[Journal of the Faculty of Science, Hokkaidô University, Japan, Ser. II, Vol. III, No. 7, 1949.]

Kroll's Expression for the Heat Resistance of the Monovalent Metals

By

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(Received February 15, 1949)*

The third approximation of Kroll's expression for the ideal heat resistance of the monovalent metals, which is considered to be a practically sufficient approximation, has been explicitly calculated. It has a maximum at an intermediate temperature, so that this maximum is not likely ascribed to the insufficient order of approximation, as hitherto stated.

Kroll[1] has derived by his method of solving Bloch's integral equation the following general expression for the ideal heat resistance of the monovalent metals (κ: the heat conductivity)

$$\frac{1}{\kappa} \sim T \frac{(b_{22}+k^2T^2a_{22})a_{22} + (b_{24}+k^2T^2a_{24})a_{24} + (b_{26}+k^2T^2a_{26})a_{26}}{\underbrace{a_{22}}_{\text{first approx.}} + \underbrace{\frac{14}{5}\pi^2a_{24} + \frac{49}{25}\pi^4a_{44}}_{\text{second approx.}} + \underbrace{\frac{62}{7}\pi^4a_{26} + \frac{434}{35}\pi^6a_{46} + \frac{961}{49}\pi^8a_{66}}_{\text{third approx.}}}, \qquad (1)$$

which should be accurate over the whole temperature range. All the notations** are the same as Kroll's. The first and the second approximations have been already calculated, which are reproduced in the appendix for the sake of comparison. Each of these approximations has a maximum at an intermediate temperature. Kroll has suggested that it is due only to the insufficient order of approximation, while Makinson[2] has stated that Kroll's expression should not show essentially this maximum. Hence it was tempting

* Presented at the first meeting of The Hokkaidô Branch of The Physical Society of Japan, December 8, 1946.

** The explicit expressions of the all quantities will be tabulated in reference (3).

to test this question by means of the higher approximations. For this purpose we have calculated the third approximation explicitly and obtained the following expression.

THE THIRD APPROXIMATION OF (1)

$$\frac{\kappa_{T=\infty}}{\kappa} = \frac{2^{\frac{2}{3}}3}{\pi^2}\,\frac{1}{X^4}\,\frac{X^6P + X^4Q + X^2R + S}{X^4A + X^2B + C},$$

$$X = \frac{x}{2^{\frac{1}{3}}} = \frac{1}{2^{\frac{1}{3}}}\,\frac{\theta}{T},$$

$$J_n(x) = \int_0^x \frac{\xi^n\,d\xi}{(e^{\xi}-1)(1-e^{-\xi})}, \qquad x = \frac{\theta}{T},$$

$$\begin{aligned}
A \equiv\ & \frac{3101696}{11025}\pi^{12}J_5^2 + \frac{311116}{2205}\pi^{10}J_5J_7 + \frac{207616}{3675}\pi^8J_5J_9 + \frac{820}{441}\pi^6J_5J_{11} + \frac{46}{75}\pi^4J_5J_{13} \\
& - \frac{544}{147}\pi^8J_7^2 + \frac{232}{21}\pi^6J_7J_9 - \frac{257}{147}\pi^4J_7J_{11} + \frac{23}{210}\pi^2J_7J_{13} + \frac{468}{175}\pi^4J_9^2 + \frac{1}{210}\pi^2J_9J_{11} \\
& + \frac{23}{420}J_9J_{13},
\end{aligned}$$

$$\begin{aligned}
B \equiv\ & \frac{41652224}{282975}\pi^{14}J_5^2 - \frac{13873408}{363825}\pi^{12}J_5J_7 + \frac{1320079}{121275}\pi^{10}J_5J_9 - \frac{179408}{77175}\pi^8J_5J_{11} \\
& + \frac{7678}{33075}\pi^6J_5J_{13} - \frac{1}{825}\pi^4J_5J_{15} - \frac{98144}{2205}\pi^{10}J_7^2 + \frac{2176}{525}\pi^8J_7J_9 - \frac{3638}{1323}\pi^6J_7J_{11} \\
& - \frac{1529}{22050}\pi^4J_7J_{13} - \frac{1}{4620}\pi^2J_7J_{15} + \frac{1444}{525}\pi^6J_9^2 + \frac{3461}{22050}\pi^4J_9J_{11} + \frac{6}{175}\pi^2J_9J_{13} \\
& - \frac{1}{9240}J_9J_{15} - \frac{7}{180}\pi^2J_{11}^2 - \frac{43}{105840}J_{11}J_{13},
\end{aligned}$$

