

## Metallic conductivity at low temperature

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**ABSTRACT.** Sodium below 20K exhibits a resistivity as a function of the temperature which apart a constant term of impurity tends to zero with  $T$ . The interpretation of this property shows that at every time, only a small fraction among the possible electrons of conduction takes part in the current flow. This result opens new perspectives for the study for the high  $T_c$  superconductors. In this approach the conductivity is calculated using the mechanical action to which is submitted the electron along its mean free path

### 1 Introduction

The current flow in metallic compounds such sodium for example was initially explained within the framework of the model of the free electron. In this model all the electrons of conduction i.e. for sodium the electron of valence, is supposed to take part in the current flow. With the appearance of the low temperatures we learned that the specific heat of the solids tends towards zero with the temperature. It was a serious difficulty since the model of the free electron inspired by that of perfect gases results in attributing to the electrons conduction a constant term of specific heat. The thermal properties of the electrons of conduction were then explained in their attributing quantum properties specific of the solid. But this approach leads to a difficulty compared to the interactions between the electrons of conduction. On the one hand, while taking as starting point the atoms of a perfect gas where the time of interaction is very short as compared to the average time between two exchanges, one supposes the free electrons i.e. without reciprocal interaction or almost and on the other hand the conduction electrons are supposed to obey the principle of exclusion of Pauli. However if there is

principle of exclusion of Pauli between the electrons of conduction, there are necessarily interactions. Indeed without interaction between them an electron cannot know the quantum state of one or more neighbours and satisfy the principle of exclusion of Pauli. In addition the balance of the charges between ions and electrons imposes on average in the case of sodium one electron of conduction by atom what implies strong interactions between electrons and ions.

Here it is necessary to recall that the quantum state is an intra-atomic property, i.e. of one electron in a central potential which is based, from the experimental point of view, on the spectroscopy. The principle of exclusion of Pauli as for it is an elegant explanation of the filling of the various atomic layers. On the other hand, the attribution of inter-atomic quantum properties as it is usually accepted in solid state physics remains an assumption made possible by the absence of interpretation of the existence of the atomic quantum state. However the intra-atomic character of the quantum state in its experimental bases makes it possible to remain reserved about the existence of inter-atomic quantum properties. The recent study "Quantum states and doublets" corroborates this criticism. Indeed the quantum state appears as the quantification of the mechanical action in a central potential [1].

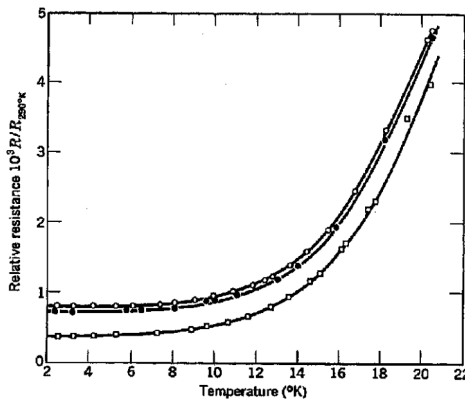


Figure 1: The resistivity of sodium below 20K by MacDonal and Mendelsohn [4,5].

We will show that in fact only a very small number of electrons of conduction really take part in the current flow. However these electrons,

except when the current flow is established, are localised at low temperature. their small number allows to explain their very large mean free path at low temperature. The other quantum homologous electrons are strongly localised on their atom. To describe the localisation of the electrons we suppose that they have a periodic motion around their atom [2] a hypothesis that we have recently used to show the compatibility between Dirac's and Sommerfeld's models [1]. Moreover we suppose that between quantum homologous electrons there is synchronisation of the motions so as to give the maximum of cohesion to the solid. The problem of correlation between electrons is consequently solved. That of the electronic specific heat which tends towards zero comes from what the solid forms a whole. It will be tackled in a separate study. The assumption that only a small number of electrons of conduction take part in the current flow is suggested by the study of the high-Tc superconductors in which the existence of defects is necessary to be conductor and superconductor [3].

