) of the plane perpendicular to the direction of incidence which by its intersection of the sphere of propagation defines  $\varphi$  (See fig. 3).

The integration in (23) can be done numerically, since we can calculate readily the values of Y corresponding to different values of  $f$  in the range  $0 \leq f \leq 2$ .

The elastic constants of sodium crystal have been determined by Quimby and Siegel (1938) at different low temperatures, which on extrapolation, give for room temperature (see Mrs. Lonsdale, 1940)

$$c_{11} = 0.52; \quad c_{12} = 0.40; \quad c_{44} = 0.41;$$

all of them in  $10^{11}$  dynes/cm<sup>2</sup>.

Or

$$c_{12} = 0.77 c_{11}; \quad c_{44} = 0.79 c_{11}; \quad \epsilon = -1.35 c_{11}.$$

Using these data, we have calculated the values of Y for different values of  $f$  in the range  $0 \leq f \leq 2$  at intervals of 0.2. The values are entered in Table I.

Table I.....

TABLE I

$f$	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	<i>Backward direction</i>
$Y \cdot c_{11} / 2\pi$	0.84	0.77	0.69	0.60	0.53	0.50	0.59	0.74	0.86	0.95	1.0	

It will be seen from the expression for  $B'$  that it becomes zero ~~zero~~ when  $\sin^2 \frac{\varphi}{2} = -b'/c'$ , or when  $f = 0.62$ . Since  $B'$  appears as a multiplying factor in the denominator of both the terms in expression (22) for  $Y$ , it ~~may~~ appears at first sight that  $Y$  <sup>may</sup> become infinite at  $f = 0.62$ . But actually on making  $B'$  small, and expanding the two terms and taking them together and then making  $B'$  tend to zero, the  $Y$  vs  $f$  curve is found to decrease smoothly at this point.

$B'$  becomes again zero at  $\varphi = \pi$ , i.e. <sup>at</sup>  $f = 2$ ; but it can be readily seen that <sup>both the</sup> terms in (22) are separately finite at this point since  $B'$  occurs in the combination  $B/B'$ , and  $B/B'$  remains finite at  $\varphi = \pi$ .

Using the values given in Table I, and Simpson's rule for numerical integration, we obtain

$$J = 2\pi \times 1.52/c_{11},$$

and hence for incidence of long electron waves along  $[100]$

$$1/l = 0.76 v^2 k T \sigma / c_{11},$$

as against

$$1/l = v^2 k T \sigma / c_{11}$$

for the elastically isotropic crystal (see (18)).

The calculation of  $1/l$  for other directions of incidence in the crystal, even  $[110]$  or  $[111]$ , becomes laborious. But one can see in a general way that for long waves  $1/l$  will be roughly of this magnitude for all directions of incidence.

We may also note here that because of the  $1 - \cos \varphi$  factor the bulk of the contribution to  $1/l$  comes from large angle scatterings, the small angle ones contributing very little to it.

In the special case where we can regard the integral of  $S_{\mathbf{r}\mathbf{k}'}$  over all azimuths  $\theta$  to be practically independent of  $t$  — which actually is found, from (16), to be a good approximation <sup>(for sodium and for incidence along [100])</sup> in our crystals, the integral will be just proportional to  $f^2$ .

This will mean for example that the contribution to  $1/\ell$  from scattering in the forward directions ( $0 < \varphi < \pi/2$ ) will be one fourth, and that from scattering in the backward directions ( $\pi/2 < \varphi < \pi$ ) three fourths, of the total contribution.