$$\begin{aligned}
C \equiv\ & \frac{196608}{11319}\pi^{16}J_5^2 - \frac{20826112}{848925}\pi^{14}J_5J_7 + \frac{474868}{121275}\pi^{12}J_5J_9 - \frac{1546763}{1131900}\pi^{10}J_5J_{11} \\
& + \frac{8}{315}\pi^8J_5J_{13} - \frac{4}{13475}\pi^6J_5J_{15} - \frac{468736}{99225}\pi^{12}J_7^2 + \frac{116192}{66150}\pi^{10}J_7J_9 - \frac{29072}{231525}\pi^8J_7J_{11} \\
& - \frac{11}{3969}\pi^6J_7J_{13} + \frac{1}{4950}\pi^4J_7J_{15} - \frac{328}{2205}\pi^8J_9^2 + \frac{326}{11025}\pi^6J_9J_{11} + \frac{11}{26460}\pi^4J_9J_{13} \\
& - \frac{1}{19800}\pi^2J_9J_{15} - \frac{202}{77175}\pi^4J_{11}^2 + \frac{1}{7560}\pi^2J_{11}J_{13} + \frac{1}{888080}J_{11}J_{15} - \frac{1}{254016}J_{13}^2,
\end{aligned}$$

$$\begin{aligned}
P \equiv\ & \frac{65536}{245}\pi^{12}J_5^3 + \frac{11264}{63}\pi^{10}J_5^2J_7 + \frac{2432}{45}\pi^8J_5^2J_9 + \frac{752}{441}\pi^6J_5^2J_{11} + \frac{184}{315}\pi^4J_5^2J_{13} \\
& - \frac{256}{21}\pi^8J_5J_7^2 + \frac{1096}{63}\pi^6J_5J_7J_9 - \frac{25}{21}\pi^4J_5J_7J_{11} + \frac{23}{126}\pi^2J_5J_7J_{13} \\
& + \frac{32}{15}\pi^4J_5J_9^2 - \frac{1}{18}\pi^2J_5J_9J_{11} + \frac{23}{420}J_5J_9J_{13} - \frac{361}{7056}J_5J_{11}^2 - \frac{940}{63}\pi^6J_7^3 - \frac{4}{3}\pi^4J_7^2J_9 \\
& - \frac{115}{252}\pi^2J_7^2J_{11} - \frac{23}{504}J_7^2J_{13} + \frac{1}{3}\pi^2J_7J_9 + \frac{19}{252}J_7J_9J_{11} - \frac{1}{30}J_9^3,
\end{aligned}$$

$$
\begin{aligned}
Q \equiv\ & \frac{17226752}{72765}\pi^{14}J_5^3 + \frac{679808}{14553}\pi^{12}J_5^2J_7 + \frac{169984}{3465}\pi^{10}J_5^2J_9 - \frac{2108}{1323}\pi^8J_5^2J_{11} \\
& + \frac{2866}{6615}\pi^6J_5^2J_{13} - \frac{4}{3465}\pi^4J_5^2J_{15} - \frac{305045}{1386}\pi^{10}J_5J_7^2 + \frac{8744}{945}\pi^8J_5J_7J_9 \\
& - \frac{209}{63}\pi^6J_5J_7J_{11} + \frac{277}{1764}\pi^4J_5J_7J_{13} - \frac{1}{2772}\pi^2J_5J_7J_{15} + \frac{128}{63}\pi^6J_5J_9^2 + \frac{4}{45}\pi^4J_5J_9J_{11} \\
& + \frac{173}{3780}\pi^2J_5J_9J_{13} - \frac{1}{9240}J_5J_9J_{15} - \frac{1093}{21168}\pi^2J_5J_{11}^2 - \frac{43}{105840}J_5J_{11}J_{13} \\
& - \frac{4000}{189}\pi^8J_7^3 + \frac{58}{189}\pi^6J_7^2J_9 - \frac{55}{126}\pi^4J_7^2J_{11} - \frac{143}{1512}\pi^2J_7^2J_{13} + \frac{1}{11088}J_7^2J_{15} \\
& + \frac{4}{9}\pi^4J_7J_9^2 + \frac{19}{84}\pi^2J_7J_9J_{11} - \frac{1}{1512}J_7J_9J_{13} + \frac{19}{6048}J_7J_{11}^2 \\
& - \frac{11}{90}\pi^2J_9^3 - \frac{1}{504}J_9^2J_{11}\,,
\end{aligned}
$$