The resistivity of metals at low temperature allows to highlight this conception of the electrons of conduction. Indeed the resistivity  $\rho$  can be expressed by the relation:

$$\rho = \rho_i + \rho_L \quad (1.1)$$

The  $\rho_L$  term tends towards zero with the absolute temperature T, the  $\rho_i$  term depends on the sample. It is consequently attributed to impurities. The example of sodium on figure 1, highlights well this property [4,5]. The resistivity of the sodium and that of other metals was studied to establish a law of variation at low temperature in  $T^5$ . MacDonal and Mendelssohn the authors of the study on sodium [4] underline that below 8°K it is impossible to check the law in  $T^5$  while Kittel [5] underlines that discrepancies with this law are usually observed. In fact the analysis of the experimental data shows an exponential growth of the resistivity on the whole of the points of measurement. The study of the slope of the logarithm of the resistivity gives access to the number of the electrons which take part really in the current flow. It is the goal of this work which we will tackle after having discussed calculation of electrical conductivity.

## 2 The conduction electrons.

Let us consider the resistivity of sodium below 20°K. After having subtract from  $\rho$  the contribution  $\rho_i$  the variation of the logarithm of  $\rho_L$

is practically linear between 2°K and 20°K figure 2. The slope of the curve is very close to 0,27. To understand this result let us start from the assumption of the localisation of the electrons of conduction at 0°K [3].

The various curves of resistivity according to the samples have very close slopes of the variation of  $\ln\rho$ . This property shows that the resistivity  $\rho_L$  depends little on the sample. It results from it that the proportion of the electrons which take part in conduction is practically independent of the sample. We will call electrons of conduction the totality of those which, in a material, are likely to take part in conduction. Indeed, even if only a fraction of them are involve in the current flow during a short interval of time, all over a sufficiently long time, are likely to take part in it. For sodium and metals in general, it should be concluded that the proportion of the electrons which take part in conduction is practically always the same one. We are there in a situation apparently different from the high Tc superconductors where we supposed that the electrons which take part in conduction are by assumption originating in structural impurities which are in a variable number. However this assumption allows to think that, for metals also, upon a short interval of time only a weak fraction of the conduction electrons of metal take part in current flow [3]. In fact for the superconducting compounds we will see that the structural defects allow, as for metals, to a weak fraction of conduction electrons to take part in the current flow.

Let us see now how with localised conduction electrons a weak fraction of them can take part in the current flow. In fact the barrier of potential or gap which retains each conduction electron to its atom fluctuates in the time and has a certain probability to become practically null. They are these fluctuations which allow to an appreciably constant proportion of atoms to have a very small gap during a short interval of time to participate in the current flow.

### 2.1 *Attraction.*

To describe the gap and its fluctuation it is necessary to describe the mechanism of cohesion between the atoms. Cohesion comes from the structure of the atom of metal which is made of an ion around of which revolves the most external electrons  $ns$ , these two parts contributing both to cohesion of the solid. The most significant term of cohesion of the solid arise from that the ion is not a constant charge in the various directions of space and in time. There are directions where the screening constant is

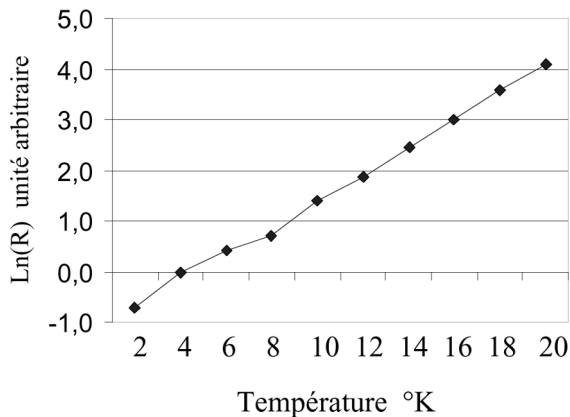


Figure 2: Variation of the logarithm of the resistance given by the resistivity term  $\rho_L$  of sodium below 20°K, from the numerical values of MacDonal and Mendelssohn [4].

weaker than the others, they are directions of positive attraction. These directions interact mainly with the electrons  $ns$ ,  $(n-1)s$  et  $(n-1)p$  of the neighbour atoms when they pass in their vicinity. This interaction gives rise to the concept of attraction which it is important to apprehend to understand the behaviour of the conduction electrons.