### § 8. VARIATION OF R WITH THE WAVE-LENGTH $\lambda$

In the region of reciprocal space close to (000), corresponding to  $\lambda \gg 2d \sin \frac{\varphi}{2}$ , the velocities  $V_i$  and the directions of displacement defined by  $A_i$   $B_i$   $C_i$ , and hence also  $R$ , will be independent of the magnitude of the elastic wave-vector  $\vec{K}$  (but will of course depend on the direction of  $\vec{K}$ ). This will not be true, however, when the pole of diffusion  $P$  approaches the boundary of the Brillouin zone. One has a rough idea how at least the velocity varies as one approaches the boundary, which may be taken to indicate in a general way the variation of the displacements also. Calculations have been made by Kellerman (1940) of the <sup>phase</sup> velocities  $V_i$  of the elastic waves in rock salt crystal. Though the velocities decrease as one approaches the boundary, the total drop, even for the [111] direction, for which it is a maximum, is only 25%, and much of this drop is confined to the close neighbourhood of the boundary. Calculations have also been made for tungsten (Fine 1939), and for KCl (Blackman 1937), of the density of distribution of the normal modes of vibration of the crystal, on the frequency scale, i.e.  $\mu(N)$  as a function of the frequency  $N$ , where  $\mu(N)dN$  gives the number of normal modes of vibration whose frequencies lie between  $N$  and  $N+dN$ . Now the corresponding distribution on the  $K$  scale, i.e.  $P(K)$  as function of  $K$ , where  $P(K)dK$  gives the number of normal modes of vibration between  $K$  and  $K+dK$ , is known to be uniform over the whole of the Brillouin zone.

run on

A comparison of the distributions on the two scales, using the simple relations \*

$$N/K = V, \text{ and } dN/dK = G,$$

where  $V$  is the phase-velocity, and  $G$  the group velocity of the elastic waves, gives a rough estimate of the change in the *phase* velocity as we approach the boundary of the zone. These estimates also show that the total drop in the phase-velocity as we approach the boundary is a fraction, of the order of  $1/4$ , most of the change again occurring in the neighbourhood of the boundary. (The group velocity  $G$  will of course diminish much more rapidly than  $V$  in this region, and tend to zero at the boundary of the zone.) The result will be <sup>a corresponding</sup> an excess of scattering in the close neighbourhood of the boundary of the Brillouin zone, which, however, being highly localized, will contribute little to the total scattering taken over all directions.

When we move ~~outside~~ <sup>of</sup> the first Brillouin zone, the value of  $R$ , which is now determined by  $\vec{K}_r$ , will naturally vary not only with the direction of  $\vec{K}_r$  but also with its magnitude, as can be seen from (7). In order to get an idea of the variation of  $R$  in this region, we have calculated for sodium the variation of  $R$  with  $\sin \frac{\phi}{2} / \lambda$  for two directions of  $\vec{K}_r$ , namely  $[100]$  and  $[110]$ . The special advantage of these directions is that for all positions of  $P$  on these lines,  $\vec{K}_r$  can be obtained in a unique way, and the directions of  $\vec{B}$ ,  $\vec{K}$  and  $\vec{K}_r$  are identical (neglecting the sense of the direction) so that  $R$  will continue to be a function of  $\sin \frac{\phi}{2} / \lambda$ , as in the central region

\* In the special case when the medium is non-crystalline and  $P(K) = 3 \times 4\pi K^2$

we obtain

$$\mu(N)dN = 3 \times 4\pi N^2 dN / (V^2 G).$$

The values of R for different positions of P along  $[100]$  and  $[110]$  for sodium crystal, and along  $[100]$  and  $[111]$  for copper ~~crystal~~ are entered in tables II to V. The distances from the origin are expressed in terms of  $1/d_{110}$  for sodium ~~crystal~~, and in terms of  $1/d_{111}$  for copper, i.e. in terms of the distance in reciprocal space of the first Bragg spot from (000).

TABLE II (Sodium crystal)

$K_r$  along  $[100]$

$K_r \cdot d_{110}$	$< .707^* = 1/\sqrt{2}$	0.75	0.80	0.877 <sup>†</sup>
$R \cdot \frac{c_{11}}{e^{-2M} \cdot 2KT}$	1.0	1.31	1.70	2.73

TABLE III (Sodium crystal)

$K_r$  along  $[110]$

$K_r \cdot d_{110}$	$< 0.5^*$	0.55	0.60	0.70	0.80	0.85	0.877 <sup>†</sup>
$R \cdot \frac{c_{11}}{e^{-2M} \cdot 2KT}$	0.60	0.89	1.34	3.12	9.55	19.2	30.5

