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## Electronic specific heat of aluminium.

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### 1. Introduction.

In a solid at any temperature the mass centres or nuclei of the atoms are not at rest but vibrate about mean position. In insulators the specific heat of the solids is, in general, due entirely to these vibrations; in metals a part of the specific heat is due to the motion of free electrons, but this part is usually very small. At low temperature, however, it should become comparable with the contribution from lattice vibrations, which according to Debye's computations is equal to

$$k \frac{12\pi^4}{5} (T/\Theta_D)^3, \quad (1)$$

where  $k$  is the Boltzmann's constant,  $T$  the absolute temperature and  $\Theta_D$  is the Debye characteristic temperature. We shall show in the following paragraphs that the contribution due to the free electrons is

$$\frac{1}{6}\pi^3 \frac{k^2 T}{\varepsilon'_0}, \quad (2)$$

where  $\varepsilon'_0$  means the certain energy of the order of 1 eV. The ratio of (1) to (2), namely,

$$\frac{5}{72\pi} \frac{kT}{\varepsilon'_0} \left(\frac{\Theta_D}{T}\right)^3$$

approaches unity in the neighbourhood of 1° K when  $\Theta_D$  is of the order of 100°. We see, therefore, that according to this result, an appreciable part of the specific heat of metals in the neighbourhood of 1° K should have electronic origin.

In order to observe the electronic part of the specific heat it is thus necessary to carry out the measurements at very low temperature. The most accurate measurements have been made on aluminium by Kok and Keesom,<sup>1)</sup> for which the molar heat is

$$C_v = 1,742 \cdot 10^{-4} RT + 3Rf_D\left(\frac{419}{T}\right), \quad (3)$$

where  $f_D(\Theta_D/T)$  is the well known Debye function, which at the low temperatures has the form of (1). The last expression is valid only above 1,13° K, for the metal changes to the superconducting phase at this temperature.

If we compare (1) and (2) with the empirical formula (3) we see at once that the term corresponding to the electronic specific heat is given by the term, which increases linearly temperature, i. e. by  $1,742 \cdot 10^{-4} RT$ .

The purpose of the present paper is to show, how it is possible to calculate this electronic specific heat from the known distribution of electrons in the zone picture of aluminium, as it was derived by the author in the previous paper<sup>2</sup>).

## 2. Model of zone structure of aluminium.

The three valence electrons of aluminium are distributed in the first and second Brillouin's zones. A face-centered cubic lattice of this metal has a body-centered lattice as its reciprocal and then it is easy to show that the first Brillouin's zone is truncated octahedron, marked out by the planes (111) and (200). The second zone is bounded by the same set of planes. Figure 1. represents the section through these zones in the plane containing the axis  $k_z$  and the direction [111] respectively, together with the position of the surfaces of Fermi energy, as they were derived in the paper mentioned above. The shaded area means the levels occupied by electrons.

The first zone is approximately full, it contains, therefore, nearly two electrons and the Fermi surface lies near to the square faces (200), bounding the zone in the [100]-directions. There is no overlap in the [100]-direction into second zone. The third electron is situated in the second zone, where the Fermi surface has the shape of semi-spheres, surrounding the eight points  $\left[ \pm \frac{\pi}{a}, \pm \frac{\pi}{a}, \pm \frac{\pi}{a} \right]$ . The energy of the electrons at this part of the Fermi surface is given by the formula:

$$E = E_0 + \frac{\hbar^2}{8\pi^2m} k_m^2, \quad (4a)$$

where  $E_0$  means the lowest energy of the second band, which is according to our calculations<sup>3</sup>) equal to 9,5 eV and  $k_m$  denotes the

maximal wave vector, with the value:  $k_m = \pi/a$  ( $a$  being the lattice constant of aluminium).

In the first zone the shape of the Fermi surface has the form of the planes parallel with the square faces (200), which are only curved near the corners of this zone. The energy ( $\epsilon_0$ ) corresponding to the Fermi limit is about 12,0 eV.

