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Exercise 3

Excercises to the Lecture

Superconductivity and Low Temperature Physics I
WS 2022/2023

2 Thermodynamic Properties of Superconductors

2.1 Specific Heat of Superconductors

Exercise:

We consider the superconducting materials Al, Nb and Pb with the characteristic parameters listed in Table 1.

Table 1: Material properties of Al, Nb and Pb.

Material	T_c	$B_{cth}(0)$	$\Delta c/c_n$	$\Delta(0)$	γ	M	ρ
	(K)	(mT)	exp.	(meV)	(mJ/mol K^2)	(g/mol)	(g/cm^3)
Al	1.2	10	1.4	0.17	1.35	27.0	2.7
Nb	9.2	206	1.9	1.52	7.79	92.9	8.4
Pb	7.2	80	2.7	1.37	2.98	207.2	11.4

(a) Calculate the jump in the specific heat of a superconductor at T_c, $\Delta c/c_n = (c_s - c_n)/c_n$, from the free enthalpy density.

(b) Calculate $\Delta c/c_n$ for Aluminium, Niobium and Lead from the measured thermodynamic critical magnetic field $B_{\rm cth}(0)$ and the transition temperature T_c listed in Table 1.

(c) According to microscopic (BCS) theory of superconductivity the difference in the free enthalpy densities of the normal and superconducting state is given by $\frac{1}{4V}D(E_{\rm F})\Delta^2(0)$. Here, $D(E_{\rm F})$ is the electronic density of states (for both spin directions) at the Fermi energy and $\Delta(0)$ the energy gap of the superconductor at $T = 0$. The latter can be derived from the low temperature dependence of the specific heat c_s, or can be obtained from tunneling and optical experiments. Use the Sommerfeld expression for the normal state specific heat c_n to derive $\Delta c/c_n$ from the microscopic quantities.

(d) Compare and discuss the results of (b) and (c).

Solution:

(a) With the differential of the inner energy, $dU = TdS - pdV + VB_{\rm ext}dM$, where $VB_{\rm ext}dM$ is the magnetization work performed on the system, and the free energy $F = U - TS$ we obtain the differential of the free energy as

$$dF = -SdT - pdV + VB_{\rm ext}dM \ . \tag{1}$$

In order to be able to neglect the terms $-pdV$ and $VB_{\rm ext}dM$ we would have to perform experiments at constant volume and magnetic moment (magnetization). However, this is difficult to realize. Therefore, it is more appropriate to consider the free enthalpy $G = U - TS + pV - VMB_{\rm ext}$, with its differential given by

$$dG = -SdT + Vdp - VMdB_{\rm ext} \ . \tag{2}$$

If we perform an experiment at constant pressure and external magnetic field (what is easy to realize) we obtain $dG = -SdT$ and hence

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,B_{\rm ext}} \ . \tag{3}$$

The specific heat at constant pressure and magnetic field is then given by

$$\begin{aligned} c_p &= \frac{C_p}{V} = \frac{1}{V}\left(\frac{\delta Q}{\delta T}\right)_{p,B_{\rm ext}} \overbrace{=}^{\delta T\to 0} \frac{T}{V}\left(\frac{\partial S}{\partial T}\right)_{p,B_{\rm ext}} \\ &= -\frac{T}{V}\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,B_{\rm ext}} = -T\left(\frac{\partial^2 \mathfrak{g}}{\partial T^2}\right)_{p,B_{\rm ext}} \ . \end{aligned} \tag{4}$$

Here, we have used the free enthalpy density $\mathfrak{g} = G/V$.

The difference of the free enthalpy densities in the superconducting and normal conducting state is given by

$$\Delta\mathfrak{g}(T) = \mathfrak{g}_s(0,T) - \mathfrak{g}_n(0,T) = -\frac{B_{\rm cth}^2(T)}{2\mu_0} \ , \tag{5}$$

where $B_{\rm cth}$ is the thermodynamical critical field of the superconductor. Using eq. (4) we obtain

$$\Delta c_p = c_{p,s} - c_{p,n} = \frac{T}{\mu_0}\left[B_{\rm cth}\frac{\partial^2 B_{\rm cth}}{\partial T^2} + \left(\frac{\partial B_{\rm cth}}{\partial T}\right)^2\right] \ . \tag{6}$$

This relation is usually called ***Rutgers Formula***.[1] For $T \to T_c$, we can neglect the first term in the brackets, since $B_{\rm cth} \to 0$. Using $c_{p,n} = \gamma T$, where γ is the Sommerfeld coefficient, and the empirical temperature dependence $B_{\rm cth} = B_{\rm cth}(0)\left[1 - (T/T_c)^2\right]$, we obtain for $T = T_c$

$$\frac{\Delta c_p}{c_{p,n}} = \frac{c_{p,s} - c_{p,n}}{c_{p,n}} = \frac{1}{\gamma T_c}\frac{T_c}{\mu_0}\left(\frac{\partial B_{\rm cth}}{\partial T}\right)^2_{T=T_c} = \frac{8}{\gamma T_c^2}\frac{B_{\rm cth}^2(0)}{2\mu_0} \ . \tag{7}$$

[1] A.J. Rutgers, *Bemerkung zur Anwendung der Thermodynamik auf die Supraleitung*, Physica **3**, 999 (1936).