TABLE IV (Copper crystal)

$K_r$  along  $[100]$

$K_r \cdot d_{111}$	$< 0.58^* = 1/\sqrt{3}$	0.60	0.70	0.80	0.90 <sup>†</sup>
$R \cdot \frac{c_{11}}{e^{-2M} \cdot 2KT}$	1.0	1.17	2.36	5.08	12.6

TABLE V (Copper crystal)

$K_r$  along  $[111]$

$K_r \cdot d_{111}$	$< 0.5^*$	0.55	0.60	0.70	0.80	0.85	0.90 <sup>†</sup>
$R \cdot \frac{c_{11}}{e^{-2M} \cdot 2KT}$	.71	1.06	1.60	3.72	11.4	22.8	58.8

\* These values of  $K_r$  correspond to the upper limit of the first Brillouin zone. For values of  $K_r$  both greater ~~or~~ smaller than this limiting value, but not close to it, R can be calculated on the basis of formula (8), and the values entered in the Table are those calculated on the basis. When  $K_r$  is close to this limiting value, the value of R given by (8) will be too low, as we mentioned earlier in this section.

† These values of  $K_r$  correspond to backward scattering ( $\varphi = \pi$ ) of electrons having the Fermi wave-length.

~~The gap in the middle of the curve corresponds to the region adjoining the boundary of the zone, in which region, as we mentioned, our calculation of R on the basis of formula (8) is uncertain.~~

9. THE ATOM FORM FACTOR  $\Delta$  AND ITS VARIATION WITH  $\varphi$

We have seen that for the Fermi wave-length the sphere of propagation extends much beyond the first Brillouin zone, and that for the regions on the sphere remote from (000), R may vary rapidly. Though this will be the major factor affecting S, two other factors also affect it considerably.

(1) the factor  $e^{-2M}$ , which in the region near (000) is practically unity, will now be appreciably less, and will diminish with increase of  $\varphi$ . For sodium crystal at room temperature (300°K), and for its Fermi wave-length  $\lambda = 2.28d_{110} = 6.93 \text{ \AA} (3.12 \text{ eV})$ ,  $e^{-2M} = e^{-0.27 \sin^2 \frac{\varphi}{2}}$  decreases by about 26% as we pass from the forward to the backward direction;

(2) the atom form factor  $\Delta$ , which in the region near (000) is practically independent of  $\varphi$ , will not be so now. Knowing, however, the Fermi wave-length  $\lambda$ , and the electronic distribution in the atoms of these metals, it is possible theoretically to calculate the variation of  $\Delta$  with  $\varphi$ . The calculation is rather laborious. But we can get the data concerning the variation of  $\Delta$  with  $\varphi$  required for our present purpose from the extensive measurements made by Ramsauer and Kollath (1932) on the scattering coefficients  $S_\varphi$  of rare gases for different angles of scattering  $\varphi$  and for different wave-lengths  $\lambda$ . The scattering medium in those experiments being gaseous, these data give directly the atom form factors  $\Delta_\varphi$ , since  $\Delta_\varphi = S_\varphi / \nu$ . The data for <sup>neon gas</sup> ~~the~~ for 3.12  $\times$  volt electrons, i.e. ~~of~~ <sup>for</sup> electrons having the same wave-length as the Fermi electrons in sodium metal, are given in the following table.

\* The value  $2M = 0.27 \sin^2 \frac{\varphi}{2} / \lambda^2$  given ~~TABLE~~ ... here is on the basis of the Debye temperature of Sodium being 150 K.

TABLE VI.