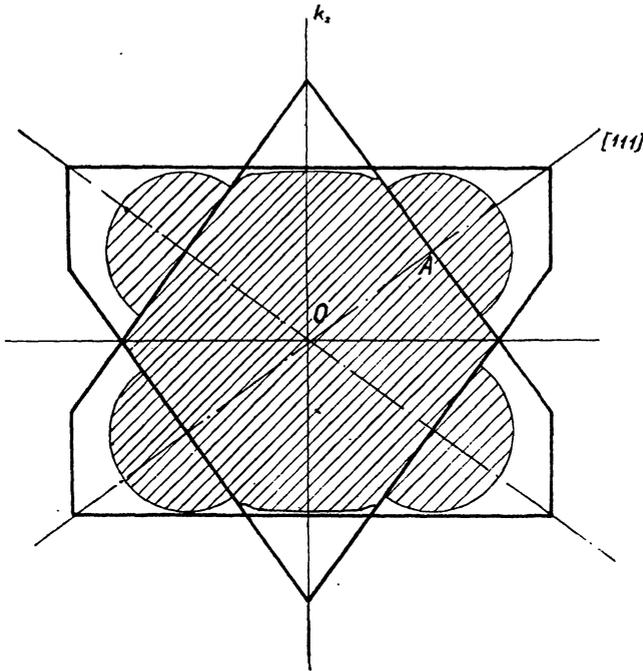


Fig. 1.

For further consideration it will be important to know the number of the stationary states  $N(E)$ , per unit volume of the metal, having the energies between the values  $E, E + dE$ , near the top of the Fermi distribution. We have shown<sup>3)</sup> that these electrons at the Fermi surface in the second zone behave as if they were free. The density of the states is then given by

$$N^{(II)}(E) = c \sqrt{E - E_0}, \quad (4b)$$

where  $c$  is the constant and  $E_0$  means the lowest energy of the second zone. Quite another situation is in the first zone. In this case we have deduced that the density curve has a peak value for the energy  $\epsilon_0$  corresponding to the Fermi energy at zero temperature

(fig. 2). The density of states for the energy higher than  $\epsilon_0$  decreases abruptly to very small value.

It is possible to show that the energy of electrons at the point  $a$  in [111]-direction in the first zone is about 6,5 eV (fig. 1).<sup>3)</sup> The

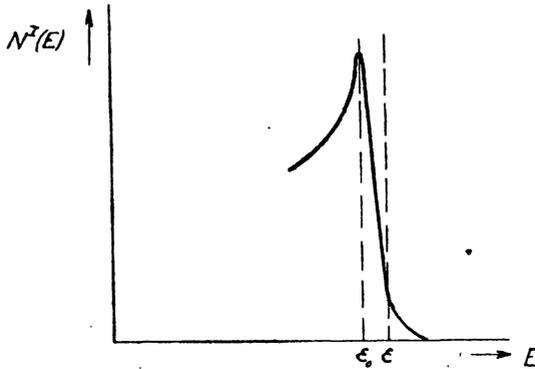


Fig. 2.

energy gap across the plan of discontinuity (111) in this direction has the value 3 eV. Therefore, the value of energy of the state at the same point  $a$  in the second Brillouin's zone is 9,5 eV and this is the lowest energy of the second band.

Thus the distribution of electrons and the relative position of these two bands in aluminium is such, as it is depicted in fig. 3.

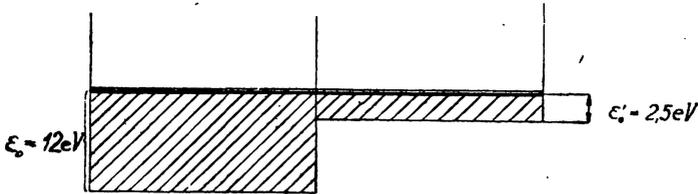


Fig. 3.

The first band is represented at the left side and its width of energy corresponds to 12 eV. The third electron is situated in the second band, which we represent at the right side of the figure. The shaded area means again the occupied levels.