Thus the positive directions attract the electrons of the neighbour atoms. This aspect of the phenomena has as for result that each electron is subjected to the interactions of the neighbour atoms which correspond to a variable potential which is added to the central potential of its atom. As a result each electron describes an energy band while remaining in a quantum state well defined. There is a significant difference with the model of the free electron where the energy band are supposed the result of the multiplication of the quantum states in the solids.

## 2.2 Cohesion and attraction.

With the study of the doublets, we introduced the assumption that the electric potential is matter and that there is a continual exchange between the electron and the electric potential [1]. The density of this matter characteristic of the electric potential is supposed by assumption inversely proportional to the distance which separates the zone of con-

sidered space from the centre of the positive charges. A given quantum state corresponds to a number  $n$  of quanta of action  $h$  (Where  $h$  is the Planck constant) along a period of the motion. If  $E$  is the energy of the state and  $p$  the momentum, the quanta of action  $nh$  are the sum of the elementary actions  $Edt$  or  $pdl$ . If the density of matter increases because of an external cause to the atom, the energy and the momentum exchanged on the interval  $\{dt, dl\}$  increases. Consequently the period and the length of the trajectory decreases in such a way to keep constant the action  $nh$  during a period of the motion. If the majority of the electrons of an atom as a result of the presence of the neighbour atoms have their trajectories which decrease in length the volume of the atom decreases. It is this phenomenon which is at the origin of attraction between the atoms of a solid. Thus attraction far from delocalising the conduction electrons brings them closer to their atom.

### 2.3 Synchronisation.

Beside the attraction there is the repulsion between electrons which generates the fluctuation of the gap. To describe its influence on the gap let us consider the motion of the corresponding electrons of neighbouring atoms which gives rise to the concept of synchronisation. To characterise synchronisation let us consider in a crystal a chain of atoms of the same chemical species, of a same crystallographic site and upon each of them an electron in a same quantum state. To simplify let us suppose a close and periodic motion. Let us then consider for example two neighbour atoms A and B each one having a conduction electron  $e_A$  and  $e_B$  (figure 3).

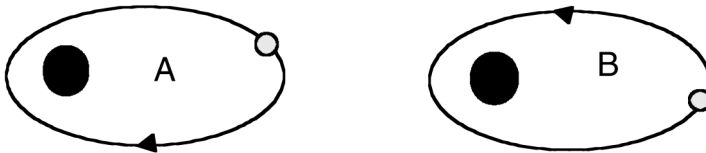


Figure 3: The synchronised motion

Without disorder at zero degree Kelvin there is correlation between the motions of the conduction electrons in such a way to have the maximum cohesive energy. For example the electron  $e_A$  comes between A and B when  $e_B$  is as far as possible from  $e_A$ . The interaction of the electron

$e_A$  with the atom core B is thus maximum. In a similar way for  $e_B$  with its other neighbour in the same chain and so on. It is the same for all the directions where there are identical chains. There is synchronisation of the motion of the electrons in the same quantum state on an atom of the same chemical species located in the same crystallographic site.

#### 2.4 *The fluctuation of the gap.*

Let us return to the cohesion of the solid. There is also a term of cohesion which comes from the synchronous motion of the electrons of neighbour atoms which are quantum and structural homologous. There is thus for the most important terms of cohesion one term for the electrons  $ns$ , another for the electrons  $(n-1)s$  and another for the electrons  $(n-1)p$ . But these electrons having different periods generates an oscillating term of repulsion which contributes to the fluctuation of the gap. This oscillating term of repulsion also involves a local variation of the interatomic distance which is another aspect of the fluctuations of the gap. We admit that it is the oscillations of this term which allow to a proportion appreciably constant  $\zeta$  zeta of atom to be temporally in position allowing to their conduction electrons to take part in the current flow.