$$
\begin{aligned}
R \equiv\ & \frac{1150976}{17325}\pi^{16}J_5^3 - \frac{11020432}{218295}\pi^{14}J_5^2J_7 + \frac{8398328}{121275}\pi^{12}J_5^2J_9 - \frac{15536}{10395}\pi^{10}J_5^2J_{11} \\
& + \frac{10198}{99225}\pi^8J_5^2J_{13} - \frac{17}{24255}\pi^6J_5^2J_{15} - \frac{7898543}{145530}\pi^{12}J_5J_7^2 + \frac{608}{105}\pi^{10}J_5J_7J_9 \\
& - \frac{6848953}{1746360}\pi^2J_5J_7J_{11} - \frac{2311}{39690}\pi^6J_5J_7J_{13} + \frac{1}{4620}\pi^4J_5J_7J_{15} \\
& - \frac{16}{45}\pi^8J_5J_9^2 + \frac{1957}{13230}\pi^6J_5J_9J_{11} + \frac{221}{18900}\pi^4J_5J_9J_{13} - \frac{1}{13860}\pi^2J_5J_9J_{15} \\
& - \frac{61}{3780}\pi^4J_5J_{11}^2 - \frac{251}{10584}\pi^2J_5J_{11}J_{13} + \frac{1}{388080}J_5J_{11}J_{15} - \frac{1}{254016}J_5J_{13}^2 \\
& - \frac{32}{27}\pi^{10}J_7^3 + \frac{4003}{1890}\pi^8J_7^2J_9 + \frac{2557}{15876}\pi^6J_7^2J_{11} - \frac{13}{540}\pi^4J_7^2J_{13} + \frac{1}{5544}\pi^2J_7^2J_{15} \\
& - \frac{368}{945}\pi^6J_7J_9^2 + \frac{103}{756}\pi^4J_7J_9J_{11} + \frac{1}{945}\pi^2J_7J_9J_{13} + \frac{5}{10584}\pi^2J_7J_{11}^2 \\
& + \frac{73}{635040}J_7J_{11}J_{13} - \frac{19}{150}\pi^4J_9^3 - \frac{13}{5040}\pi^2J_9^2J_{11} - \frac{59}{151200}J_9^2J_{13} + \frac{1}{3920}J_9J_{11}^2\,,
\end{aligned}
$$

$$
\begin{aligned}
S \equiv\ & \frac{65536}{11319}\pi^{18}J_5^3 - \frac{575488}{51975}\pi^{16}J_5^2J_7 - \frac{4340857}{727650}\pi^{14}J_5^2J_9 - \frac{1173289}{2546775}\pi^{12}J_5^2J_{11} \\
& + \frac{8}{945}\pi^{10}J_5^2J_{13} - \frac{4}{40425}\pi^8J_5^2J_{15} - \frac{2699264}{130977}\pi^{14}J_5J_7^2 - \frac{5137519}{485100}\pi^{12}J_5J_7J_9 \\
& + \frac{1168}{31185}\pi^{10}J_5J_7J_{11} - \frac{307}{59535}\pi^8J_5J_7J_{13} + \frac{359}{1746360}\pi^6J_5J_7J_{15} \\
& - \frac{3704}{10395}\pi^{10}J_5J_9^2 + \frac{1627}{66150}\pi^8J_5J_9J_{11} + \frac{11}{79380}\pi^6J_5J_9J_{13} - \frac{1}{59400}\pi^4J_5J_9J_{15} \\
& - \frac{1}{1890}\pi^6J_5J_{11}^2 + \frac{1}{22680}\pi^4J_5J_{11}J_{13} + \frac{1}{1164240}\pi^2J_5J_{11}J_{15} - \frac{1}{762048}\pi^2J_5J_{13}^2 \\
& + \frac{32416}{59535}\pi^{12}J_7^3 + \frac{608}{2835}\pi^{10}J_7^2J_9 + \frac{524}{19845}\pi^8J_7^2J_{11} - \frac{61}{23814}\pi^6J_7^2J_{13} \\
& + \frac{1}{41580}\pi^4J_7^2J_{15} - \frac{478}{4725}\pi^8J_7J_9^2 + \frac{121}{7560}\pi^6J_7J_9J_{11} + \frac{1}{22680}\pi^4J_7J_9J_{13}
\end{aligned}
$$

$$-\frac{1}{166320}\pi^2 J_7 J_9 J_{15} - \frac{1}{1890}\pi^4 J_7 J_{11}^2 + \frac{1}{63504}\pi^2 J_7 J_{11} J_{13} - \frac{1}{2328480} J_7 J_{11} J_{15}$$
$$+\frac{1}{1524096} J_7 J_{13}^2 - \frac{1}{315}\pi^6 J_9^3 + \frac{1}{2100}\pi^4 J_9^2 J_{11} + \frac{1}{30240}\pi^2 J_9^2 J_{13}$$
$$+\frac{1}{1108800} J_9^2 J_{15} - \frac{1}{17640}\pi^2 J_9 J_{11}^2 - \frac{1}{211680} J_9 J_{11} J_{13} + \frac{1}{246960} J_{11}^3 .$$