$\varphi$ in degrees	$\Delta_{\varphi}$ in $\text{\AA}^2$	$\varphi$ in degrees	$\Delta_{\varphi}$ in $\text{\AA}^2$
15	0.220	105.5	0.148
28	.214	121	.131
43	.218	137	.120
59	.220	152	.117
74.5	.207	167	.112
90	.173		

It will be seen from the table that  $\Delta_{\varphi}$  is practically independent of  $\varphi$  up to about  $\varphi = 75^{\circ}$ , after which it drops down, ~~to~~ <sup>reaching</sup> about half the value <sup>at about  $\varphi = 125^{\circ}$</sup>  and remains <sup>wards</sup> after ~~it~~ practically constant at this value. The general variation of  $\Delta_{\varphi}$  with  $\varphi$  <sup>(electrons, but also for electrons having energies in the neighbourhood</sup> observed here holds not only ~~for~~ <sup>too.</sup> for 3.12 volt of this value, and for other rare gases. We may, therefore, take this result to be applicable to the scattering atoms in the alkali metals also, and to a rough approximation take  $\Delta_{\varphi}$  to be constant and equal to  $\Delta_1$  over the whole of the range  $0 \leq \varphi \leq \varphi_0$ , and again constant and equal to  $\Delta_2 = \Delta_1/2$  over the remaining angles of scattering  $\varphi_0 < \varphi \leq \pi$ , where  $\varphi_0$  is about ~~100~~  $100^{\circ}$ .

10. CALCULATION OF  $\tau$  FOR THE FERMI ELECTRONS IN SODIUM CRYSTAL.

We now proceed to calculate  $1/l$  for one typical crystal, namely sodium, and for its Fermi wave-length of 6.93A, when the direction of incidence is along (110), i.e to evaluate the integral

$$1/l = \int_{\varphi=0}^{\pi} \int_{\theta=0}^{2\pi} S_{kk'} (1 - \cos \varphi) \sin \varphi d\varphi d\theta$$

over the whole of the corresponding sphere of propagation. The value of  $1/l$  will be a maximum for this direction of incidence in the alkali metals. For the purpose of the integration we split the surface of the sphere into two parts, namely that included in the central zone, and that outside respectively. The critical angle of scattering  $\varphi_0$  defining the transition from the former to the latter region is about  $98^{\circ}$ , corresponding..

corresponding to (see Section 7)  $f_0 = 1 - \cos 98^\circ = 1.14$ , and in view of the remarks made at the end of the previous section we may to a first approximation take  $\Delta_\varphi$  to be constant and equal to  $\Delta_1$  over the whole of the former part,  $0 \leq \varphi \leq 98^\circ$ , ~~over~~ and again constant and equal to  $\Delta_2 = \Delta_1/2$  ~~over~~ the latter part  $98^\circ < \varphi \leq \pi$ , the average value of  $\Delta$  over the whole of the sphere being given by

$$\bar{\Delta} = \sigma/4\pi = (1.14\Delta_1 + 0.86\Delta_2)/2 = 0.79\Delta_1. \dots$$

Let us denote by  $(1/l)_1$  the contribution to  $1/l$  from the part of the sphere included in the first Brillouin zone, corresponding to  $0 \leq \varphi \leq 98^\circ$ , and by  $(1/l)_2$  the contribution from the part of the sphere that lies outside the first zone ~~and~~ ~~corresponding~~ ~~ing~~ to  $98^\circ < \varphi \leq \pi$ .

The calculation of  $(1/l)_1$  is done immediately. Since  $(1/l)_1$  ~~which~~ is the contribution to  $1/l$  from forward scattering ~~and~~ ~~is~~ a ~~very~~ small part of  $1/l$ , we may in view of (23) take it to be just  $(f_0/2k)^2$  times the value of  $1/l$  for the complete sphere of propagation, the whole of the sphere being taken for this purpose to be well within the first Brillouin zone, or

$$\begin{aligned} (1/l)_1 &= v^2 k T \cdot 4\pi \Delta_1 (0.76/c_{11}) \cdot (1.14 R/2k)^2 \\ &= 0.31 v^2 k T \sigma / c_{11}. \dots (28) \end{aligned}$$

