Ya I Frenkel's studies of the theory of the electric conductivity of metals

R A Suris, V Ya Frenkel'

Abstract. The bulk of this contribution is a paper by Ya I Frenkel' on the theory of the electric conductivity of metals, written in 1928 and published in the same year in Uspekhi Fizicheskikh Nauk. Much of this paper is based on the original results of Frenkel' himself obtained in the years 1924–1927. An introductory section provides a brief review of Frenkel's main investigation in the fields of quantum mechanics and the kinetic theory of he condensed state, applied to specific problems in physics. Frenkel's paper is accompanied by necessary comments relating mainly to the current state of the art of the subject.

Much has been written about Yakov II'ich Frenkel' [1-3], including also in *Uspekhi Fizicheskik h Nauk* [4, 5]. We shall therefore preface Frenkel's paper with just a brief biographical sketch.

Yakov Il'ich was born on 10 February (new style) 1894 in Rostov-on-Don in a family of an office worker. His father had been a member of the 'Narodnaya Volya' ('People's Freedom') organisation and had spent seven years in Siberian exile because of this activity. In 1913, after finishing the well-known K Mai high school in St Petersburg, Frenkel' entered the St Petersburg University in the Physicomathematical Faculty. He completed a full course in three years and stayed to train for a university teaching job. In the autumn of 1917 Yakov Il'ich passed in record time all the relevant examinations and was awarded a Master's degree.

This helped him to gain in 1918 the position of a privatdozent (unestablished university lecturer) at the Tauric University in Simferopol. He worked there for three years. The very hard conditions during the Civil War in Crimea were aggravated in Frenkel's case by his imprisonment for participating in the government of the Tauric Republic: he worked as Deputy People's Commissar of Education and was a member of the editorial board of the newspaper *Krasnyi Krym* (Red Crimea). Frenkel' was arrested by the intelligence service of Denikin's Army and spent a few months in prison. When he left prison he was prevented from continuing his teaching. One should mention also the practically complete isolation of Crimea from St Petersburg (at that time called Petrograd) and Moscow, where new physics schools began to evolve

R A Suris, V Ya Frenkel' A F Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politekhnicheskaya ul. 26, 194021 St Petersburg

Received 29 December 1993 Uspekhi Fizicheskikh Nauk **164** (4) 379–396 (1994) Translated by A Tybulewicz rapidly beginning from 1918. This is the reason why, after a successful start in St Petersburg, the subsequent scientific achievements of Frenkel' were very modest. He did however gain teaching experience and, moreover, established professional and personal relationships with outstanding scientists working in Simferopol: the mathematicians N M Krylov and V I Smirnov, the physicist I E Tamm, the biologist A G Gurvich and A A Lyubishchev, and the literature specialist N K Gudzii.

In March 1921 Frenkel' returned to Petrograd and began to work simultaneously at the Physicotechnical Institute (in his absence he was elected a staff member and researcher back at the time of foundation of the Institute in 1918-see p. 73 in Ref. [1]) and in the Physicomechanical Faculty of the Polytechnic Institute. He soon became head of the Theoretical Division at the Physicotechnical Institute (PTI) and held the Chair of Theoretical Physics at the Polytechnic Institute. All the scientific activities of Yakov Il'ich took place at these two institutes which could justifiably be regarded as the leading scientific and teaching centres for physics during the first quarter of a century of the existence of the USSR. At various times Frenkel' worked simultaneously at the Institute of Chemical Physics, the Main Geophysical Observatory in Leningrad, the Institute of Theoretical Geophysics, the All-Union Institute of Aviation Materials in Moscow, and Kazan University.

Frenkel' travelled several times abroad: in 1925-1926 he went to Germany, France, and England as a Rockefeller Foundation fellow; in 1930-1931 for ten months he was a visiting professor at the Minnesota University in the USA, and in 1927 he spent two months in Italy and France.

Frenkel' became professor when still in Crimea at the end of 1920 and was elected a corresponding member of the Academy of Sciences in 1929 together with his friends and colleagues P L Kapitza and N N Semenov, who had been his colleagues at A F loffe's seminar on new physics held in Petrograd (1916–1917), and then at the PTI. This was the end of the official career of Yakov Il'ich. To a considerable extent this was because of his uncompromising struggle with the official Marxist philosophy, which had imposed restrictions on the development of theoretical physics, and even physics as a whole, in the thirties and forties.

Censorship has prevented inclusion of these aspects of Frenkel's biography in the books cited earlier [1-3]. Therefore, we shall try (at least briefly) to give an account of his relationships with the official Soviet philosophy. When visiting the USA in the early thirties, Yakov Il'ich had tried to gain the attention and sympathy of American scientists and intellectuals for his mother country, and particularly to the policy of the development of science



Yakov Il'ich Frenkel', Leningrad, 1936

and culture, which has undoubtedly had a major positive impact. In his own words, on return home this gave him the right to criticise sharply the distortions of such policy which he saw with a 'fresh eye'. At that time such policy distortions in science affected most strongly the physicists because of the attempts of Marxist philosophers to impose the dogma of Marxist–Leninist philosophy. In the opinion of and in accordance with the demands of the heralds of this philosophy, it should direct and control the development of new physics, particularly quantum mechanics and relativity theory. These philosophers rejected almost completely the universally recognised achievements of these fields of physics.

At the Third Physicochemical Conference, held in November 1931, Frenkel' spoke against such guardianship of physics. The published proceeding of this Conference make no mention of his speech. However, in the subsequent publications of these philosophers, above all those of A A Maksimov, there have been frequent citations of Frenkel's opinions. It has been found subsequently that these citations have been based on the minutes of a special meeting of the Conference Communist Party Group, held on 14 November. Frenkel' was called to this meeting and, in answer to questions from some philosophers among the members of this Group, stated that "The dialectical method has no right to claim the leading role in science" and that what he "read in the works of Lenin and Engels could not change [his] gnosiological views." In reply to a direct question from the chemist S A Balezin "Is it possible to conclude from your statement that dialectical materialism is an obstacle in the development of science and particularly natural science?" Frenkel' replied "Yes, it is an obstacle, at least in the dogmatic form in which it is taught now." He also added, in answer to another question, that "I am not enthusiastic about what I read in the books of Engels and Lenin. Neither Lenin nor Engels are authorities for physicists" (p. 141 in Ref. [6]).

Yakov Il'ich confirmed later his negative attitude to the regime of Arakcheev, which the official philosophers tried to impose on physics. He did this in the middle thirties when the journal Pod Znamenem Marksizma (Under the Banner of Marxism) launched a campaign of defamation (with a clear political slant) of a number of Soviet physicists including S I Vavilov, A F Ioffe, L D Landau, I E Tamm, V A Fok, Ya I Frenkel', and some others. The majority of these leading physicists responded with dignity to this 'criticism' and defenced with courage modern physics from the attacks of the 'physics ignoramuses' such as A A Maksimov, V F Mitkevich, and others. It was surprising not to find Yakov Il'ich among those who answered the attacks, since he had the reputation of a resolute and uncompromising person, as often confirmed later by his colleagues and friends [2]. The answer to this puzzle has been found in the archives[†]. A A Maksimov's papers have been found to include an article by Ya I Frenkel' counterattacking Maksimov and others with him so strongly that the editors of the journal Pod Znamenem Marksizma refused to publish it (this article has been published quite recently; see Ref. [7]).

The spectrum of Frenkel's scientific interests was exceptionally wide and included classical electrodynamics, electron theory, quantum mechanics, kinetic theory of solids and liquids, optics of crystals, physics of semiconductors, nuclear physics, as well as astrophysics, biophysics, and geophysics. He belonged to the galaxy of polymath scientists who have now passed away and whose kind would be hard to find in the history of physics of our country.

To conclude, we must mention that Frenkel' was the founder and continued to be the leader, right to his last days, of the first seminar on theoretical physics, in the USSR. This seminar met weekly at the PTI. Frenkel' was the author of the first complete course of theoretical physics (theoretical mechanics, electrodynamics, statistical physics, wave mechanics) written in 1925-1940 and published fully in Russian, as well as partly in German and in English. He wrote a total (apart from translations and new editions) of 22 monographs and over 200 scientific and popular papers.

Yakov Il'ich Frenkel' died at night on 23 January 1952.

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The above list of active scientific interests of Ya I Frenkel' can be grouped into three main trends, which have attracted him practically throughout the whole period of his scientific work. The first was the physics of real crystals (Frenkel defects, Frenkel solitons, theory of strength) and the kinetic theory of liquids. The problems in these branches of physics occupied Yakov II'ich beginning from 1923 to the end of his life. In his autobiography, published in 1946, he wrote decisively: "Although I have been concerned with a number of problems belonging to different branches of physics, physical chemistry, and geophysics, the mainstream of my work has been the

†G A Savina (staff member of the Archives of the Russian Academy of Sciences, Moscow) kindly drew our attention to this article (which exists in typescript form).



Ya I Frenkel' lecturing at the Physicomechanical Faculty of the Leningrad Polytechnic Institute, 8 March 1937.

structure of matter, particularly of liquids and solids" (p. 470 in Ref. [2]).

The second of his main preoccupations have been the problems in nuclear physics. The master thesis of Yakov Il'ich, published in three issues of *Zhurnal Russkogo* Fiziko-Khimicheskogo Obshchestva, Chast' Fizicheskaya (Journal of the Russian Physicochemical Society, Physical Part) in 1917–1919 [8] was then, and for a long time after, the fullest scientific review of the subject in the Russian physics literature of the time. Frenkel' was most active in nuclear research in the years 1936–1939 (developing the concept of the temperature of nuclei and applying the ideas of statistical physics to the description of nuclei, proposing an electrocapillary theory of fission), but this continued well into the late forties.

The last but not the least was his interest in the electron theory of solids. This included quantum (1924) and wavemechanical (1927–1928) theories of metallic conduction, a theory of paramagnetism and ferromagnetism (1927–1930), physics of semiconductors and insulators, and physics of quasiparticles which have become known as the Frenkel excitons (1931–1936). Frenkel' continued work on these subjects also later and gave a full account of the majority of his results in the second edition of his book *Vvedenie v Teoriyu Metallov* (Introduction to the Theory of Metals), which had ten editions in Russian and foreign languages.

In 1967 on the occasion of the fiftieth anniversary of the October Revolution Uspekhi Fizicheskikh Nauk published

in two issues [9-10] the most important papers of Soviet physicists. Yakov Il'ich was represented in these jubilee issues by his paper on excitons [11]. This tradition was followed by a jubilee issue of *Uspekhi Fizicheskikh Nauk* published on the occasion of the 75th anniversary of the foundation of the journal [12][†].