If there is no difference of potential between the ends of the conductor, the presence of the neighbour atoms with their electron of conduction prohibited to the electrons to conduction of the atoms zeta to leave their atom. The possibility for a fraction of electron of being able to leave their atom makes that their binding energy to their atom is temporarily almost null, these electrons are temporarily almost free.

#### 2.5 *The zeta electrons.*

Let  $N$  be the number of atoms per unit of volume likely to give an conduction electron. The fraction  $N_i$  of the electrons which take part in conduction during the relaxation time  $\tau$  is in mean value zeta. We have :

$$N_i = \zeta N \quad (2.1)$$

It is interesting to recall that at low temperature the conduction electrons are known to have a mean free path  $\lambda$  much higher than atomic dimensions. At low temperature  $\lambda$  can reach values from  $10^8$  to  $10^9$  interatomic distances [6,7]. In the traditional expression of conductivity  $N_i$  is supposed equal to  $N$ . The expression (4.6) giving conductivity

shows, for a given experimental value, that the smaller factor  $\zeta$  is, the larger the collision time  $\tau$  between two shocks is large and consequently also the mean free path.

### 3 The transport of the electrical energy

By assumption the electrons of conduction are released during the application of a difference of potential. For simplicity we suppose it applied at the boundaries of the conductor. It is thus, initially, during the establishment of the current that the electrical energy is absorbed by the electrons to leave their atom. Then in the second time, when the current is established and stable, each time that an electron leaves its atom it does it by absorbing electrical energy. The expression (1.1) shows that sodium metal will have when the temperature  $T$  tends towards zero, a resistance tending towards zero if there was no impurities. This fact leads to suppose that for the resistivity  $\rho_L$  the absorbed electrical energy is then gives back because of thermal agitation when the electron itself is absorbed on another atom. As a result if the electrical energy is absorbed in an ordered way in the direction of the current, it is given back in a disordered way in all the directions of the space, and is transformed consequently into heat. It is this transport of the electric energy given back in the form of heat which determines the potential fall associated with transport of the current. In this approach it is thus a discontinuous absorption of the electric power which takes place in the solid. In the theory of the free electron one supposes initially, that the electron between two collisions is continuously accelerated by the electric field. Thereafter for the calculation of electrical conductivity the electron is supposed to move at constant speed but acceleration is supposed to be null [6]. There is a difficulty compared to the concept of electrical field which one can avoid by considering only the energy of the electron in a potential.

Leaving its atom a zeta electron becomes a free electron. Its energy  $E$  is given by the potential difference at the ends of the conductor giving it a speed  $v_D$ . It exchanges continuously this energy with the potential in which it moves in such a way to keep the balance between the spatial and temporal action. Let us then be  $m$  the mass of the electron. During a short interval of space and time  $\{dl, dt\}$  the spatial and temporal action gives :

$$mv_D \delta l = E \delta t \quad (3.1)$$



Then let us consider  $\tau$  the relaxation time between the emission of an electron of conduction and its absorption and  $\lambda$  the mean free path associated to  $\tau$ . The energy  $E$  being constant during the interval  $\{\lambda, \tau\}$  we have :

$$mv_D\lambda = E\tau \quad (3.2)$$

Thus when an conduction electron is emitted, it acquires an energy and momentum which are provided to it by the electrical potential. It transports them in the direction of the current flow, at the distance  $\lambda$  during the mean time  $\tau$ , then it is stabilised on another atom where it releases the energy and momentum in a disordered way.