The contribution to  $1/l$  from the part of the sphere outside the central zone, which we have denoted by  $(1/l)_2$ , and which is the major contribution to  $1/l$ , is calculated in the following manner, remembering that in this region also  $\Delta$  may be taken to be independent of  $\varphi$ , but equal to  $\Delta_2$ . The major factor that determines variation of  $S$  in this region will be the variation of  $R$ , which will be particularly marked in the regions of the sphere facing the reciprocal point (110). Jahn has discussed in the case of X-rays the variation of  $R$  for scattering by sodium crystal, for different positions of  $P$  in the neighbourhood of the reciprocal point (110), and has investigated in particular the shape of the 'isodiffusion'

~~29~~

surfaces, i.e. the loci of P corresponding to different constant values of the coefficient  $R_e$ . The portions of these isodiffusion surfaces in the neighbourhood of the line  $[110]$  and the reciprocal point  $(110)$ , are found to be portions of highly oblate ellipsoids, with their short axis along  $[110]$ , and hence the ~~portions~~ <sup>intersections</sup> of these surfaces ~~included in~~ <sup>with</sup> the sphere of propagation will be ~~practically~~ practically planes perpendicular to the above line and perpendicular to the plane of the paper in Fig. 4.

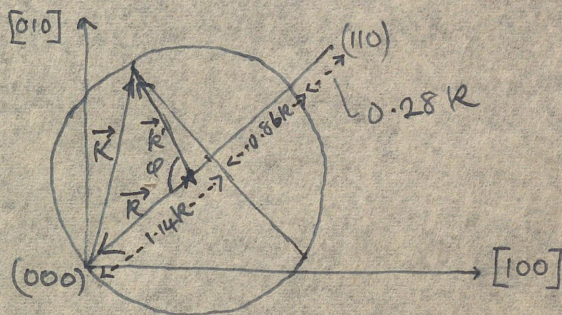


Fig. 4

In order to give an idea how flat these surfaces are, we give in Table VII for a few of the isodiffusion ellipsoids surrounding  $(110)$ , the magnitudes of the semi-axes along the three principal directions of the ellipsoid, which are also the directions of displacement  $\vec{e}_i$ , I along  $[110]$ ; II along  $[\bar{1}10]$ ; and III along  $(001)$ . The semi-axes are all expressed in terms of  $\sqrt{R} = 1/(2.28d_{110})$  as unit. (The shortest distance from  $(110)$  to the surface of the sphere of propagation is  $0.28k$ .) The calculation of the axes is based on the data for the elastic constants of sodium crystal given in Section 7.

TABLE VII

Semi-axes of some of the isodiffusion ellipsoids

(around  $(110)$  and close to their  $[110]$  axes

I	II	III	$R_e = \frac{c_{11}}{e^{2M} \cdot \nu RT}$
0.28	1.23	0.48k	30.5
0.4	1.90	0.73	13.2
0.5	2.55	1.00	7.6
0.75	4.90	2.10	2.48
0.9	7.06	4.04	1.40
1.0	10.89	..	0.98

It will be seen that the II and III semi-axis are much greater than I, especially as we move out some distance from  $(110)$  and as the area of intersection of these isodiffusion surfaces....

surfaces with the sphere of propagation expands; and hence we may take these intersections practically as planes perpendicular to  $[110]$ .

This feature of the isodiffusion surfaces makes the computation of the structure factor  $R_q$ , and the scattering coefficient  $S_q$ , for the portions of the sphere of propagation outside the central Brillouin zone, and facing  $(110)$ , and the numerical integration of  $S_q(1-\cos\varphi)$  over this region of the surface of the sphere, easy; since for the purpose of this integration we may divide the surface of the sphere in the neighbourhood of B into zones of equal area, by equally spaced planes perpendicular to  $[110]$ . In other words  $S$  in this region, ~~besides being a function of  $\varphi$~~ , is determined wholly by the distance  $fK$  from  $(000)$  measured along  $[110]$ , where  $f = 1 - \cos\varphi$ ,  $90^\circ < \varphi \leq \pi$ .