When planning to present Frenkel's contribution to the theory of metals on the centenary of his birth we decided, in a sense to supplement Ref. [12] and to reproduce here Frenkel's review "Theory of metallic conduction" written at the invitation of the editorial board of *Uspekhi Fizicheskikh Nauk* in 1928 and presenting an extended summary of his own results [13]. We decided to introduce this paper by this short biographical note and to follow it by a number of appendices and comments. We hope that these additions will not be regarded as intrusions into Frenkel's text and will help to guide the reader to some of the early original work of Frenkel' as well as to some of the subsequent trends of research in this branch of physics.

The physics of metals can be regarded as a kind of a proving ground where new physical principles are being tested. The concept of free electrons has been developed by Drude. His theory has been refined by Lorentz, who took into account the Maxwellian distribution of the electron velocities in a metal. Then, in 1924, Frenkel' applied the Rutherford – Bohr model of an atom to an electron gas and was thus able to resolve the paradox of the nonparticipation of free electrons in the specific heat of metals, which was called the 'specific heat catastrophe' by P S Ehrenfest[‡].

Two new approaches to the problem of the electric conductivity of metals were proposed in 1927. Both were presented at the A Volta Memorial Congress held in Como in 1927 on the centenary of Volta's death. One approach, proposed by A Sommerfeld, was related to the fundamental—for the theory of metals—transition from the Maxwell–Boltzman classical statistics to the Pauli–Fermi quantum statistics. The other, put forward by Ya I Frenkel', was based on a direct extension of the ideas of de Broglie on the wave process, associated with the motion of electrons in empty space, to electrons moving in a metal. The stages of the development of this approach are described in the paper of Yakov II'ich published in 1928 and reprinted below§.

We are very indebted to V I Perel' for valuable comments and suggestions which he made in the course of a review of the material presented here.

\$This paper of Ya I Frenkel' is the core of the article presented here. The general list of references appended at the end includes the main papers of Yakov II'ich on the theory of the electric conductivity of metals as well as some more general work on the physics of metals where detailed discussions are given of the relevant problems [16–28].

[†]None of the papers of Yakov Il'ich, who published 17 of them in *Uspekhi Fizicheskikh Nauk* between 1924 and 1951, have been reprinted in this issue.

[‡]It is appropriate to point out here that Frenkel' was the first to apply the ideas of Rutherford and Bohr on the nuclear model of atoms to contact phenomena in metals. A theory he developed in 1916 made it possible in particular to provide a theoretical basis of the Volta sequence of metals (Volta series) in which each metal acquires a positive charge when brought into contact with the next term of the series. An interesting assessment of this paper of Yakov II'ich was given by T P Kravets (p. 74 in Ref. [1]). The relevant papers of Frenkel', which were published simultaneously in 1917 in Russia [14] and in England [15] and had become widely known, served in 1927 as one of the reasons for inviting Yakov II'ich to the Volta Memorial Congress in Como.

Theory of metallic conduction

Ya I Frenkel' (Leningrad)[†]

1. Drude theory

The main and most characteristic property of metallic materials is their electric conductivity. The electric conductivity of metals not only is quantitatively much higher than the conductivity of any of the other materials, but it also differs qualitatively. The passage of a current through a metal is not accompanied by the transport of matter in the ordinary sense of that word, in contrast to what happens in electrolytes. This property of the metallic electric conductivity has been explained soon after the appearance of the electric theory by the postulate that electricity is transported in metals not by ions, i.e. not by charged atoms or groups of atoms, but by 'free' electrons which become separated from the individual atoms and move independently. Drude was the first to formulate quantitatively the theory of free electrons. Drude based his theory on an analogy between the motion of free electrons in a metal and the motion of molecules in a gas. In both cases the particles (electrons or molecules) are not bound at specific equilibrium positions, but move over the whole volume occupied by the investigated body; the difference is only that gas molecules are confined within this volume by solid walls of some vessel, whereas in a metallic body the role of these walls is played by its surface.

This circumstance by itself does not yet provide grounds for drawing the analogy between electrons in a metal and gas molecules (for example, in liquids again molecules are not bound at some equilibrium positions). Moreover, there is every reason to assume that free electrons experience, in contrast to gas molecules, enormous forces which are exerted on them by atoms, positive ions, and other electrons and which continuously bend their paths. The gas molecules, on the other hand, usually move rectilinearly and uniformly in the intervals between very brief collisions. Therefore, the identification of the motion of free electrons with the motion of molecules in a gas has no reasonable basis. It was introduced by Drude mainly, if not exclusively, in order to simplify his calculations.

Drude left open the question of the number of free electrons n (per unit volume) and of the mean free path l, selecting *a priori* only their mean-square velocity v, defined by the familiar equation

$$\frac{1}{2}mv^2 = \frac{3}{2}kT , (1)$$

where k is the Boltzmann constant and T is the absolute temperature. It then immediately follows that the number of free electrons should be very small compared with the number of neutral atoms which hold firmly on to their own electrons. Otherwise the heat capacity of metals would have been considerably greater than the value (6 calories per one gramme-atom), which is predicted by the Dulong-Petit law and which follows from the theorem on the equipartition of energy. This theorem of classical statistical mechanics becomes invalid in the case of solids at low temperatures: according to Nernst's theorem the heat capacity of solids tends to zero as temperature is lowered. On the other hand, the heat capacity of a monatomic gas retains a

†First published in Usp. Fiz. Nauk 8 (2) 155-193 (1928).

constant value (three calories per one gramme-atom). Therefore, the theory of an electron gas confined in a solid metal can be reconciled with the experimental observations only if the number of free electrons is small compared with the number of atoms.

If we assume that n is known, we can readily calculate the electric conductivity of a metal. According to Drude, this can be done as follows. In the presence of an external electric field E the motion of free electrons between two collisions is subject to an acceleration w = eE/m (e is the charge and m is the mass of an electron) and electrons seem to 'fall' along the direction of this field. In a collision of an electron with any atom (neutral or positively charged) the electron loses its kinetic energy and transfers it to the atom, which releases it in the form of heat (Joule heat). The increment in the velocity of an electron at the end of its path is wt, where t is the travel time. If this additional velocity is small compared with the average velocity v of chaotic thermal motion, we can assume that t = l/v. Therefore, the average additional velocity imparted to electrons by the field E is

$$u = \frac{1}{2} wt = \frac{1}{2} \frac{eE}{m} \frac{l}{v}.$$

The product of this velocity and *ne* is simply the density of the electric current, equal by definition to σE , where σ is the electric conductivity of the metal. Therefore, the conductivity is described by the expression

$$\sigma = \frac{e^2 n l}{2m\nu} \,. \tag{2}$$

A comparison of this expression with the experimental results is pointless because we do not yet know n or l.

However, Drude did not stop at the result given above, but calculated the additional thermal conductivity which metallic bodies should have because of the presence of an electron gas. In so doing he put forward the hypothesis that the additional electron thermal conductivity is equal to the thermal conductivity of the electron gas itself, and he used an expression familiar from the kinetic theory to describe the latter:

$$\kappa = \frac{1}{2} vlc , \qquad (3)$$

where c denotes the specific heat per unit volume of the gas (at constant volume). In this case we have

$$c = \frac{3}{2} kn \tag{4}$$

and, consequently,

$$\kappa = \frac{1}{2} \, kvnl \ . \tag{5}$$

A comparison of this expression with Eqn (2) gives

$$\frac{\kappa}{\sigma} = \frac{kmv^2}{e^2}$$

i.e. it follows from Eqn (1) that

$$\frac{\kappa}{\sigma} = 3\left(\frac{k}{e}\right)^2 T \ . \tag{6}$$

Metals are known to be not only excellent conductors of electricity, but equally good heat conductors. Experiments show that the ratio of the total thermal conductivity of various metals to their electric conductivity is the same for all metals at the same temperature and directly proportional to temperature. Therefore, this law (discovered by Wiedmann and Franz) is described correctly by Eqn (6) if σ is understood to be not the additional but the total electric conductivity of a metal. The numerical value of the coefficient of proportionality $3(k/e)^2$ then agrees accurately with the experimental value (it should be pointed out that the ratio κ/σ does not contain the unknowns *n* and *l*).

At first sight this result seems to represent a triumph of the Drude theory, but in reality it suffers from an internal inconsistency. The thermal conductivity of a metal can be practically equal to the thermal conductivity of an electron gas only if the number of free electrons is very large. In reality Eqn (5) is based on the assumption that the temperature of a nonuniformly heated metal is governed by the kinetic energy of free electrons at a given point, i.e. the thermal energy of atoms is equal to that of free electrons. This is obviously possible only if the number of free electrons is equal to the number of atoms. However, under these conditions the specific heat of metals would have been considerably greater than the quantity predicted by Dulong and Petit in accordance with statistical mechanics.

2. Lorentz theory

The Drude theory has been improved by Lorentz, who has taken into account the distribution of the electron velocities on the basis of the familiar Maxwellian law. According to this law, the number of electrons whose projections of the velocities along the coordinate axes x, y, and z lie within the intervals $(\xi, \xi + d\xi), (\eta, \eta + d\eta), (\zeta, \zeta + d\zeta)$, is

$$\mathrm{d}n = A \, \exp\left(-\frac{W}{kT}\right) \mathrm{d}\xi \, \mathrm{d}\eta \, \mathrm{d}\zeta \,, \tag{7}$$

where $W = (1/2)m(\xi^2 + \eta^2 + \zeta^2) = (1/2)mv^2$ is the kinetic energy of an electron and A is a constant given by

$$A = n \left(\frac{m}{2\pi kT}\right)^{3/2} \,. \tag{8}$$

The Maxwellian velocity distribution has played an important role in a theoretical explanation of the Richardson effect (emission of electrons by heated bodies), but it contributes only an unimportant correction to the theory of electric and thermal conductivities of metals. The following values are then obtained for σ and κ :

$$\sigma = \frac{4}{3} \frac{e^2 ln}{\sqrt{2\pi mkT}} = \sqrt{\frac{8}{3\pi}} \frac{e^2 ln}{mv} , \qquad (9)$$

$$\kappa = \frac{8}{3} \sqrt{\frac{kT}{2\pi m}} kln = \frac{4}{3} \sqrt{\frac{2}{3\pi}} klnv , \qquad (10)$$

where v is the mean-square velocity defined by Eqn (1). The ratio κ/σ is then $2(k/e)^2T$; the rigorous theory is thus in *poorer* agreement with experiments than the approximate Drude theory.