### 3. The specific electronic heat.

In our first and second band there are a series of possible stationary states for an electron. We know also that the Pauli

exclusion principle forbids more than two electrons to be in any one stationary state; it follows that at the absolute zero of temperature, all states with energy below a certain maximum energy  $\epsilon_0$  are doubly occupied, and higher states empty.  $\epsilon_0$  is given by the equation

$$2 \int_0^{\epsilon_0} N(E) dE = N, \quad (5)$$

where  $N$  is the total number of electrons per unit volume.

At finite temperature there will be a number of electrons with energies greater than  $\epsilon_0$ ; according to the Fermi-Dirac statistic, the probability<sup>5)</sup> that a given quantum state of energy  $E$  is occupied, is given by the „Fermi-Dirac distribution function“

$$f(E) = \frac{1}{e^{(E-\epsilon)/kT} + 1}, \quad (6)$$

the number of electrons having energy between  $E$  and  $E + dE$  is thus

$$2N(E) f(E) dE = \frac{2N(E) dE}{e^{(E-\epsilon)/kT} + 1}. \quad (7)$$

$\epsilon$  is here the thermodynamic potential per electron and may be determined from the equation

$$2 \int_0^{\infty} N(E) f(E) dE = N, \quad (8)$$

the integration being over all energies for which  $N(E)$  is finite. At the absolute zero temperature the constant  $\epsilon$  is equal to the maximum electronic energy  $\epsilon_0$  at this temperature, which in our case is equal to  $\epsilon_0 = 12,0$  eV.

More difficult is to evaluate the integral (8) in the case of temperature different from zero. Sommerfeld and Bethe have developed a convenient method for evaluating integrals of this type when  $kT \ll \epsilon$  and this is a case in which are interested here. Denoting by  $F(E)$  any function of  $E$  which vanishes for  $E = 0$ , we have<sup>6)</sup>

$$\int_0^{\infty} f(E) \frac{d}{dE} F(E) dE = F(\epsilon) + \frac{1}{6} \pi^2 (kT)^2 F''(\epsilon) + \dots \quad (9)$$

If we put into the last expression for  $F(E)$  the integral:

$$F(E) = \int_0^E N(E) dE,$$

the left side of eq. (9) is identical with the integral in (8) and hence we can determine  $\epsilon$ .

To calculate the specific heat due to the electrons it is necessary to know the total energy of electrons ( $\bar{E}$ ) in the conducting bands. If we take the lowest energy in the first band as zero, we can write:

$$\bar{E} = 2 \int_0^{\infty} N(E) f(E) E dE. \quad (10)$$

Denoting by  $N^I(E)$  or  $N^{II}(E)$  the density of states in the first or second zone respectively we can express the last integral as the sum of two integrals ( $N(E) = N^I(E) + N^{II}(E)$ ):

$$\bar{E} = 2 \int_0^{\infty} N^I(E) f(E) E dE + 2 \int_0^{\infty} N^{II}(E) f(E) E dE. \quad (11)$$

The first integral on the right side may be evaluated again according to the formula (9) by putting  $F(E)$  equal to  $\int_0^E N^I(E) E dE$ .

We shall get:

$$\begin{aligned} 2 \int_0^{\infty} N^I(E) f(E) E dE &= 2 \int_0^{\infty} N^I(E) E dE + \frac{1}{3} \pi^2 (kT)^2 \left[ \frac{d(EN^I)}{dE} \right]_{E=\infty} = \\ &= 2 \int_0^{\infty} N^I(E) E dE + 2 \int_0^{\infty} N^I(E) E dE + \\ &+ \frac{1}{3} \pi^2 (kT)^2 \varepsilon \left[ \frac{dN^I}{dE} \right]_{E=\infty} + \frac{1}{3} \pi^2 (kT)^2 N^I(\varepsilon). \end{aligned} \quad (12a)$$