On this basis expression (7) for  $R$ , for the part of the sphere outside the central zone at a distance  $fK$  from  $(000)$  measured along  $[110]$  will be given by

$$R = e^{-2M} \cdot \frac{\nu K T}{\rho V_l^2} \left( \frac{K_r}{K} \right)^2$$

$$= e^{-2M} \cdot \frac{\nu K T}{\rho V_l^2} \left( \frac{f}{2.28-f} \right)^2 \quad (\text{of wave-number } K)$$

where  $V_l$  is the velocity of the longitudinal elastic wave travelling along  $[110]$ , and is given by (see (12))

$$\rho V_l^2 = (c_{11} + c_{12} + 2c_{44})/2,$$

which for sodium crystal becomes  $c_{11}/0.60$ . Hence we obtain

$$R = e^{-2M} \cdot \nu K T (0.60/c_{11}) \cdot f^2 / (2.28-f)^2$$

and

$$(1/l)_2 = \int_{\varphi_0}^{\pi} R \nu S_2 (1-\cos\varphi) 2\pi \sin\varphi d\varphi$$

$$= \frac{\nu^2 K T \sigma}{c_{11}} \cdot 0.190 \int_{0.14}^2 e^{-2M} \frac{f^3 df}{(2.28-f)^2}$$

The integral can be evaluated numerically, and is found to be equal to about 12.0, whence we obtain

$$(1/l)_2 = 2.28 \nu^2 K T \sigma / c_{11}$$

Hence  ~~$1/l = 2.59 \nu^2 K T \sigma / c_{11}$~~

BEESWING MANIFOLD

$$(1/l)_2 = 2.3 v^2 R T \sigma / c_{11} \dots\dots\dots(33)$$

From (28) and (33) we obtain

$$\begin{aligned} 1/l &= (1/l)_1 + (1/l)_2 \\ &= 2.6 v^2 R T \sigma / c_{11} \dots\dots\dots(34) \end{aligned}$$

Though the above method of calculating  $(1/l)_2$  by taking the intersections of the sphere of propagation by the iso-diffusion surfaces to be planes is a good approximation, it can be readily seen that it is on the side of an over-estimate, since  $R$  will fall off slightly more rapidly as we move away from (110) than is implied in the above approximation. Hence we may express  $1/l$  for the Fermi electrons in sodium crystal in the form

$$1/l = \Phi \cdot v^2 R T \sigma / c_{11}, \dots\dots\dots(35)$$

where for incidence along  $[110]$ ,  $\Phi$  is slightly less than 2.6, which as we mentioned is the highest value of  $\Phi$  for any direction of incidence of the Fermi electrons.

#### 11. INCIDENCE OF FERMI ELECTRONS ALONG $[100]$

The calculation of  $\Phi$  for other directions of incidence of the Fermi electrons is more laborious, but one can see in a general way that in a body-centred cubic crystal, just as  $\Phi$  is a maximum for incidence along  $[110]$ , it is a minimum for incidence along  $[100]$ . For the latter direction of incidence the portion of the sphere of propagation that is included in the first Brillouin zone varies with the azimuthal plane of scattering, and for (001) and similar azimuthal planes corresponds to  $0 \leq f \leq 0.66$ . Now the structure factor  $R$  does not reach a high value in any part of the sphere of propagation, as it does when the incidence is along  $[110]$ , the highest value of  $R c_{11} / (e^{-2M} \cdot v^2 R T)$  now reached being only 2.7 (see Table II), for the backward direction of scattering, i.e. for  $f = 2$ , and falling down to unity as we move back to the boundary of the Brillouin zone. The above value of  $R$  would correspond to

$$\begin{aligned} S_{\text{Max}} &= e^{-0.27} \cdot 2.7 v^2 R T \sigma_2 / c_{11} \\ &= 1.3 \frac{v^2 R T \sigma}{c_{11}} \cdot \frac{\sigma}{4\pi} \end{aligned}$$

Hence for this direction of incidence  $\Phi$  should lie between 1.3 and 0.76, and a rough estimate shows it is about 1.1.