Lorentz calculated σ and κ by a method which will be described here, because it will be used later. The Maxwellian distribution of Eqn (7) should be slightly distorted by the presence of gradients of the potential or temperature (or at least, a temperature gradient). In the first approximation, this distortion has the following effect: at each point in space the distribution of the electron velocities is not that which corresponds to the temperature or potential of this point, but the distribution corresponding to the temperature and potential of those points at which the electrons have just collided with the atoms (we shall consequently assume that any specific distribution of the electron velocities is established by such collisions). Electrons crossing any plane perpendicular to the x axis at velocities which are within the intervals $d\xi$, $d\eta$, and $d\zeta$ have experienced the last collision in a parallel plane separated from the plane in question by a distance $\Delta x = -\xi t$, where t = l/v is the time from this collision $[v = (\xi^2 + \eta^2 + \zeta^2)^{1/2}]$. Therefore, the number of electrons of this kind, taken per unit volume, is not $f_0(x, W) d\omega$ where for brevity we assume that $Ae^{-W/kT} = f_0(x, W)$ and $d\omega = d\xi d\eta d\zeta$, but is instead given by

 $f(x, W) d\omega = f_0(x + \Delta x, W + \Delta W) d\omega$.

Here, ΔW denotes the change in the kinetic energy of an electron in the interval Δx . In view of the smallness of this interval, we can assume quite accurately that

$$f_0(x + \Delta x, W + \Delta W) = f_0(x, W) + \left(\frac{\partial f_0}{\partial x} \Delta x + \frac{\partial f_0}{\partial W} \Delta W\right),$$

or, since

$$\Delta W = eE\Delta$$

(the change in the energy is equal to the work done by the acting force in the interval Δx),

$$f(x, W) = f_0(x, W) - \left(\frac{\partial f_0}{\partial x} + \frac{\partial f_0}{\partial W} eE\right) \xi \frac{l}{v}.$$
 (11)

This is the approximate expression for that distorted velocity distribution which originates from the presence of the temperature and potential gradients along the x axis. Knowledge of the function f(x, W) allows us to calculated the density of the electric current and of the heat flux (i.e. the amounts of the electric charge or kinetic energy transported by electrons per unit time across an area of 1 cm² perpendicular to the x axis) from the expressions

$$I = e \int \xi f \,\mathrm{d}\omega \,, \qquad Q = \frac{m}{2} \int v^2 \xi f \,\mathrm{d}\omega \,. \tag{12}$$

The earlier expression for the electric conductivity [Eqn (9)] follows directly from the first of the above expressions since $I = \sigma E$ when dT/dx = 0. In the calculation of the thermal conductivity from $Q = -\kappa \partial T/\partial x$ it is necessary to introduce an additional condition I = 0 (which is far from being automatically valid). This gives Eqn (10) for κ .

3. Sommerfeld theory

As pointed out above, the Lorentz theory does not alter significantly the Drude theory and in any case the former does not resolve the main conflict between the small number of free electrons required by the specific heat and the large value of this number which follows from the thermal conductivity. Last year this conflict was resolved by A Sommerfeld, who retained all the ideas of Drude and Lorentz on the motion of electrons in metals and simply replaced the Maxwellian velocity distribution with what is known as the Fermi distribution[†]

[†]The physical meaning of the Fermi distribution is discussed later in Section 4. At this stage we note that this distribution follows from certain general principles of quantum theory.

Here, *h* is the Planck constant and *c* is a certain fairly complex function of the temperature *T* and of the electron density *n* (i.e. the number of electrons per unit volume)^I[†]. At very high values of *T* or for very low values of *n* this function is identical with the coefficient *A* introduced above and divided by $(m/h)^3$. In the opposite case, i.e. when *n* is large and *T* is low, the function c(n, T) is given by the equation[‡]

$$\frac{4}{3\sqrt{\pi}} \left(\ln c \right)^{3/2} \left[1 + \frac{\pi^2}{8(\ln c)^2} + \dots \right]$$
$$= \left(\frac{h}{m} \right)^3 A = \frac{nh^3}{(2\pi mkT)^{3/2}} . \tag{14}$$

In the former case it is found that $c^{-1} \exp(W/kT)$ is very large compared with unity, so that the Fermi distribution reduces in practice to the Maxwellian form. In the latter case the value of $c^{-1} \exp(W/kT)$ is conversely small compared with unity and we obtain a very different velocity distribution as well as a temperature dependence of the average kinetic energy which is of completely different nature from that given by Eqn (1). It is in fact found that

$$\frac{1}{2}mv^2 = \frac{3}{2}kT \times \frac{2}{5}\ln c \left[1 + \frac{1}{2}\frac{\pi^2}{(\ln c)^2} + \dots\right].$$
 (15)

In particular, if T = 0, we obtain

$$\frac{1}{2}mv_0^2 = \frac{3}{10}\frac{h^2}{m}\left(\frac{3}{4\pi}n\right)^{2/3}.$$
(16)

It therefore follows from the Fermi distribution that the average kinetic energy of electrons at absolute zero does not vanish but retains a finite value which increases with the electron gas density. We can moreover show readily that this average energy increases with increase in temperature more slowly than its initial ('zero') value; at high temperatures we come back to the linear dependence of the classical theory: $\frac{1}{2}mv^2 = kT$. These relationships are illustrated in Fig. 1.

If we identify the number *n* with the number of atoms per unit volume, i.e. we assume that there is one electron for each atom in a metal, then the velocity v_0 deduced from Eqn (16) is of the order of 10^8 cm s^{-1} , i.e. it is comparable with the velocities of revolution of the outer (valence) electrons in isolated atoms. The increase in the velocity between absolute zero and normal temperatures is very slight. The 'atomic specific heat' of such extremely dense electron gas is negligible (about one-hundredth of a calorie). Therefore, the 'electron gas' contributes practically nothing to the total specific heat of a metal. The electric and thermal conductivities due to this gas are described by the following

[†]The Roman superscripts (i.e. ^{I, II} etc.) will be used to identify our comments on Frenkel's paper. These comments can be found at the end of the paper (R A Suris, V Ya Frenkel').

‡The exact form of this equation is as follows:

$$\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{c\sqrt{x} e^{-x}}{1 + c e^{-x}} dx = \left(\frac{h}{m}\right)^3 A .$$



approximate expressions:

$$\sigma = \frac{4\pi}{3} \frac{e^2 l}{h} \left(\frac{3n}{4\pi}\right)^{2/3} = \sqrt{\frac{3}{5}} \left(\frac{4\pi}{3}\right)^{1/3} \frac{e^2 n l}{m v_0} \qquad (v \approx v_0) \ (17)$$

and

$$\kappa = \frac{4\pi^3}{9} \frac{lk^2 T}{h} \left(\frac{3n}{4\pi}\right)^{2/3} = \frac{\pi^2}{\sqrt{15}} \left(\frac{4\pi}{3}\right)^{1/3} \frac{k^2 T n l}{m v_0}, \qquad (18)$$

which gives

$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3} \left(\frac{k}{e}\right)^2 T \ . \tag{19}$$

The above expression is in excellent agreement with the experimental results. However, this is not true of the preceding two expressions, because they contain the unknown mean free path l. It should be noted that Eqn (17) is of approximately the same form as the Drude [Eqn (2)] or Lorentz [Eqn (9)] formulas. The only difference between them is that in the former formulas the velocity vrepresents a relatively small quantity proportional to the square root of the absolute temperature (at normal temperatures we have $v = (3kT/m)^{1/2} \approx 6 \times 10^6$ cm s⁻¹), whereas in Eqn (17) the velocity v_0 is of the order of 10^8 cm s⁻¹. If the number *n* of electrons is also regarded as constant, the temperature dependence of σ should reduce as a whole to the temperature dependence of the mean free path *l*. Experiments showed that the electric conductivity of various metals at normal temperatures is inversely proportional to the absolute temperature. We should therefore have l = const/T. The absolute value of l can be obtained by substituting the experimental values of σ in Eqn (17) and this gives a value of the order of 10^{-5} cm at T = 300 K. Therefore, the mean free path of electrons in a metal should have approximately the same value as the mean free path of molecules in a gas at normal temperature and pressure, i.e. when the concentration of molecules is negligible. The familiar expression

$$l = \frac{1}{n\pi r^2} \,, \tag{20}$$

where r is the effective radius of atoms (we are assuming that electrons do not collide with one another at all), allows us to show readily by calculation that the effective radius r, which governs the magnitude of the deflecting action of atoms on electrons, is approximately 3×10^{-9} cm, i.e. it is 10 times less than that which is usually attributed to atoms and corresponds to the average distance between neighbouring atoms in any metal. Since, moreover, the number nis independent of temperature, we have to assume that this effective radius varies with temperature approximately proportionally to the square root of temperature. It seems that we are dealing not so much with the radius of atoms, but with the amplitude of their thermal vibrations near the equilibrium positions. It should be noted that the energy of such vibrations is αr^2 , where α is the coefficient of proportionality representing the strength of the binding of an atom to its equilibrium position. Therefore, from this point of view the mean free path of electrons l should be inversely proportional to the thermal energy of a metal (per unit volume). The thermal energy of solids is known to be proportional to the absolute temperature only at moderate temperatures. Cooling causes this energy to decrease much faster than the absolute temperature, so that the specific heat (i.e. the derivative of the energy with respect to temperature) vanishes at absolute zero. Consequently, if the above interpretation of Eqn (20) corresponds to reality, i.e. if the motion of electrons in a metal is hindered not by atoms themselves but only by the spheres formed around their centres because of thermal vibrations, then on the basis of Eqn (17) we can expect the electric conductivity to increase faster as a result of cooling than in inverse proportion to temperature, namely it should be inversely proportional to the thermal energy of metals. This conclusion is in qualitative agreement with the experiments. However, it is in reality found that this energy can be replaced by the product of the (atomic) specific heat c and temperature. This law, established empirically by Gruneisen, is given by the expression

$$\sigma = \frac{\text{const}}{cT} \,. \tag{21}$$

It is therefore clear that the above interpretation is supported only qualitatively by experiments.