#### 4 The electrical conductivity

We have just seen how the electron of conduction transports the electrical energy in the direction of the electrical current. But the electrons of conduction also receive thermal energy. This point is fundamental because each electron transporting thermal energy leaves an ion likely to be an obstacle to the current flow. Consequently the number of these ions determines that of the obstacles to the current flow. It is this number which determines the mean free path  $\lambda$  and the relaxation time  $\tau$  between the emission and the absorption of the electrons of conduction.

Let us then  $V$  be the average fall of potential on the mean free path  $\lambda$  and  $e$  the electron charge, the transported energy is :

$$E = eV \quad (4.1)$$

Taking into account (3.2) it comes :

$$mv_D\lambda = eV\tau \quad (4.2)$$

Let us then  $j$  be the density of current and  $\sigma$  the electrical conductivity. As  $V$  is the difference of potential between two points  $\lambda$  apart, we have :

$$j\lambda = \sigma V \quad (4.3)$$

Let  $N_i$  be the number of atoms per unit of volume providing an electron of conduction during the relaxation time  $\tau$ . We have :

$$j = N_i e v_D \quad (4.4)$$

Using the relation (4.2), it comes :

$$j = N_i e^2 V \tau (m \lambda)^{-1} \quad (4.5)$$

Comparing to (4.3) one obtains the expression of the conductivity :

$$\sigma = N_i e^2 \tau (m)^{-1} \quad (4.6)$$

We thus find the classical expression of electrical conductivity by introducing only the transport of the electrical energy which is then dissipated in the form of heat during the collisions which are the result of thermal agitation.

## 5 The resistivity as a function of the temperature.

To study the resistivity it is necessary now to calculate the collision time, the only term in electrical conductivity which varies with the temperature. To this end it is important to determine how an atom can become an obstacle for an electron of conduction.

### 5.1 The mechanism of the conductivity.

By assumption at low temperature only a fraction of the electrons of conduction called  $dzta$ , takes part effectively in the current flow. The other quantum homologous electrons have a too high gap to leave their atom at low temperature. During the current flow the electrons  $zeta$  are consequently generally in excess on an atom which has kept its electron of conduction. Let us then consider a  $zeta$  electron. As long as it is in excess it cannot be stabilised on the atom. Let us now suppose that it gravitates in space of an atom which has lost its electron of conduction, i.e. an ion. If there is no thermal disorder it will just carry on its path as the electron which it has preceded it and which left itself the atom. On the other hand if this zone of space is subjected to thermal agitation then it exists a certain probability so that the electron of conduction is stabilised on the ion which thus becomes again a neutral atom. The electrical energy that it transported is then dissipates in the form of heat, it is the Joule effect. Thus the only possible obstacles to the current flow are the atoms which lost their electrons of conduction. At low temperature, the field that we consider for the resistivity of sodium, their number is equal to that of the electrons  $zeta$ .

5.2 *The calculation de la resistivity*

Let then  $P$  be the probability for an atom of having thermal energy higher than that necessary to become an obstacle. Among the  $N_i$  atoms there are constantly creation and annihilation of obstacles. Let  $p_c$  and  $p_a$  be the corresponding probabilities. The maximum number of possible obstacles is  $N_i P$ . The number of the obstacles destroyed per unit of time is  $N_i P p_a$ . The number of the obstacles created per unit of time is  $N_i(1 - P)p_c$ . In stable current, at the macroscopic scale, there are necessarily balance between creations and annihilations of obstacles. Consequently it comes :

$$N_i P p_a = N_i(1 - P)p_c \tag{5.1}$$

whence :

$$\frac{p_a}{p_c} = \frac{1 - P}{P} \tag{5.2}$$

The annihilation of obstacles generates a conducting term, consequently the collision time  $\tau$  is proportional to  $p_a$ . On the other hand the creation of obstacles generates a resistant term,  $\tau$  is consequently inversely proportional to  $p_c$ . It comes :

$$\tau = \tau_a \frac{p_a}{p_c} = \tau_a \frac{1 - P}{P} \tag{5.3}$$

The term  $\tau_a$  is a time to determine. Taking  $P = \frac{1}{2}$  it comes  $\tau = \tau_a$ . Thus  $\tau_a$  is the value of  $\tau$  when  $P = \frac{1}{2}$ .