12. THE AVERAGE VALUE OF  $1/l$  TAKEN OVER ALL DIRECTIONS OF INCIDENCE

Having fixed the approximate upper and lower limits for  $\Phi$ , namely 2.6 and 1.1, for incidence of the Fermi electrons along  $[110]$  and  $[100]$  respectively, it now remains to determine the average value of  $\Phi$  taken over all directions of incidence of these electrons. The high value of  $\Phi = 2.6$  for incidence along  $[110]$  is due to the close proximity of the extreme outer regions of the sphere of propagation to the reciprocal lattice point  $(110)$ ; indeed of the total value of 2.6 for  $\Phi$  for this direction of incidence, about 1.7 is contributed by the small region  $1.75 < f < 2$ , the rest of the sphere, namely  $0 \leq f \leq 1.75$ , contributing about 0.9 only. Hence as the direction of incidence is varied even slightly away from  $[110]$ ,  $\Phi$  will drop down considerably, and hence one can reasonably take the average value of  $\Phi$  to be very close to its minimum value of 1.1, and take the mean value of  $1/l$  or  $1/v\tau$  required <sup>for the</sup> ~~in~~ calculating <sup>on</sup> ~~of~~ the specific resistance <sup>a</sup> of sodium to be given by

$$\overline{1/l} = \overline{\Phi} \cdot v^2 k T \sigma / c_{11}$$

where  $\overline{\Phi}$  is about 1.2 or 1.3.

Till now we ~~have~~ <sup>have</sup> expressed  $1/l$  <sup>for sodium</sup> in terms of ~~the~~ its elastic constant  $c_{11}$  ~~of the cubic crystal~~. We may also, for convenience, express it in terms of ~~the~~ <sup>its</sup> compressibility  $\beta$ , which in a cubic crystal is given by

$$\beta = 3 / (c_{11} + 2c_{12}),$$

and which in sodium ~~crystal~~ is equal to  $3 / (2.54c_{11}) \neq 1.18/c_{11}$ . The mean free path  $1/l$  can then be expressed in the form

$$\overline{1/l} = \Psi \cdot v^2 k T \beta \sigma, \quad \dots (35)$$

where  $\Psi$  is a numerical factor, which in sodium crystal <sup>(will be seen to be)</sup> is close to unity. With  $\Psi = 1$ , one can easily recognise the right-hand side of equation (35) to be just <sup>the</sup> Einstein -

Smoluchowski expression for the attenuation coefficient of a liquid medium for long waves.

Now in a liquid, the local inhomogeneities produced by thermal agitation, which ultimately account for the scattering, is represented almost wholly by the local fluctuations in density. In a crystalline medium, however, the local inhomogeneities, which produce scattering will naturally be more complicated, and will involve, besides the compressibility  $\beta$ , the other elastic constants too. As a result of this, in sodium crystal, and for small values of  $\sin \frac{\varphi}{2} / \lambda$ , the structure factor  $R$  is considerably less than the Einstein value, almost half of it when  $\vec{K}$  is along  $[110]$ . On the other hand when the pole of diffusion  $\vec{K}$  moves out of the first Brillouin zone,  $R$  as we have seen rises above the Einstein value, and for certain directions of incidence, and in the neighbourhood of the backward direction, becomes several times the Einstein value. But since these high values are highly localized their contribution to  $1/\ell$  is not so large. Indeed the average value of  $1/\ell$  for the Fermi electrons, (as we have seen, is) gives roughly just the Einstein value, as though we might regard the mean free path  $\ell$  of the Fermi electrons in sodium to be just the reciprocal of the attenuation coefficient due to scattering, and the scattering to be determined almost wholly <sup>by the</sup> local thermal fluctuations in density.

This simple approximation is a result of the rough balancing of the different varying factors that determine the mean free path,  $R$  and  $1 - \cos \varphi$  increasing, <sup>and  $e^{-2M}$</sup>  and  $\Delta \varphi$  decreasing, as we pass from the forward to the backward directions of scattering.

Had  $\lambda$  been considerably shorter, i.e. had the Fermi surface been much closer to the boundary of the Brillouin zone, owing to the rapid increase of  $R$  as one approaches the boundary, and the consequent increase of the scattering

coefficient  $S$ , the free path and the relaxation time would be much shorter. The result would be <sup>correspondingly</sup> an enhanced specific resistance.