4. Pauli and Fermi distributions of the electron velocities

We shall not analyse in detail Eqn (17)-(19) but consider briefly the physical meaning of the velocity distribution law from which these equations follow. This law was established in 1926 by a young Italian theoretician E Fermi, who extended the Pauli principle, governing the structure of individual atoms, to gases. In more or less complex atoms the electrons are distributed around a central nucleus in a series of layers or groups which correspond to specific terms in the X-ray spectra of these atoms[†]. The first, nearest to the nucleus, always consists of just two electrons (K group). The next (L) group contains eight electrons. In the group M there can be a maximum of 18 electrons and so on. Both K-group electrons move along one-quantum orbits (i.e. along orbits with the principal quantum number 1), the L- and M-group electrons move along a two- and three-quantum orbits, respectively, and so on. Each group is divided in general into subgroups and it is found that each set of the quantum numbers (principal, azimuthal, internal, and magnetic) corresponds to no more than one electron. This is the Pauli principle. It can be

†The terms represent the energies needed to extract these electrons outside.

formulated also as follows: an atom cannot have two or more 'equivalent' (in respect of the nature of their motion) electrons; each electron of a given atom differs in some respects (at least by one quantum number) from the rest.

At absolute zero the atoms are in the normal state corresponding to the minimum of their energy. However, this minimum is not absolute, but relative and its satisfies the Pauli principle or the 'equivalence principle', which was the name given by Pauli himself. If there had been no such restriction, then all the electrons (no matter how large their number) would have arranged themselves at the same (nearest) distance of the nucleus, i.e. they would have moved along identical one-quantum orbits. In reality, these orbits carry just two electrons on condition that their magnetic axes are oppositely directed[‡]. The other electrons must therefore occupy more distant orbits. Why and how this happens we do not know, but it remains a fact. The Pauli principle is only regulative and it represents the principle governing the electronic 'communal life', and a kind of 'housing law' of the electron community. In this community each pair of electrons is given a separate 'apartment' and the presence of a third electron in any 'apartment'-occupied by such an 'electron couple'-is never permitted (this applies also to the 'unnatural cohabitation' of two electrons with identically directed moments). Some electrons may of course remain in the 'bachelor' state occupying a whole 'apartment' by themselves. The number of such elementary 'apartments' occupied by single electrons or by pairs in an atom cannot be expressed in terms of any volume. The number in question is therefore described differently by attributing it a unit 'weight' (in the statistical sense of this word). Several 'apartments' with the same energy (if there are any) usually join to form a larger 'apartment' whose weight is equal to the sum of the individual 'apartments'.

The concept of such discrete 'apartments' is completely alien to classical statistical mechanics. This mechanics deals with a continuous set of spatial points and velocities with the a priori admission of the possibility of any state, i.e. of any position and any velocity of the investigated particles. The state of a system that consists of a large number of identical particles (for example, an electron gas discussed in the preceding section) is described by specifying the number of particles $f(x, y, z; \xi, \eta, \zeta) dx dy dz d\xi d\eta d\zeta$, whose coordinates and velocities are limited to the intervals dx, dy, dz, $d\xi$, $d\eta$, $d\zeta$, i.e. by the form of the distribution function f. This method of representing the state of a complex system is retained also in new statistical mechanics, related to quantum theory, in those cases when each of the particles under consideration can have arbitrary coordinates and velocities in specified fairly wide intervals (which is true, for example, of an electron gas or any other gas). The new statistics does however introduce an important addition that these intervals are separated into elementary cells the dimensions of which are given by the expression

$$\int dx \, dy \, dz \, d\xi \, d\eta \, d\zeta = \left(\frac{h}{m}\right)^3.$$
(22)

[‡]The magnetic properties of electrons and their importance in the mechanics of atoms can be judged on the basis of my earlier paper [29]. If we ignore these magnetic properties, i.e. if we regard as equivalent the electron orbits differing only in respect of the direction of the magnetic moment, the Pauli principle reduces to the statement that each orbit can be present in an atom in no more than two 'copies'.

The cells (with the shape to be determined) represent in this case the basic 'apartments' for separate electron pairs, in the sense defined above. It was Planck back in 1916 who pointed out that such cells correspond to distinct quantum orbits, all with the same statistical weight of unity. However, it is to Fermi that we owe the extension of the Pauli principle, i.e. of the 'housing law of the electron community', to such cells.

Let us now see what is the result of application of the Pauli–Fermi theory to an electron gas at absolute zero [16]. From the point of view of the classical theory, electrons can be at rest at a position which corresponds to a minimum of the potential energy, i.e. in one specific cell of the phase space $(x, y, z; \xi, \eta, \zeta)$. However, this is as impossible as the placing of all the electrons of an atom at the same onequantum orbits. In fact, the 'most convenient' cell just mentioned can accommodate just one pair of electrons; other pairs are distributed, possibly at a higher density, in cells with higher values of both the kinetic and potential energies. If the potential energy is the same for the whole of the spatial volume under consideration, the distribution of electrons in this volume remains uniform.

We shall use v_{max} to denote the maximum velocity of one out of N electrons in a volume V. The points representing electrons in the velocity space (where the coordinates are the velocity components ξ , η , ζ) should then lie within (or on the surface of) a sphere of radius r_{max} , i.e. in the 'velocity volume' $(4\pi/3)v_{\text{max}}^3$. Combining this sphere with the spatial volume V, we obtain the following product for the phase volume:

$$\Phi = \frac{4\pi}{3} v_{\max}^3 V .$$
 (23)

Since the volume of a basic 'phase apartment' is $(h/m)^3$, the number Z of such 'apartments' in the phase volume Φ is

$$Z = \Phi\left(\frac{m}{h}\right)^3 = \frac{4\pi}{3} \left(\frac{m}{h} v_{\text{max}}\right)^3 V .$$
 (24)

The various 'apartments' can be imagined in the form of a combination of the spatial volume V and concentric spherical layers of the same velocity volume:

$$4\pi v^2 \Delta v = \frac{1}{V} \left(\frac{h}{m}\right)^3.$$
⁽²⁵⁾

At absolute zero the number of 'apartments' should be identical with half the number of electrons N (when there is not a single free place!), which corresponds to the minimum kinetic energy of an electron gas. If we substitute Z = N/2and N/V = n in the electron density in Eqn (24), the result is

$$\frac{m}{h}v = \left(\frac{3}{8\pi}n\right)^{1/3},\tag{26}$$

so that as a consequence we have

$$\frac{1}{2}mv_{\max}^2 = \frac{1}{2}\frac{h^2}{m}\left(\frac{3n}{8\pi}\right)^{2/3}.$$
(27)

This is the maximum energy of one of the electrons at T = 0. The average energy $\frac{1}{2}mv_0^2$ is found by summing the values of $\frac{1}{2}mv^2$ for different spherical layers of Eqn (25)

and dividing by the number of electrons N. At high values of N the summation can be replaced with integration, i.e. we can assume that

$$\frac{1}{N}\sum_{v=1}^{\infty}\frac{1}{2}mv^{2} = \frac{1}{N}\int_{0}^{v_{max}}mv^{2}\frac{4\pi v^{2} dv}{V^{-1}(h/m)^{3}}$$
$$= \frac{1}{n}\left(\frac{m}{h}\right)^{3}4\pi m\int_{0}^{v_{max}}v^{4} dv,$$

which on the basis of Eqn (26) gives

$$\frac{1}{2}mv_0^2 = \frac{3}{10}\frac{h^2}{m}\left(\frac{3}{8\pi}n\right)^{2/3}.$$
(28)

The above expression differs from Eqn (16), which I took from Fermi's paper [31], by the replacement of 4π with 8π . This can be explained by the fact that Fermi, and following him Sommerfeld, applied the Pauli principle in a form which is not quite accurate, namely by assigning basic 'apartments' $(h/m)^3$ to single electrons and not to electron pairs.^{II}

The above ideas can readily be generalised to the case when T > 0. The number Z of the phase cells can then be greater than half the number of electrons N; some of the cells thus remain unoccupied. The probability of a particular electron distribution (which is not in conflict with the Pauli principle) with a total energy W should then be propor- tional to $\exp(-W/kT)$ or to $\exp[W - W_0)/kT]$, where $W_0 = N \times \frac{1}{2}mv_0^2$ is the energy at absolute zero. This principle, inherited by the new quantum statistics from classical statistical mechanics, leads to the Fermi expression (13) for the distribution of the velocities subject to a small correction, which reduces to the replacement of $(h/m)^3$ in Eqns (13) and (14) with $\frac{1}{2}(h/m)^3$.

5. Physical picture of the motion of electrons in metals

In 1924, i.e. before the appearance of the new statistics associated with the pauli principle, I developed an electron theory of metals[†] on the same basis as the Sommerfeld theory, namely on the assumption that at absolute zero the kinetic energy of free electrons is very high and it remains almost constant when temperature is increased, and that the number of such electrons is approximately equal to the number of atoms.^{III}

This approach follows from an analysis of the process of formation of a solid or liquid metal by condensation of the vapour of this metal.

Metal vapours are not electrically conducting. It follows that they do not contain any free electrons. Experiments show that the outer electrons of metal atoms are bound less strongly to the atoms than the corresponding electrons in the case of metalloids, which are insulators (nonconductors) in the solid state. Moreover, according to the Bohr theory the outer electrons of metal atoms follow strongly extended orbits resembling the orbits of comets, whereas the outer electrons of nonmetal atoms have orbits similar to those of the familiar planets of the solar system.

The interaction of metal atoms with metalloids results in the transfer of some of the electrons from the former to the

†See Ref. [16].

latter. These easily transferred electrons are usually called the valence electrons since their number determines the positive valence of a metal or an ion. The valence electrons are simply the 'cometary electrons', just mentioned above.^{IV} The capture of these electrons by a metalloid atom is not so much due to their weak binding to the parent (metal) atom, as due to their considerable distance from the centre of this atom because the orbits are elongated. If the aphelion of the undisturbed elliptic orbit of such electrons is close to the position of a metalloid atom, they fall within the sphere of attraction of the latter and no longer return to the metal. In a similar manner the comets in the solar system may be captured by some other system of the same type if they approach the sun sufficiently close.

In a metal vapour the average distances between atoms are very large compared with the dimensions of the orbits of the various electrons, including the cometary electrons. Therefore, the latter remain bound to the corresponding atoms. However, when a vapour is condensed into a solid, these atoms are located in the direct vicinity of one another and the cometary electrons can pass from one atom to its neighbour. In each atom they can make one or at most several revolutions (if the aphelion distance of their unperturbed orbit is sufficiently large) and then join one of the adjacent atoms. In this way the cometary electrons are converted by the condenstation of a metal vapour into 'itinerant' electrons, i.e. they travel over the whole volume occupied by a metallic body. These itinerant electrons, which have lost their binding to specific 'hosts' and continuously pass from one atom to another, represent what are usually known as free electrons. Their 'freedom' is very limited. These electrons are converted from the private property of atoms isolated from one another in a metal vapour into the collective property of the community formed when these atoms combine into a solid or a liquid. However, the binding of these electrons to the community does not become weaker than the binding to the previous hosts; just the opposite, the binding becomes even stronger, because each itinerant electron located inside the metal is held there not by one but by several (adjacent) atoms[†].