It comes for the conductivity :

$$\sigma = \sigma_a \frac{P - 1}{P} \quad \text{avec} \quad \sigma_a = \frac{N_i e^2 \tau_a}{m} \tag{5.4}$$

and for the resistivity :

$$\rho = \rho_a \frac{P}{1 - P} \quad \text{avec} \quad \rho_a = \frac{m}{N_i e^2 \tau_a} \tag{5.5}$$

To determine the variations of  $\rho$  it is necessary to study those of  $P$ . The function  $P$  is the probability for an atom of having thermal energy higher than that necessary to become an obstacle.

### 5.3 Mean energy and dispersion

The function  $P$  comes from the integration of the densities of probability for an electron to have an energy higher than the barrier of potential  $E_g$  which retains it to its atom at zero Kelvin degree. Let  $D(E, U)$  be the representative function of the densities of probability. In this expression  $E$  is the thermal energy of the particle and  $U$  is the average thermal energy by particle, as a result it characterises the dispersion of energy. Indeed more  $U$  is high more the density of probability takes significant values for high energies.

At high temperature the atoms of a solid tend in an asymptotic way to absorb thermal energy proportionally at the absolute temperature. It is the law of Dulong and Petit. This property authorises to describe the distribution of their energy as for the atoms of a gas while taking for their mean thermal energy  $U = 3kT$  with corrective terms if one want a better approximation.

At low temperature the situation is different, the atoms tend to behave like a whole. It is in particular what shows the specific heat of the solids which tends towards zero with  $T$ . In fact the zeta electrons can be regarded as privileged receivers of the thermal energy received on the surface of the solid. By assumption we suppose zeta atoms disordered. Now as a result of the very small number of the zeta electrons, we suppose that they practically do not exchange directly between them their energy. Under this angle the zeta electrons can be considered independent from each other as the atoms of a perfect gas. We can thus take as representative function of the distribution of the thermal energy of the electrons zeta that of the atoms of gas. The calculation itself of the energy of the electrons zeta comes out of the framework of this work and we will propose it in a separate study.

### 5.4 The calculation of number of the zeta electrons.

Let us consider the  $N_i$  electrons which take part in conduction. The energy of the barrier of potential which retains them to their atom at zero Kelvin degree is  $E_g$ . Their participation to the current flow depends on a probability during which  $E_g$  is practicaly zero. Before this participation when the temperature increases the electrons receive an average thermal energy, let  $E_m$  be this energy. The barrier of potential decreases as much. Let  $E_g(T)$  be this barrier, one has :

$$E_g(T) = E_g - E_m \quad (5.6)$$

They are the ions left by the electrons having a thermal energy  $E_m$  which are likely to contribute to the formation of the obstacles to the current flow.

In the expression (5.5) giving the resistivity  $\rho = \rho_a P / (1 - P)$ , the temperature  $T$  being low the probability  $P$  is low, one can thus consider that :

$$\rho = \rho_a P \quad (5.7)$$

We defined  $P$  as the probability for an atom to have a thermal energy higher than that necessary to become an obstacle. It is thus the probability for a conduction electron to have a thermal energy higher than energy  $E_g(T)$ . The determination of  $P$  [8,9] gives :

$$P = A^{-1} \ln \left[ 1 + \exp -\alpha \left( \frac{E_g(T)}{U} - 1 \right) \right] \quad (5.8)$$

with  $A = 1,7054$  and  $\alpha = 1,5049$

In this expression  $U$  is the average thermal energy of the atoms of the gas. This energy is  $\frac{1}{2}kT$  for each of the three degrees of freedom. In addition as we are at low temperature, in the expression of the logarithm the exponential is small and we have with a good approximation:

$$P = A^{-1} \exp -\alpha \left( \frac{E_g(T)}{U} - 1 \right) \quad (5.9)$$

Taking into account (5.4), (5.5) and (5.7) it comes :

$$\ln \rho = \ln \rho_a - \ln A - \alpha \frac{E_g}{U} + \alpha \frac{E_m}{U} + \alpha \quad (5.10)$$