Similarly we obtain for the second integral:

$$\begin{aligned} 2 \int_0^{\infty} N^{II}(E) f(E) E dE &= 2 \int_0^{\infty} N^{II}(E) E dE + 2 \int_0^{\infty} N^{II}(E) E dE + \\ &+ \frac{1}{3} \pi^2 (kT)^2 \varepsilon \left( \frac{dN^{II}}{dE} \right)_{E=\infty} + \frac{1}{3} \pi^2 (kT)^2 N^{II}(\varepsilon). \end{aligned} \quad (12b)$$

Putting these expressions back into (11) we can write the formula for energy  $\bar{E}$  in the form:

$$\begin{aligned} \bar{E} &= 2 \int_0^{\infty} N(E) E dE + 2 \int_0^{\infty} N(E) E dE + \\ &+ \frac{1}{3} \pi^2 (kT)^2 \varepsilon \left[ \frac{dN}{dE} \right]_{E=\infty} + \frac{1}{3} \pi^2 (kT)^2 (N^I(\varepsilon) + N^{II}(\varepsilon)). \end{aligned} \quad (13)$$

The first integral on the right side is equal to the energy of electrons at the absolute zero of temperature. The sum of the next two terms is zero. This we can prove in the following way: we set again

$F(E) = \int_0^E N(E) dE$  into (9) and hence obtain for the total number

of electrons per unit volume

$$N = 2 \int_0^{\infty} f(E) N(E) dE = 2 \int_0^{\varepsilon} N(E) dE + \frac{1}{3} \pi^2 (kT)^2 \left( \frac{dN}{dE} \right)_{E=\varepsilon}.$$

If we now subtract the equation (5) from the last equation, we obtain

$$0 = 2 \int_{\varepsilon_0}^{\varepsilon} N(E) dE + \frac{1}{3} \pi^2 (kT)^2 \left[ \frac{dN}{dE} \right]_{E=\varepsilon}. \quad (14)$$

Further we know that  $\varepsilon$  is only slightly different from  $\varepsilon_0$ , we may thus write second integral in (13) with sufficient accuracy in the form:

$$2 \int_{\varepsilon_0}^{\varepsilon} N(E) E dE = 2\varepsilon \int_{\varepsilon_0}^{\varepsilon} N(E) dE.$$

Multiplying, therefore, eq. (14) by  $\varepsilon$ , we see at once that the sum of the second and the third term in (13) is equal to zero.

We can also neglect in (13) the term  $\frac{1}{3} \pi (kT)^2 N^I(\varepsilon)$ , as we know, from the previous paragraph, that the density of states in the first zone for energy  $\varepsilon$  (e. i.  $N^I(\varepsilon)$ ) is much more smaller than  $N^{II}(\varepsilon)$  (fig. 2).

Thus we obtain for the total energy  $\bar{E}$  the following expression:

$$\begin{aligned} \bar{E} &= 2 \int_0^{\varepsilon_0} N(E) E dE + \frac{1}{3} \pi^2 N^{II}(\varepsilon) (kT)^2 = \\ &= 2 \int_0^{\varepsilon_0} N(E) E dE + \frac{1}{3} \pi^2 N^{II}(\varepsilon_0) (kT)^2, \end{aligned} \quad (15)$$

where we have put for  $N^{II}(\varepsilon)$  the density of states for the energy  $\varepsilon_0$  (e. i.  $N^{II}(\varepsilon_0)$ ), as we know safely that the density of states at the Fermi energy in the second zone do not change suddenly and  $\varepsilon_0 \doteq \varepsilon$ .

In order to evaluate  $\bar{E}$  it is thus necessary to know the density of states on the Fermi surface:  $N^{II}(\varepsilon_0)$ . We have remarked already in the second paragraph that the electrons in this state are practically free and the density of the states must be given by (4b). The value of the constant  $c$  in the expression (4b) we can find easily as follows: it is well known that the density of the states  $N(E)$  is expressed by the general formula<sup>7)</sup>:

$$N(E) = \frac{1}{8\pi^3} \iint \frac{dS}{|\text{grad } E|},$$

where the integration is over the surface in  $k$  space on which the energy is constant and has the value  $E$ . In our case it means that