In the case of isolated atoms the outer (cometary) electrons revolve along orbits at a velocity[‡] of the order of 10^8 cm s⁻¹.

When a metal vapour condenses, these electrons continue to move at approximately the same velocity and even, as can easily be demonstrated, at a somewhat higher velocity. In fact, the stronger the forces acting on the electrons, the greater the acceleration induced by these forces and, consequently, the greater the velocity. This relationship can readily be made more specific by the use of what is known as the *virial theorem*. According to this theorem, in a system of particles acting on one another with forces inversely proportional to the square of the distance and remaining at a finite distance from one another, the average kinetic energy W of all the particles should be

numerically equal to their total energy with the reversed sign, i.e. it should be equal to the work needed to separate the system into its components§. Since in the condensation of a metal vapour the total energy decreases by an amount equal to the latent heat of condensation, the kinetic energy of electrons and protons should then increase by the same amount. This increase applies if not completely then at least mainly to the cometary electrons, because the motion of the other electrons is distorted only slightly and the kinetic energy of the vibrational motion of atoms taken as a whole can be ignored. If the kinetic energy of electrons is measured in volts (i.e. in terms of that potential drop in volts which is necessary to acquire this energy), we find that the kinetic energy of electrons of isolated atoms is of the order of 5-7 V, and the additional energy acquired due to the vapour condensation process \P is 1-2 V.

The application of the virial theorem to the process of 'socialisation' (collectivisation) of the valence electrons^V shows that the velocities of these electrons are of the same order of magnitude as those that follow from the Pauli-Fermi statistical theory (discussed above). It should be pointed out that the virial theorem is applicable in the above form only at absolute zero. At T > 0 there should be a partial spontaneous dissociation of a metal in the gaseous and solid (by evaporation) states. If the virial theorem is extended into this case, it is necessary to allow also for the vapour pressure (or, more accurately, for the pressure of a mixture of ions, electrons, and neutral atoms) on the walls of the enclosing vessel. The agreement between the 'zeropoint energy' of free electrons predicted by the Pauli-Fermi-Sommerfeld theory with the quantity calculated by us on the basis of an analysis of the condensation process is not quite exact, which in all probability is due to inaccuracies of our theory, which obviously represents only a fairly rough approximation. We shall discuss the meaning of such agreement, even though it is approximate (see Section 8).

6. Theory of electric and heat conduction deduced from the foregoing picture

These ideas on the number and motion of free electrons in a metal were used by me to develop in 1924 a theory of electric and thermal conduction of metals, which differs considerably from the classical theories of Drude and Lorentz, and from the similarly developed Sommerfeld theory.

There should be a correlation between the motion of various electrons, so that the position vacated by one electron, which moves away from a given atom, should be occupied immediately by another electron. We shall

§In the simplest case of the hydrogen atom we find that, for example, $mv^2 = e^2/v$. The left-hand side of this expression represents the doubled kinetic energy and the right-hand side is the potential energy with the reversed sign. The total energy is consequently

$$\frac{1}{2}mv^2 - \frac{e^2}{r} = -\frac{e^2}{2r} = -\frac{1}{2}mv^2.$$

[†]These conditions change somewhat for electrons that manage to reach somehow to the surface of a metal. There they can become separated from the metal quite readily (at the expense of about half the energy otherwise required for separation).

[‡]For example, in the case of an electron orbiting around a proton (hydrogen atom) along a circle of radius *r*, the attractive force is equal to the centrifugal force, $e^2/r^2 = mv^2/r$, which gives $v = (e^2/mv)^{1/2}$, which gives $v = 2 \times 10^8$ cm s⁻¹ for $e \approx 5 \times 10^{-10}$, $m = 10^{-27}$, and $r = 10^{-8}$.

[¶]The average kinetic energy of a valence electron in an atom of a univalent metal, such as sodium or potassium, is equal—in accordance with the virial theorem—to the ionisation energy of this atom, i.e. to the work needed to separate the electron in question. The latent heat of condensation amounts to about 20-40 kilocalories per one gramme-atom, i.e. per 6×10^{23} atoms. When this is attributed to the same number of electrons, it is found that 23 kcal are equivalent to 1 V.

ignore this correlation and try to follow the path of any one electron in a metal. The metal can be considered as one molecule of giant dimensions so that the whole path of an electron can be regarded as one unbroken 'quantum' orbit. However, it can readily be shown that this applies only at absolute zero. The thermal motion of atoms should, because of its disordered nature, so to speak break the electron orbit into longer or shorter quantised sections related to one another by the stochastic laws only. We shall call the rectilinear displacements corresponding to such sections the 'elementary electron displacements'.

These elementary displacements evidently play the same role as the free paths in the theory of an electron gas. At absolute zero they become infinite. Then a metallic body does not resist more the motion of electrons than does a single atom. The direct cause of the electric resistance of metals is the presence of irregularities in the distributions of atoms which are due to their thermal motion.

At sufficiently high temperatures these elementary displacements of electrons should reduce to the minimum value which is equal to the distance between the adjacent atoms. This means that in the absence of an external electric field the elementary displacements along different directions from any atom A_0 to one of its *s* neighbours $A_1, A_2, \ldots A_s$ are equiprobable irrespective of the direction of the preceding $(A_k \rightarrow A_0)$ elementary displacement. In the presence of an electric field *E* the elementary displacements in the direction of this field (or, more correctly, in the direction of the corresponding force F = eE) become more probable than the opposite displacements. This change in the probability in the course of the displacement $\overline{A_0A_i}$ is proportional to $\exp(-U_i/kT)$, where

$$U_i = -eEd \cos \theta_i$$

is the potential energy of an electron at the point A_i compared with the point A_0 , and θ is the angle between the segment $\overline{A_0A_i}$ and the vector E (or eE). This modified probability p_i can consequently be represented in the form

$$p_{i} = p_{i}^{0} \frac{\exp(-U_{i}/kT)}{\sum_{k=1}^{s} \exp(-U_{k}/kT)},$$
(29)

where $p_i^0 = 1/s$ is its value for E = 0.

If t is the time in which an elementary displacement is completed, the average displacement velocity of an electron in the direction of the external force eE is given by

$$u = \sum_{i=1}^{s} p_i \frac{d \cos \theta_i}{t}, \qquad (30)$$

or, in the first approximation on the assumption that $\exp(-U_i/kT) = 1 - (U_i/kT)$ and, bearing in mind that $\sum_{i=1}^{s} \cos \theta_i = 0$, we obtain

$$u = \frac{ed^2}{tkT} \overline{\cos^2 \theta} E , \qquad (31)$$

where $\overline{\cos^2 \theta}$ denotes the average value of $\cos^2 \theta_i$ for all *s* displacements $\overline{A_0 A_i}$ (if they are regarded as equiprobable). Since the number *s* is usually quite large (it is either 12 or 8), we can assume that $\cos^2 \theta = 1/3$. Since the current density is *neu* = σE , we obtain the following expression for the electric conductivity of a metal:

$$\sigma = \frac{e^2 n d^2}{3kTt} \,. \tag{32}$$

The same result can be deduced from the familiar relationship between the friction coefficient ϑ and the diffusion coefficient D:

$$D\vartheta = kT , \qquad (33)$$

which was first established by Einstein in the theory of Brownian motion. Here, ϑ is defined by $\vartheta = eE/u$ and the diffusion coefficient is given by $D = dv'/3 = d^2/3t$, where v' = d/t is the average displacement velocity of electrons in a metal. In general, this velocity is somewhat less than the intrinsic velocity v, but it is approximately equal to the latter if an electron does not stay too long at the individual atoms but makes just one revolution around each of them and passes immediately to a neighbouring atom[†].

This condition can be regarded as satisfied in the case of alkali metals the atoms of which have only one cometary electron with a very elongated orbit. If we assume that $d \approx 10^{-8}$ and $v' \approx 10^{8}$, we find that the diffusion coefficient of electrons is of the order of unity and, moreover, it is independent of temperature. If we rewrite Eqn (32) in the form

$$\sigma = \frac{e^2 nD}{kT} \,, \tag{34}$$

we can then see that the electric conductivity should be inversely proportional to the absolute temperature (in the range of temperatures where the length of elementary displacements reduces to the interatomic distance d) and it is of the order of e^2n/kT . If we assume that $e = 4.7 \times 10^{-10}$, $n \approx 10^{22}$, and $k = 1.3 \times 10^{-16}$, we in fact obtain numbers which are quite close to the experimental results (the electrostatic cgs units are used here; the electric conductance in terms of reciprocal ohms can be obtained if the values are divided further by 9×10^{11}). More accurate numerical data will not be given here; the reader can find them in the paper cited above. I shall simply note that in the case of divalent (alkalineearth) metals the velocity v' is approximately half v; in this case the cometary electrons follow approximately two revolutions around the same atom before passing to the next one.

According to the proposed viewpoint, free electrons do not participate directly in the thermal motion of atoms and, therefore, they do not increase significantly the specific heat of a solid or liquid metal, since they do not increase the specific heat of a metal vapour (apart obviously from very

† If the electron density falls along the x axis, we find that the 'diffusion' electric current along this direction has the density $-cD\partial n/\partial x$. In the presence of an electric field we have to add the usual conduction current $neu = ne^2 E/\vartheta$. Here under equilibrium conditions the two currents compensate one another. We therefore find, denoting the potential energy of an electron by

$$U\left(eE = -\frac{\partial U}{\partial x}\right), \quad D\frac{\partial n}{\partial x} + \frac{n}{\vartheta}\frac{\partial U}{\partial x} = 0,$$

i.e. $n = \operatorname{const} \times \exp(-U/D\vartheta)$.

On the other hand, according to the Boltzmann theorem, we should have $n = \text{const} \times \exp(-U/kT)$. A comparison of this expression with the preceding one yields Eqn (33).

high temperatures where significant ionisation of atoms begins). Therefore, the specific heat of a solid metal at normal temperatures is $c = 3kn_a$, where n_a is the number of atoms per unit volume, in agreement with the Dulong–Petit law.