The terms  $\ln \rho_a$ ,  $\ln A$  and  $\alpha$  are constant. When  $T$  tends towards zero the term  $-\alpha E_g / U$  tends towards minus the infinite, the probability  $P$  tends towards zero. The compound tends towards the superconducting state. In fact impurities for sodium and the conductors which side with in this type of compounds, are responsible for the  $\rho_i$  term of the relation

(1.1). At low temperature we know that the specific heat  $C_e$  of the electrons of conduction varies linearly with  $T$ , we have  $C_e = \gamma T$  where  $\gamma$  is the linear coefficient. Thus one has  $E_m = \frac{1}{2}\gamma T^2$ . The term  $\gamma$  is generally expressed by mol, as the disorder results from collisions in all the directions of space, one has, for a mole, to replace  $U$  by  $3RT/2$ . But for one gram atom carrying the conduction electrons only the fraction  $\zeta$  receives energy  $E_m$ . To take this point into account one has to replace  $R$  by  $\zeta R$ . It comes :

$$\alpha \frac{E_m}{U} = \alpha \frac{\gamma T}{3\zeta R} = dT \quad (5.11)$$

In this expression  $d$  is the slope of the logarithm of the resistivity. Thus resistivity has at low temperature an exponential term of variation with temperature. When this term overrides the  $\alpha E_g/U$  term in the expression (5.10) the logarithm of  $\rho$  presents a linear variation to low temperature. It is what shows figure 2. Let us write,  $E_g = kT_g$ , the experiment for sodium shows that  $T_g$  is lower than two Kelvin [4 and figure 1]. For Na we have  $\gamma = 1,381$  mJ/mol-degr<sup>2</sup>. It comes :

$$\zeta = \frac{\alpha\gamma}{3Rd} \quad (5.12)$$

The experiment gives for sodium  $d=0,269$  and  $\zeta = 3.1 \cdot 10^{-4}$ . There are thus very few atoms whose electron takes part in the current flow and one understand that the mean free path is much higher than the computed values while supposing than all the sodium atoms bring an electron of conduction.

Thus there is a small number of electrons contributing to the current flow associated to a gap. This result makes closer the metallic conductivity to that of the semiconductors and to that of the metallic glasses.

### 5.5 The mean free path

To calculate the mean free path at low temperature let us notice that conductivity is proportional to the average time between the emission and the absorption of an electron. According to the experimental data of MacDonald and Mendelssohn [4] to 2°K the relationship between resistance to this temperature and that to 300°K is  $R(2^\circ\text{K})/R(300^\circ\text{K}) \approx 10^{-3}$ . This result combined with factor  $\zeta$  leads to  $\lambda(2^\circ\text{K}) \approx 10^6 \lambda(\text{free-electrons } 300^\circ\text{K})$ . With  $\lambda(\text{free-electrons } 300^\circ\text{K})$

$\approx 100\text{\AA}$  one obtains  $\lambda(2^\circ\text{K}) \approx 1\text{cm}$ , result which up to now remained surprising in the frame of the classical model of the free electron as underlines it Kittel [5,7].

Among the experiments which put in view large mean free path within the framework of the model of the free electron there are those of Bernamont and Surdin on the fluctuations of current in a conductor [10-12]. To explain their results they admit the existence of rare soft collisions i.e. obstacles on which the electrons dissipate the electrical energy, as a result a mean free path much larger. In the model developed in this study the number of the atoms likely to lead to a soft collision is equal to that of the electrons zeta. Moreover absorption of an electron on an obstacle is the result of a certain probability, it is thus natural to observe fluctuations of resistance. We thus find a great similarity with the analysis of Bernamont and Surdin.