we must integrate over the Fermi surface which is composed of the eight semi-spheres with the radii  $\pi/a$ . From the expression for energy (4a):  $E = E_0 + \hbar^2/8\pi^2m \cdot k^2$ , where  $\vec{k}$  means the wave vectors with the origin in the points  $\left(\pm \frac{\pi}{a}, \pm \frac{\pi}{a}, \pm \frac{\pi}{a}\right)$  and ending on the Fermi surfaces of the second zone, we have

$$N^{II}(\varepsilon_0) = \frac{\pi}{a^3} \frac{1}{\varepsilon'_0}; \quad (16)$$

$\varepsilon'_0$  is equal to  $\varepsilon_0 - E_0 = 12,0 \text{ eV} - 9,5 \text{ eV} = 2,5 \text{ eV}$ . The number of atoms in the elementary cell of the face-centered cubic lattice of aluminium is four. Thus the number of electrons in the second zone per unit volume in aluminium is given by:

$$N = \frac{4}{a^3}.$$

Putting this expression into (16) we can write:

$$N^{II}(\varepsilon_0) = N \frac{1}{4} \pi \frac{1}{\varepsilon'_0}. \quad (17)$$

The final expression for the total energy of electrons is then as follows:

$$\bar{E} = \bar{E}_0 + \frac{1}{12} \pi^3 N \frac{1}{\varepsilon'_0} (kT)^2, \quad (18)$$

where  $\bar{E}_0$  denotes the energy of electrons at the zero temperature.

To obtain the contribution to the specific heat at constant volume we must divide by the density  $\rho$  and differentiate with respect to  $T$ :

$$c_v = \frac{1}{6} \pi^3 n \frac{k^2 T}{\varepsilon'_0},$$

where  $n = N/\rho$  is the number of electrons per unit mass.

The molar heat is then given by

$$C_v = \frac{1}{6} \pi^3 \frac{kT}{\varepsilon'_0} R, \quad (19)$$

where  $R$  is the gas constant.

Comparing this last expression with the first term of the empirical equation (3) we must expect that the value of  $\frac{1}{6} \pi^3 \frac{k}{\varepsilon'_0}$  ought to be equal to  $1,74 \cdot 10^{-4}$ . According to our band model of aluminium we must put for  $\varepsilon'_0 = 2,5 \text{ eV}$ . Taking this theoretical con-

stant we shall get for our constant the following value:

$$\frac{1}{6}\pi^3 \frac{k}{2,5 \text{ eV}} = 1,755 \cdot 10^{-4}.$$

The agreement between the theory and experiment seems to be rather good.

#### References:

1. Kok and Keesom, *Physica*, Volume IV, p. 835 (1937).
2. Matyáš, *Phil. Mag.:* Ser. 7, XXXIX, 420 (1948).
3. Matyáš, *Phil. Mag.:* „Age hardening of aluminium-copper alloys“; in print (1948).
4. See e. g. Mott-Jones: *Properties of Metals and Alloys*; Oxford (1936), p. 84.
5. Sommerfeld, Bethe: *Hand. d. Physik*, Vol. 24/2 (1933), p. 339.
6. Sommerfeld, Bethe: *op. cit.*
7. See e. g. Mott-Jones: *Properties of Metals and Alloys*; Oxford (1936), p. 85.

\*

#### Elektronické specifické teplo hliníku.

(Obsah předešlého článku.)

Specifické teplo kovů má původ ve dvou, svou povahou odlišných, zjevech. K celkovému specifickému teplu přispívají jednak termické kmity pozitivních iontů a jednak elektronový plyn ovládaný Fermiho statistikou (elektronická část specifického tepla).

Autor v předechozích pojednáních zjistil strukturu obou Brilloninových pásem hliníku. Na podkladě tohoto výsledku je poměrně snadné dokázat, že jen elektrony z druhého Brilloninova pásma přispívají podstatně k celkovému specifickému teplu tohoto kovu. Velikost tohoto příspěvku možno určit pomocí kvantově mechanických method a výsledek je v dobré shodě s přesnými měřeními Kok a Keesoma.