Although they do not participate directly in thermal motion, free electrons may nevertheless transfer thermal energy from one atom to another in approximately the same manner, as happens in gases. In the presence of a temperature gradient in a metal the temperature distribution is described by the familiar equation

$$\frac{\partial T}{\partial t} = \frac{\kappa}{c} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) ,$$

where κ denotes as usual the thermal conductivity.

A comparison of this equation with the diffusion equation

$$\frac{\partial n'}{\partial t} = D\left(\frac{\partial^2 n'}{\partial x^2} + \frac{\partial^2 n'}{\partial y^2} + \frac{\partial^2 n'}{\partial z^2}\right),\,$$

which determines the changes in space and time of the density n' of an arbitrary selected set of electrons (n') should not be mixed up with the total density n, yields the result

$$\frac{\kappa}{c} = D , \qquad (35)$$

which expresses the identity of the processes of the transport of electric charges and heat in a metal (it should be noted that this relationship applies also to gases). If we substitute in this expression the quantities $c = 3kn_a$ and $D = \sigma k/ne^2$ [on the basis of Eqn (34)], the result is

$$\frac{\kappa}{\sigma} = \frac{3n_a}{n} \left(\frac{k}{e}\right)^2 T , \qquad (36)$$

i.e. the Wiedemann-Franz law. However, it must be pointed out that the agreement with the experimental value of the coefficient of proportionality is obtained only for $n = n_a$ and that at low temperatures the specific heat is no longer constant. This results in the replacement of T on the right-hand side of Eqn (36) with a more complex function of temperature. Experiments however show that the Wiedemann-Franz law is valid right down to the lowest temperatures.

At low temperatures the electric conductivity also ceases to vary proportionally to T, but can be described—as pointed out earlier—by the Gruneisen formula

$$\sigma = \frac{\text{const}}{cT} \,,$$

where c is the specific heat of the metal or, more correctly, a certain function of temperature such that it varies with temperature at approximately the same manner as the specific heat, but not the heat of the metal in question but of some other metal.

A qualitative interpretation of the above formula on the basis of the proposed theory is quite easy. Cooling continuously increases the length of the elementary displacements (which become infinite at T = 0). If this limit of length is denoted by l, the diffusion coefficient is given by D = lv'/3, where v' has approximately the same value as before.

Hence it follows from Eqn (34) that

$$\sigma = \frac{\text{const}}{(d/l)T}$$

Therefore, we can derive the Gruneisen formula of Eqn (21) by assuming that the ratio d/l varies in direct proportion to the specific heat c. However, it is impossible to derive this result in a rigorous quantitative form from the principles stated above.

The proposed theory differs from that developed by Sommerfeld in this respect: the influence of an external field on the motion of electrons reduces it to a change in the probability of elementary displacements of an electron along different directions, whereas according to Sommerfeld (also according to Drude and Lorentz), this influence is due to an additional velocity acquired by an electron during an elementary displacement (i.e. between two collisions). According to our ideas, this additional velocity plays no role whatever. Let us assume that, for example, electrons can move only parallel to the x axis. In this case in the presence of a field they travel a distance between two atoms A_1 to A_2 somewhat faster in one direction, for example, from A_1 to A_2 , than in the opposite direction. However, since both directions are equiprobable and since, as found later, the length of elementary displacements along one or the other directions remains the same, then - on averageit is not possible to induce any additional motion along the direction of action of the applied forces, irrespective of the value of the above-mentioned additional velocity. This velocity may be important only when electrons do not encounter one another at each step, as is true evidently of metals at moderate temperatures, but few steps apart and only if the number of such steps (interatomic spacing) along the direction of action of the active force is (in the final analysis) greater than in the opposite direction. It is this concept (although not stated explicitly) that is the basis of the calculations reported by Sommerfeld, Lorentz, and Drude. It is interesting to note that in the case of the last two theories (Lorentz and Drude), postulating that the average electron velocity is given by the expression $\frac{1}{2}mv^2 = \frac{3}{2}kT$, the electron mobility can be calculated by either method (additional velocity or additional probability) and the result is practically the same in both cases.^{VI}

7. Principles of wave mechanics. Cathode rays and waves

I shall now present new and very special ideas on the motion of electrons in metals, which follow from the new wave (or quantum) mechanics developed in the last few years by L de Broglie and E Shrodinger, and also from an equivalent (although superficially different) form proposed by W Heisenberg, M Born, and P Jordan.

The essence of wave mechanics reduces to a closer analogy between the motion of material particles and propagation of light rays. This analogy is implied also by the name 'cathode rays' given from the time of Crookes to a stream of electrons emitted by the cathode of a discharge tube. In this case the rays are the paths of single electrons (which may be rectilinear or curvilinear). On the other hand, the corpuscular theory of light, proposed by Einstein, makes light waves resemble a flux of electrons the role of which is then played by light quanta. Such phenomena as the reflection and refraction of light, i.e. the geometric-optics effects, can readily be explained by the quantum theory of light subject to some very general assumptions about the interaction of light quanta with 'ordinary' matter. However, the phenomena of interference and diffraction of light do not fit at all the framework of corpuscular theory and can be explained solely by the wave theory of light. In this theory the light rays and the light quanta, the former being the paths of the latter, represent geometric functions and should be regarded simply as lines perpendicular to the surfaces of optical waves. The reality and 'essence' of light is represented by these waves and not by rays.

The main idea in the de Broglie-Schrodinger theory is that in the case of a material flux, such as cathode rays, we are not dealing with individual particles similar to light quanta, but with waves of a special kind analogous to light waves. In no way does it imply that there are no electrons as such (i.e. as discrete material particles). It simply means that their motion in space cannot be deduced from the principles of classical corpuscular mechanics. We have to replace the concepts of cathode rays with that of cathode or (as they are called by de Broglie) phase waves, establish the relationship between the wave and corpuscular representations, similar to the relationship between light waves and quanta, and finally find the laws of propagation of cathode waves in space, being guided again by their analogy with optical waves. This procedure can be reduced to the following. The action of light on material bodies can be described in terms of the corpuscular theory if we consider light quanta as particles of energy hv and with a momentum $h/\lambda = hv/c$ (c is the velocity of light)[†]. Hence it follows that in the case of cathode rays we should define the oscillation frequency and the wavelength of the corresponding cathode waves as follows:

$$hv = V$$
, $\frac{h}{\lambda} = mv$, (37)

where V is the total energy of an electron and mv is the electron momentum. The energy V should be defined in such a way that an electron at rest has the energy mc^2 . Subject to this condition, the velocity λv of cathode waves is approximately c^2/v , i.e. it is as many times higher than the velocity of light as the latter is higher than the velocity of electrons.^{VII} If we consider only low (compared with c) velocities v, we can describe the kinetic energy by the usual expression $\frac{1}{2}mv^2$. If W is the sum of this kinetic energy and of the potential energy U(x, y, z), we can assume that $m^2v^2 = 2m(W - U)$ and, consequently, it follows from Eqn (37) that

$$\frac{h}{\lambda} = \sqrt{2m[W - U(x, y, z)]} .$$
(38)

This expression provides a 'single-valued' relationship between the wavelength of cathode waves and the coordinates (the oscillation frequency ν remains independent of the coordinates, i.e. it is the same at all points in space).

The amplitude ψ of light waves with a definite frequency, propagating in a certain isotropic but inhomogeneous medium where the wavelength of these waves λ varies continuously from one point to its neighbours, is described as a function of the coordinates by the familiar equation:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{4\pi^2}{\lambda^2} \psi = 0 .$$
(39)

Optical oscillations at each point are described by the product of this amplitude and $\cos 2\pi vt$. The square of the amplitude (or, more correctly, its absolute value) determines the average energy of waves or the intensity of rays at the point in question.

Schrodinger assumed that the propagation of cathode rays is governed by the same differential equation as the propagation of optical waves if the wavelength λ is expressed as a function of the coordinates in accordance with Eqn (38). The Schrodinger equation then has the form

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{4\pi^2 m}{h^2} \left(W - U \right) \psi = 0 .$$
 (40)

Born has suggested however that the energy of cathode waves, i.e. the square of the function ψ , is a measure of the intensity of cathode rays or, more correctly, of the density of the electron flux which forms these rays. The intensity of this flux is found from this energy $(\psi)^2$ (which can also be treated as a measure of the probability of finding an electron at a given space) multiplied by the velocity of rays v, i.e. by $h/m\lambda$.

8. Application of the theory of cathode waves to metals[‡]

If we apply these ideas to the motion of free electrons in metals, we first of all obtain a very simple and clear interpretation of that velocity distribution at absolute zero which follows from the Pauli-Fermi principle. The substitution of $mv_{\text{max}}/h = 1/\lambda_{\text{min}}$ in Eqn (26) yields, on the basis of Eqn (37), the expression

$$\lambda_{\min} = \left(\frac{8\pi}{3n}\right)^{1/3} . \tag{41}$$

This means that the minimum wavelength of cathode waves, 'ploughing' along all directions in a metal, is approximately equal to the average distance between the adjacent electrons if we assume that they are distributed in the from of a regular cubic lattice. Next, we can readily show that the condition (25) is equivalent to the following: at absolute zero the motion of electrons in a metal can be described by a superposition of a system of N/2 standing cathode waves, which represent resonant oscillations in a body of a given volume and shape§. For example, in the case of a metal in the shape of a rectangular parallelepiped with the edges a_1 , a_2 , a_3 the wavelength of different waves is

$$\frac{1}{\lambda} = \sqrt{\left(\frac{k_1}{a_1}\right)^2 + \left(\frac{k_2}{a_2}\right)^2 + \left(\frac{k_3}{a_3}\right)^2},$$
(42)

§Each standing wave can be regarded as a set of two ordinary travelling waves propagating in opposite directions.

[‡]The results presented in this section were obtained by me in the summer of last year (1927) and had been included partly in my paper presented at the International Physics Congress in Como. Similar ideas were put forward simultaneously by Sommerfeld, but de did not develop them into a quantitative theory.^{VIII}

where k_1 , k_2 , k_3 are integers. Exactly similar relationships are obtained when thermal vibrations of atoms in a metal (or any other monatomic solid) are represented by superposition of a system of elastic standing waves, as is done for example in the familiar Debye theory of specific heat.