### 5.6 *The case of the high $T_c$ superconductors.*

The assumption that only a low number of electrons among those possible take part in conduction comes from the study of the high  $T_c$  superconductors [3]. The study of these compounds shows the need of structural impurities to observe metallic conductivity and superconductivity. There is a difference compared to metals that is only apparent. Indeed the structural defects introduce a first reduction of the gap. The fluctuations of this gap related to the various electronic periodic motions are then sufficient to make it almost zero. The corresponding zeta electrons are then practically free as with traditional metals. Under this angle the role of the structural impurities is to allow the gap, thanks to the fluctuations, to reach sufficiently low values to make the compound conducting.

The experimental verification shows that with the high  $T_c$  superconductors there also is a factor  $\zeta$ . For  $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$  with the curves of Wu et al [13] one find  $d = 1$ , taking into account the value of  $\gamma = 3,1 \text{ mJ/mol-degr}^2$  given by Eckert et al. [14] one obtains  $\zeta = 1.9 \cdot 10^{-4}$ .

This result comes to supplement the interpretation of the field high temperature where the high  $T_c$  superconductors have a resistivity which varies linearly with  $T$  [15,16]. Instead of having a number of electrons and obstacles equal to the number of the atoms likely to bring conduction electrons, there is only one very weak fraction of these electrons which take part in conduction. On the other hand at high temperature all the atoms likely to bring conduction electrons can become obstacles. We

suppose that they become obstacle by thermal ionisation of their conduction electrons. This ionisation being disordered the electron emitted like this does not contribute to the intensity of the current flow but the corresponding ions are as much obstacles. Let us then  $E_{ob}$  be the energy of this barrier. If the solid is well crystallised the dispersion of the values of  $E_{ob}$  is weak, all the obstacles will be formed in the vicinity of the  $T_{ob}$  temperature such as  $E_{ob} \approx kT_c$ . Moreover the disorder causes a reduction in the  $E_{ob}$  energy of disorder and amplifies the variation of the resistivity  $\rho$  given by (5.5) which is of exponential type. These are the variations of resistivity which give in cuprates the superconductivity and which we already discussed [15,16]. What is remarkable it is that because of the very small number zeta of the electrons taking part in the current flow, superconductivity is the result of a phenomenon of order-disorder not on the conduction electrons but on the obstacles to the current flow. Now for metals as sodium one does not observe abrupt variation of the resistivity. We suppose that this absence comes from the dispersion of the values of the  $E_{ob}$  energy of disorder.

Finally it is necessary to distinguish the superconductivity observed with cuprates for example from that observed with metals or alloys as for gallium [17]. For gallium indeed the specific heat exhibits a  $\gamma T$  term for temperature higher than  $T_c$  but this term is present in cuprates below this temperature. That comes from the two types of atoms carrying the conduction electrons: those carrying the  $\zeta$  electrons and the others. For different compounds or metals the zeta atoms and consequently the corresponding electrons can be ordered at a temperature sufficiently low. Then they have a temperature of order-disorder as the other atoms than the zeta atoms. It is like this that one has to understand the variations of specific heat observed on the gallium on which we will return in a separate study.

## 6 Conclusion

Thus with localised electrons on their atom, the study of metallic conductivity at low temperature shows that in metals only a small zeta fraction among the possible electrons of conduction are involve in the current flow. At low temperature they are the atoms of these electrons which play the role of obstacles. For the other electrons the potential energy cannot excite them. There is a point which makes it possible to clarify the study of the superconductors because there are two types of atoms carrying the electrons of conduction: those carrying the zeta



electrons and the others. The atoms of these two types can each one give rise to an order-disorder transition which generates each one a transition superconductor-conductor. We will propose in a separated study the calculation of the heat capacity of the zeta electrons which was a fundamental difficulty of the free electron model.

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