This third approximation has also a maximum at an intermediate temperature, as seen in Fig. 1 in which the three approximations of (1) are plotted as functions of the temperature. The

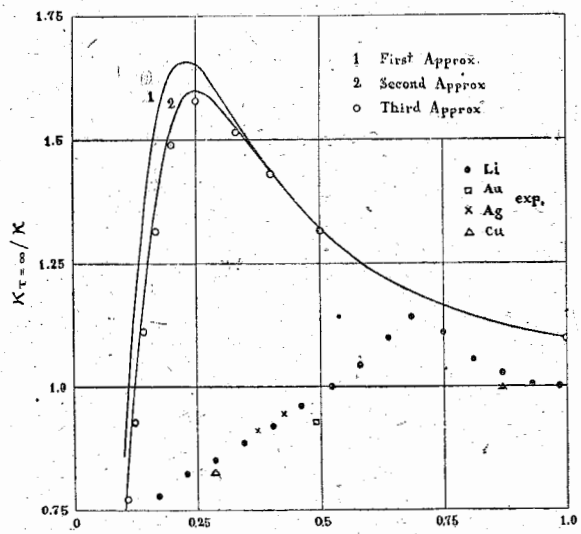

Fig. 1. *Ideal heat resistance of the monovalent metals in three approximations as functions of the temperature.*

maximum is lowered in height and shifted to the higher temperature, although not markedly, as the order of approximation increases. It seems obviously difficult to fit the theoretical values to the experimental data even in the more higher approximations. Recently Toya and one of us (K.U.)[3] have shown by the investigation of the convergence of the Kroll's method that the third approximation, which corresponds to the substitution for Kroll's infinite set of equations by seven or eight ones, is practically sufficient. Therefore the questioned maximum of the heat resistance at an intermediate temperature seems to be not due to the insufficient order of approximation, as hitherto stated.

In conclusion, we wish express our thanks to Ass. Prof. Toya for his valuable advices. This work has been carried out as a research of The Special Research Committee of the Theoretical Physics in The National Research Council of Japan, aided by the research grant given from The Department of Education.

Appendix

The First Approximation of (1)

Kroll has already shown that this approximation is nothing but Wilson's expression[4]:

$$\frac{\kappa_{T=\infty}}{\kappa} = \frac{2^2 3}{\pi^2}\frac{1}{X^4}\left[X^2 J_5 + \left(\frac{\pi^2}{3}J_5 - \frac{1}{6}J_7\right)\right], \tag{3}$$

which has been traced by Makinson[2] and Toya et al.[5] as a function of temperature.

The Second Approximation of (1)

This approximation has been given explicitly by Kroll himself[1]. But there were found unfortunately some erroneous coefficients. The correct expression is

$$\frac{\kappa_{T=\infty}}{\kappa} = \frac{2^2 3}{\pi^2}\frac{1}{X^4}\frac{X^4 L + X^2 M + N}{X^2 F + G}, \tag{4}$$

$$F \equiv \frac{84}{25}\pi^4 J_5 + \frac{3}{5}\pi^2 J_7 + \frac{3}{10}J_9,$$

$$G \equiv \frac{144}{175}\pi^6 J_5 - \frac{14}{25}\pi^4 J_7 + \frac{7}{50}\pi^2 J_9 - \frac{1}{140}J_{11},$$

$$L \equiv \frac{16}{5}\pi^4 J_5^2 + \pi^2 J_5 J_7 + \frac{3}{10}J_5 J_9 - \frac{1}{4}J_7^2,$$

$$M \equiv \frac{68}{35}\pi^6 J_5^2 - \frac{3}{5}\pi^4 J_5 J_7 + \frac{1}{5}\pi^2 J_5 J_9 - \frac{1}{140}J_5 J_{11} - \frac{1}{2}\pi^2 J_7^2,$$

$$N \equiv \frac{48}{175}\pi^8 J_5^2 - \frac{34}{105}\pi^6 J_5 J_7 + \frac{7}{150}\pi^4 J_5 J_9 - \frac{1}{420}\pi^2 J_5 J_{11}$$
$$- \frac{1}{15}\pi^4 J_7^2 + \frac{1}{60}\pi^2 J_7 J_9 + \frac{1}{840}J_7 J_{11} - \frac{1}{400}J_9^2.$$

The refinement[2][5], in which the number of conduction electrons were taken into consideration, could remove the maximum, but it has been likely not effective to reproduce the experimental data.

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