It is interesting to note also the following circumstance. The dimensions of the circular orbit followed by an electron in an isolated atom is given by the familiar Bohr condition: the angular momentum is $mvr = kh/2\pi$, where k is an integer and r is the orbit radius. Substituting $mv = h/\lambda$ in the above expression, we obtain

$$\frac{2\pi r}{\lambda} = k \ (= 1, 2, 3, ...) \ . \tag{43}$$

This equality, first obtained by de Broglie, shows that the length of the orbit of the cometary electrons in isolated metal atoms is if not exactly equal then at least comparable with the wavelength of the corresponding phase waves. If the condensation of a metal vapour converts all the cometary electrons into free electrons, the distance between them $(n^{-1/3})$ is found to be comparable with the interatomic distances. On the other hand, the interatomic distances in solids are comparable with the dimensions of orbits of the outer electrons, and we find that the minimum or average wavelength of cathode waves in a solid metal is of the same order of magnitude as in the isolated atoms. Hence it follows that the average velocity of electrons is approximately the same in both cases.

These relationships change somewhat when temperature is increased. First and foremost such an increase gives rise to shorter cathode wavelengths than those given by Eqn (41). Next, and this is particularly important to us, because of an irregular distribution of atoms associated with their thermal motion, the propagating cathode waves begin to experience diffuse scattering which reduces their intensity, i.e. which causes their apparent absorption and is the direct reason for the electric and also thermal resistance of a metal. The 'resistance' is understood to be here the reciprocal of the conductance. At absolute zero the electric and thermal conductances of a metal are both infinite, i.e. the corresponding resistances vanish. This means that from the point of view of wave mechanics the cathode waves 'ploughing' through a metal propagate without any 'absorption' or diffuse scattering, i.e. they propagate in the same way as optical waves in perfectly transparent bodies.IX

However, it is known that even perfectly transparent bodies such as pure air become more or less 'turbid' at temperatures other than absolute zero, i.e. they begin to scatter light rays passing through them. Such scattering of solar radiation is the reason for the visibility of atmospheric air (sky). The cause of such turbidity of air are the slight local increments or reductions in the density, which are the result of an irregular disordered motion of the air molecules. The coefficient of the scattering light in gases whose molecules travel completely independently of one another is, as demonstrated by the theory and experiment, temperature-independent. Conversely, in the case of solids, this coefficient decreases rapidly when temperature is lowered, but at moderate temperatures it is approximately directly proportional to temperature. One should however mention that this is true only of visible light or, more correctly, of the optical waves whose wavelength is long compared with the interatomic distances. In the case of short X-ray waves, whose wavelength is of the same order of magnitude or even less than these distances, the scattering coefficient remains constant at moderate temperatures not only for gases, but also for liquids and solids.

When these principles are applied to the scattering of cathode waves in metals, which is due to the thermal motion of the metal atoms, it is necessary to answer first the question whether these waves should be treated as 'long' or 'short', compared with the interatomic distances. In the former case they should be scattered in approximately the same way as the waves of ordinary light, i.e. approximately proportionately to T at moderate temperatures, whereas in the latter case they should be scattered in the same way as X-ray waves, i.e. approximately independently of T, naturally in the same temperature range. At very low temperatures the scattering coefficient of these waves should vanish in either case.[†]

The scattering coefficient of waves in any turbid medium is generally given by the expression

$$\mu = -\frac{1}{J} \frac{\mathrm{d}J}{\mathrm{d}x} \,, \tag{44}$$

where J is the wave intensity and dJ is the change in this intensity in an interval dx along the direction of the wave propagation. Integration of this equation gives

$$J = J_0 \exp(-\mu x) . \tag{45}$$

In the case of cathode waves the intensity J, represented by the square of their amplitude ψ , is a measure of the number of electrons participating in the motion described by these waves. Thus Eqn (45) represents the law describing the reduction in the number of electrons in a cathode beam because of that scattering which the electrons experience by colliding with atoms. The rectilinear motion of electrons is hindered not only by the atoms themselves (because at T = 0 the scattering ceases), but also by the thermal vibrations of the atoms [compare this with the interpretation of Eqn (20)]. In any case, the relative number of the 'scattered' electrons, i.e. those ejected from the beam in question in an interval of length dx, is μdx . Hence it follows that the scattering coefficient μ is simply the reciprocal of the mean free path of electrons or of their elementary displacement *l*:

$$\mu = \frac{1}{l} \,. \tag{46}$$

Therefore, if we know μ , we can calculate the electric and thermal resistances of metals (or the corresponding conductances) by means of the expressions given above.

A theory of heat conduction in solid insulators constructed in a fully analogous way was put forward by Debye in 1914. It has been established experimentally that the lowtemperature thermal conductivity of insulators becomes very high and exceeds the thermal conductivity of metals. Debye described the thermal motion of atoms in solids by a superposition of a system of elastic waves and came up with the idea that the cause of the thermal resistance lies in the scattering experienced by these waves on fluctuations of the density of the investigated body. However, since these

[†]The proof of this for the second case is not as simple as in the first case; the reader can find it in my paper presented at the Como Congress [17].

For the moment we shall not consider the determination of the numerical value of the coefficient μ (see below), but we can put forward the following qualitative propositions.

If the cathode waves in metals are regarded as long, then at moderate temperatures we can assume that

$$\mu = \operatorname{const} \times T \ . \tag{47}$$

The electric conductivity σ is inversely proportional to T if it is described by the Sommerfeld formula [Eqn (17)], which does not contain temperature explicitly, whereas the application of my formula [Eqn (34)] gives, in accordance with the equality

$$D = \frac{1}{3} lv' = \frac{1}{3} \frac{v'}{\mu} \,,$$

the expression

$$\sigma = \frac{\text{const}}{T^2}$$

Conversely, if we treat cathode waves as short (regarding them as similar to X-ray waves), we obtain under the same conditions

 $\mu = \text{const} , \qquad (48)$

and, consequently, according to my formula we have $\sigma = \text{const}/T$, whereas the Sommerfeld formula gives $\sigma = \text{const}$.

The question of which of these two formulas corresponds to reality cannot be answered simply. We have seen earlier that the average wavelength of cathode waves in a metal is indeed comparable with the interatomic distances. Therefore, these waves should not, strictly speaking, be treated as long or short. A theory of the scattering of optical waves whose wavelength is intermediate does not yet exist because the development of such a theory meets with very serious difficulties.

However, there are two circumstances which support the Sommerfeld formula rather than mine.

According to the above theory the scattering coefficient μ' of cathode waves in a metal which is not quite pure, i.e. a metal containing a small number of some impurities (if only of another highly conducting metal), should always be greater than the scattering coefficient μ of the same metal when it is perfectly pure.

Such irregularly distributed impurities should in fact act on cathode waves in approximately the same way as dust suspended in air acts on the scattering of light waves. We can consequently assume that

$$\mu' = \mu + \Delta \mu , \qquad (49)$$

where $\Delta\mu$ is an essentially positive quantity, which is practically independent of temperature. Substituting here the value of μ from Eqn (47) and applying the Sommerfeld formula for the electric conductivity, we obtain

$$\rho' = \frac{1}{\sigma'} = \rho + \Delta \rho = \text{const} \times T + \Delta \rho ,$$

where $\rho \propto T$ is the resistivity of a pure metal and $\Delta \rho$ is the additional resistivity proportional to the number of impurities and independent of temperature. This result is in full agreement with the experimental observations formulated as the Matthiessen rule. However, according to my formula the additional resistivity should be directly proportional to the absolute temperature.

It is also known that the resistivity of the majority of metals rises steeply (it approximately doubles) as a result of melting. This can be explained directly by the concept of 'long cathode waves' because inhomogeneities caused by fluctuations of the density in a liquid are stronger (approximately twice as strong) than in the case of the corre-sponding solid. If the assumption is made that cathode waves are short, the scattering coefficient should reach its maximum value $\mu = 1/d \approx 10^8$ cm⁻¹ already in a solid near the melting point, so that its significant increase as a result of melting becomes incomprehensible.

These considerations undermine the validity of the calculation of the electron mobility made in Section 6, which is based on the idea of a change in the probability of various elementary displacements under the influence of an electric field (and which is related directly to the Boltzmann distribution law of electrons in a given force field).^X As far as the numerical value of μ (at normal temperatures) is concerned, both points of view—postulating 'short' and 'long' cathode waves—lead to values which are in agreement with the experimental data on the electric conductivity of various metals if in the former case this conductivity is calculated using my formula and in the latter case the Sommerfeld formula is used.

I am unable to go into further details of the calculations in this paper. The calculation of μ is possible on the basis of the Schrodinger equation [Eqn (40)] if U is understood to be the potential energy of an electron relative to all the atoms and if the atoms are regarded as neutral. The energy of cathode waves scattered by one such atom is, as demonstrated by a new theory of collisions developed by Born and Wentzel, given approximately by

$$\mu = 4\pi \left(\frac{e^2}{mv_0^2}\right)^2 \frac{4k^2 a^2}{1 + 4k^2 a^2} \quad \left(k = \frac{2\pi}{\lambda} = \frac{2\pi mv}{h}\right), \tag{50}$$

if the energy $(\omega)^2$ of the incident waves is assumed to be unity. Here, a denotes the effective radius of an atom in the normal 'Bohr' sense, i.e. a quantity of the order of 10^{-8} cm. The total scattering coefficient for a (pure) metal containing n_a atoms per unit volume can be found if we multiply the above expression by n_a in the case of 'short' waves and by the mean square fluctuation $(\Delta n_a)^2$ in the case of long waves[†]. In the former case this gives $\mu \approx 10^8$, i.e. $l \approx 10^{-8}$ cm $\approx d$, whereas in the latter case it gives $\mu \approx 10^5$, i.e. $l \approx 10^{-5}$ cm (at $T \approx 300$ K) with the experimental electric conductivity if the latter is calculated using my formula in the first case and the Sommerfeld formula in the second case. However, I think that the temperature dependence of σ at low temperatures agrees better with the Sommerfeld formula, i.e. with the theory of an electron gas formed by long cathode waves than with my theory of itinerant comet-like electrons, which correspond to very short cathode waves. However, there

†Here, Δn_a represents the difference between the actual and mean values of n_a .

is no doubt that in reality the wavelength of these waves is comparable with the interatomic distances and, consequently, they are short rather than long.

Appendix: Comments on Ya I Frenkel's paper

^IIn terms of the more usual notation the value of c can be described as follows: $c = \exp(-E_F/kT)$, where E_F is the Fermi energy.

^{II}In Ya I Frenkel's obituary [33] A I Ansel'm specially emphasised the elegance of Yakov II'ich's derivations of the main formulas in the quantum theory of metals for an ideal electron gas at absolute zero (Ansel'm mentioned this later in one of the first sessions of a meeting devoted to the memory of Ya I Frenkel' in 1953). These relationships are derived in the first section of the famous article of A Sommerfeld and H A Bethe 'Electronentheorie der Metalle' [34] written in 1933 (and published in Russian translation in 1938). There is naturally a direct reference to Frenkel's work. Judging by all the facts, Yakov II'ich himself also liked this derivation and with obvious satisfaction he included it in a number of his papers and in a book [28].