In the usual treatment of the electrical resistivities of metals (~~Bloch, 19~~) for convenience in calculation, the medium is regarded as elastically isotropic, and the longitudinal thermal elastic waves alone as contributing to the scattering, which is equivalent to regarding the scattering as produced by the fluctuations in density due to thermal agitation. The detailed calculations made in the present paper show that in sodium metal, this is a good approximation, and it is presumably so in other monovalent metals too.

Now the Fermi wave-length  $\lambda$  <sup>(as we have seen,)</sup> is not much longer than ~~that~~ necessary to give the first Bragg reflection in the backward direction, i.e. ~~through~~  $\lambda$  is not much longer than  $2d$ . Even so, it was shown in an earlier paper (Krishnan and Bhatia, 1944) from certain general considerations, that it should be regarded as long enough for the Einstein formula — which is derived explicitly on the basis of  $\lambda$ 's being very long in comparison with the interatomic distance — to be applicable. The present calculations show that the intensity of scattering, particularly along the backward direction will deviate considerably from the Einstein value, <sup>but</sup> the total scattering in all directions, i.e. the attenuation coefficient, <sup>(remains roughly at this value.)</sup> ~~does not.~~

### 13. FERMI SURFACE CLOSE TO THE BOUNDARY OF THE BRILLOUIN ZONE

We have already emphasised that if the electronic wave-length were to be reduced considerably below the Fermi value, the total scattering, and hence the specific resistance, would increase very rapidly. This would be attributed in the usual theory of electrical conduction in metals to the approach of the Fermi surface to the boundary of the Brillouin zone, and the consequent enhanced influence

of the ionic lattice on the freedom of movement of the electrons. The effect <sup>would be</sup> ~~is~~ regarded as equivalent to either an increase in the effective mass of the electron near the boundary of the zone, or a decrease in the effective number of conduction electrons, whereas from the point of view ~~of~~ adopted in the present paper the effect is an enhanced scattering and a corresponding reduction in the mean free path, ~~and in the relaxation time~~ of the Fermi electrons. All the three alternatives are of course ~~be~~ equivalent, and correspond to an enhanced specific resistance. But the view-point adopted here, which regards the enhancement of the resistance when the Fermi surface approaches any of the reciprocal points as due to enhanced scattering of the Fermi electrons, has certain advantages, especially in dealing with the electrical resistivities of liquid metals. <sup>(Krishnan and Bhatia 1942)</sup> We postpone detailed consideration of this aspect to a separate paper.

REFERENCES

- Blackman, M. 1937 Proc. Roy. Soc. A, 159, 416.
- Darwin, C.G. 1914 Phil. Mag. 1, 315.
- Debye, P. 1914 Ann.d. Physik. 43, 49.
- Einstein, A. 1910 Ann.d. Physik 33, 1294.
- Faxén, H. 1923 Z. Phys. 17, 266.  
 \_\_\_\_\_ *and Holtsmark*
- Fine, P.C. 1939 Phys. Rev. 54, 355.
- Jahn, H.A. 1942 Proc. Roy. Soc. A, 178, 320.  
*Jauncey See Compton and Allison,*
- ~~Jauncey~~ Kellerman, E.W. 1940 Phil. Trans. Roy. Soc. A, 238, 513
- Krishnan, K.S. and Bhatia, A.B. 1944 Proc. Nat. Acad. Sc., India  
 \_\_\_\_\_ (14 153  
 \_\_\_\_\_ 19 *Nature*  
 \_\_\_\_\_ 1947 in course of publication.
- Quimby, S.L. and Siegel, S. 1938 Phys. Rev. 54, 293.
- Raman, Sir C.V. 1941 Proc. Ind. Acad. Sc. 13, 1.
- Raman C.V. and Ramanathan, K.R. 1923 Phil. Mag. 45, 213.
- Ramsauer, C. and Kollath, R., 1932 Ann. d. Physik. 12, 529.
- Waller, I. 1923 Z. Phys. 17, 398.  
 " " 1925 Diss. (Uppsala).  
 " " 1928 Z. Phys. 51, 213.