^{III}The paper mentioned by Frenkel' was presented by R Becker at a colloquium in Berlin on 24 November 1925. Four days earlier Yakov Il'ich visited Einstein, told him about his own results obtained on the theory of metals, and received his approval. This was confirmed at the colloquium itself. On 26 November Frenkel' wrote to his parents: 'The day before yesterday at a colloquium at the University in the presence of Einstein, Planck, Nernst, Laue, and other leading scientists (including Abram Fedorovich [Ioffe]) one of the subjects reported on was my theory of electric conduction of metals. Becker presented my results but differed with me on one very important topic. Einstein contradicted him strongly and declared that he "regards my ideas to be perfectly correct and the results as very remarkable" (see p. 146 in Ref. [1]). On the same day loffe wrote to his wife V A Kravtsova: "I was present at a colloquium where Frenkel's work on metals was discussed and praised very highly (particularly by Einstein)" (p. 470 in Ref. [35]).

^{IV}The concept of 'cometary' electrons was applied by Frenkel' to metals in the (chronologically) second of his publications [14] (for the English version of this paper see Ref. [15]). It is amusing to note that Ya I Frenkel' published his first work in the Petrograd journal Avtomobil (Automobile) and its title was 'Mechanical conditions of the operation of the differential' [36].

^VIn one of his postwar papers Yakov II'ich referred to the transition from the insulating to metallic type of conduction under the influence of an external pressure as the 'forced collectivisation of electrons'. This served to accuse him (at a meeting of the Academic Council of the Leningrad Polytechnic Institute in the early fifties) of mocking the Soviet collective farm system. These were difficult times!

^{VI}In contrast to Sommerfeld's work in which the influence of an external field on the motion of electrons is included automatically by the use of the Pauli–Fermi quantum statistics, Yakov II'ich tried to establish a physical model of the effect by considering diffusion jumps. However, this model provides an unsatisfactory description of the situation in ordinary metals, i.e. metals with an allowed band which is not too narrow. However, the jump ('hopping') concept applies directly to what are known as low-mobility materials.

 $^{\rm VII}Of$ course, we are dealing here with the phase velocity of waves.

^{VIII}It seems appropriate to say a few words about the relationship between Frenkel' and Sommerfeld. On 26 September 1927 he wrote to his wife from Naples: "I travelled to Naples with Sommerfeld. On the way we talked a lot, naturally about physics. He is no longer young (58 years old), but be behaves in a very simple and pleasant manner. It is a pity that ten years ago I could not be one of his students. Almost all the most talented young theoreticians (in Germany and partly elsewhere) are his students" (see p. 434 in Ref. [2]).

They evidently met in Italy. Foreign archives contain several letters from Frenkel' to Sommerfeld (the private prewar archive of Yakov Il'ich was lost during the blockade of Leningrad). These letters (see pp 337-341 in Ref. [2]) can be used to judge the profound respect and even admiration that Yakov Il'ich felt for Sommerfeld. It is interesting that Frenkel' abstracted a large paper of Sommerfeld on the electric conductivity of metals for the German abstract journal Physikalische Berichte [9 1051-1055 (1928)]. This abstract differs strikingly from the conventional form. It not only gives Sommerfeld's results, but also-with Sommerfeld' agreement-some comments which are partially polemical. Frenkel's abstract was republished by Sommerfeld (pp 103-108 in Ref. [37]) and it is a good illustration of the approach to the problem by two scientists, which supplements the paper of Yakov Il'ich reprinted above.

We shall mention two events which describe the relationship between the two theoreticians. I K Kikoin writes in Reminiscences of Frenkel' (pp 62-69): 'When I graduated from the Institute (in 1927 Kikoin graduated from the Physicomechanical Faculty of the Leningrad Polytechnic Institute) I was sent on an official trip to Germany and worked for a time at the Munich University, where Sommerfeld held the chair of theoretical physics, and I became acquainted with young postgraduate students, i.e. those who obtained a first degree, and found that they were studying Frenkel's electrodynamics. To my question what are they doing they answered: "We are preparing to be examined on electrodynamics by Sommerfeld". "But Sommerfeld has his own course of lectures on electrodynamics?". "Yes, but Professor Sommerfeld thinks there is no better course in the world than that of Frenkel'. He will examine us solely on the basis of Frenkel's book" (p. 66 in Ref. [2]).

The same Reminiscences include a paper bv G V Skrotskii. In September 1930 Sommerfeld participated in the First All-Union Congress of Physicists in Odessa. He presented there a paper on the influence of a magnetic field on the electric conductivity of metals. The paper was translated on the spot by Yakov Il'ich. Skrotskii writes: "Yakov II'ich went beyond the remit of an interpreter: he did not provide a simple translation from the German, but commented and explained various statements in Sommerfeld's paper. These improvisations did not escape the attention of Sommerfeld, who thanked him and mentioned this point especially at the conclusion. When Yakov Il'ich translated these words, Sommerfeld,

Yakov Il'ich, and many participants were laughing" (p. 164 in Ref. [12]).

^{IX}It is interesting to point out that, judging by the paper of Frenkel' presented at the Como Congress [17], he already then understood that electron diffraction by a regular crystal lattice of a metal does not give rise to the resistance. Yakov Il'ich stressed this point frequently in the paper reprinted above. The idea that the resistance of a pure defect-free metal is solely due to the thermal vibrations of the lattice is fundamental to the whole theory of the electric conductivity of metals. At present we might regard it as trivial, but we must recall that this idea was put forward in 1927-1928, and at the time it has been far from self-evident. The understanding has come only with the development of the band theory of solids. Subsequently Frenkel' has accepted his theory but has regarded its role as greatly exaggerated. His main objection was that it does not allow for the electron – electron interaction which is very strong in solids. Nevertheless, it is tempting to guess that this objection has been partly due to purely psychological and possibly even subconscious motivation. He approach very closely what is now known as the weak-binding approximation (nearly-free electron model) and is used widely in the method of pseudopotential, but did not make the next logical step of constructing a many-wave theory of diffraction of electron waves. This is particularly surprising because, judging by the list of names and references to his papers, he knew of the work of Darwin (1914), who developed a dynamic theory of X-ray diffraction in the two wave approximation. This theory is fully equivalent to the weak-binding approximation.

Here is the relevant part of his paper presented in Como: The electrical potential in an absolutely homogeneous metal crystal of infinite dimensions at absolute zero can evidently be represented by a triple Fourier series, the period of which is equal to the edge of a unit cell and the constant term is equal to the average value of the positive potential. Consequently, we have

$$W - U = W_0 + \sum_{s}' C \exp(q_1 x_1 + q_2 x_2 + q_3 x_3) , \quad (A.1)$$

where W_0 is the average kinetic energy of an electron, $q_s = (2\pi/a_s)n_s$ ($s = 1, 2, 3; n_s = 0, 1, 2, ...$) in the case of the orthorhombic lattice in which the unit cell is a parallelepiped with the edges a_1, a_2, a_3 ; the prime in the summation sign indicates that the term $n_1 = n_2 = n_3 = 0$ is excluded.

Introduction of Eqn (A.1) into the Schrodinger equation and neglect of the periodic terms compared with W_0 , gives the zeroth-order approximation in the form of a solution of the type $\psi = \psi_0 = \exp(ikx)$, where

$$k = \frac{2\pi}{\lambda} = \frac{2\pi m\nu}{h} = \frac{2\pi}{h} \sqrt{2mW_0} . \tag{A.2}$$

This solution describes the main primary waves propagating in a crystal along an arbitrarily selected direction. Each periodic term (W - U) corresponds to one side primary wave, described in the first approximation by

$$\nabla^2 \psi' + k^2 \psi' = -C \exp\left(i \sum_{s}' q_s x_s\right) \psi^0$$
$$= C \exp\left[i \sum_{s} (q_s + k_s) x_s\right], \qquad (A.3)$$

where k_1 , k_2 , and k_3 are the components of the vector k, representing the length and the direction of the main primary wave.

If it is assumed that

$$\psi' = A \, \exp\left[i\sum_{s} (q_s + k_s) \, x_s\right] \,, \tag{A.4}$$

the result is

$$\left[\sum_{s}' (q_s + k_s)^2 - k^2\right] A = C , \qquad (A.5)$$

i.e.

$$A = \frac{C}{q^2 + 2\sum_{s} q_s k_s} \,. \tag{A.6}$$

If we introduce the wavelength d of the exp($i \sum q_s x_s$) waves and use θ_q to denote the angle between the vectors kand -q, the denominator of Eqn (A.6) can be written in the form

$$q^{2} + 2\sum_{s} q_{s}k_{s} = 2\pi q \left(\frac{1}{d} - \frac{2\cos\theta_{q}}{\lambda}\right).$$
(A.7)

Hence it follows that A becomes infinite, in other words, our approximation becomes invalid at values of θ_q which satisfy the relationship

$$\lambda = 2d \cos \theta_q \; ; \tag{A.8}$$

this is the well-known Bragg or Rayleigh relationship, which determines the directions of the interference maxima.

It therefore follows that in the absence of thermal motion or any other cause of an inhomogeneity of a crystal, the main waves, like the side waves, do indeed propagate without any scattering.

The scattering and the closely related apparent absorption cannot be calculated simply. I shall not reproduce here some of the attempts which I have made in this connection. However, I shall point out one circumstance which becomes self-evident as soon as we turn to the topic. An elementary event in a crystal is the propagation not of just a single wave but of a 'packet' formed by the main and side waves. From the corpuscular point of view this effect corresponds not to a parallel beam of electrons, but to motion which is much more complex. Had we been able to solve the thermal scattering problem, could we have then found the quantity which would correspond to an 'elementary displacement' l? I do not know an answer to this question. A probable way, a possible one, is to tackle this problem without recourse to corpuscular ideas' (see pp 87-88 in Ref. [17]).

^xIt should be pointed out that fusion of these opposite points of view on the process of conduction, 'hopping' and 'free-electron', has been achieved in what are known as superlattice semiconductors. The electrons move in artificially formed layer semiconductor structures with periods of tens of angstroms, are localised by an applied electric field, and experience Bloch oscillations. The usual conduction due to almost-free electrons in weak fields changes to the hopping mechanism when the field is sufficiently high to ensure that the localisation length becomes comparable with the mean free path (or less than this path).

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