Table 2: Calculated and measured specific heat values of Al, Nb and Pb together with further material properties of Al, Nb and Pb.

Material	T_c	$B_{cth}(0)$	$\Delta c/c_n$	$\Delta c/c_n$	γ	γ	M	ρ
	(K)	(mT)	exp.	ber.	(mJ/mol K^2)	(J/m^{3}K^2)	(g/mol)	(g/cm^3)
Al	1.2	10	1.4	1.6	1.35	135	27.0	2.7
Nb	9.2	206	1.9	2.2	7.79	704	92.9	8.4
Pb	7.2	80	2.7	2.4	2.98	164	207.2	11.4

(b) Equation (7) shows that we expect a jump of the specific heat at T_c. This jump can be measured directly by calorimetric techniques. On the other hand, we can also determine $B_{\mathrm{cth}}(0)$ from magnetization measurements at low temperatures and use this value to calculate the jump in the specific heat at $T = T_c$. We will do so in the following by using the values of $B_{\mathrm{cth}}(0)$, T_c and γ listed in Table 1. For the calculation we first have to convert the units into SI units. To obtain the Sommerfeld coefficient in units of J/m^{3}K^2 we have to multiply the value given in units of mJ/mol K^2 by a factor of 1000 and then divide by the molar mass M and finally multiply by the mass density ρ. The result and the derived value of $\Delta c_p/c_{p,n}$ are also listed in Table 2. We see that the calculated values agree well with the calorimetrically measured values.

(c) We now use the prediction of BCS theory that the ground state energy density of the superconducting state at $T = 0$ is lowered by $D(E_{\mathrm{F}})\Delta^2(0)/4V$ below that of the normal conducting state. Then, the difference of the free enthalpy densities can be written as

$$\Delta \mathfrak{g} = \mathfrak{g}_s(0,T) - \mathfrak{g}_n(0,T) = -\frac{1}{4}\frac{D(E_{\mathrm{F}})}{V}\Delta^2(0) = -\frac{B_{\mathrm{cth}}^2(0)}{2\mu_0} . \tag{8}$$

Here, $\Delta(0)$ is the energy gap in the excitation spectrum of the superconductor at $T = 0$. We can use this expression to derive $\Delta c_p/c_{p,n}$. In order to do so we have to express the Sommerfeld coefficient γ as a function of the density of states, $D(E_{\mathrm{F}})$, at the Fermi energy:

$$\gamma = \frac{\pi^2}{2} n \frac{k_{\mathrm{B}}^2}{E_{\mathrm{F}}} \overbrace{=}^{D(E_{\mathrm{F}})=\frac{3}{2}\frac{nV}{E_{\mathrm{F}}}} \frac{\pi^2}{3}\frac{D(E_{\mathrm{F}})}{V}k_{\mathrm{B}}^2 . \tag{9}$$

With this expression we obtain

$$\begin{aligned}\frac{\Delta c_p}{c_{p,n}} &= \frac{8}{\gamma T_c^2}\frac{B_{\mathrm{cth}}^2(0)}{2\mu_0} = \frac{8}{\gamma T_c^2}\frac{1}{4}\frac{D(E_{\mathrm{F}})}{V}\Delta^2(0) \\ &= \frac{8}{\frac{\pi^2}{3}\frac{D(E_{\mathrm{F}})}{V}k_{\mathrm{B}}^2 T_c^2}\frac{1}{4}\frac{D(E_{\mathrm{F}})}{V}\Delta^2(0) = \frac{6}{\pi^2}\left(\frac{\Delta(0)}{k_{\mathrm{B}}T_c}\right)^2 .\end{aligned} \tag{10}$$

Using the BCS prediction $\Delta(0)/k_{\mathrm{B}}T_c = \pi/\mathrm{e}^\gamma = 1.76387699$ for weakly coupled superconductors ($\gamma = 0.5772\ldots$ is Euler's constant), we obtain

$$\frac{\Delta c_p}{c_{p,n}} = 1.8914 . \tag{11}$$

Table 3: Jump $\Delta c_p/c_{p,n}$ of the specific heat of Al, Nb and Pb calculated according to eqs. (10) and (12) with the given values of $\Delta(0)$ and T_c. For comparison, also the calorimetrically measured values are shown.

Material	$\mathbf{T_c}$	$\mathbf{\Delta(0)}$	$\mathbf{\Delta c/c_n}$	$\mathbf{\Delta c/c_n}$	$\mathbf{\Delta c/c_n}$
	(K)	(meV)	exp.	eq.(10)	eq.(12)
Al	1.2	0.17	1.4	1.6	1.2
Nb	9.2	1.52	1.9	2.2	1.7
Pb	7.2	1.37	2.7	2.9	2.2

Note that the prefactor $6/\pi^2 = 0.6079\ldots$ in eq. (10) has been calculated using the BCS condensation energy density $D(E_\mathrm{F})\Delta^2(0)/4V$ for $T = 0$ and the empirical temperature dependence $\propto [1 - (T/T_c)^2]$. Therefore, this prefactor is slightly larger than the value $0.4601\ldots$ predicted by BCS theory. The BCS theory yields (cf. R. Gross and A. Marx, *Festkörperphysik*, Oldenbourg-Verlag (2012), Section 13.5.4)

$$\frac{\Delta c_p}{c_{p,n}} = \frac{D(E_\mathrm{F})}{2\gamma T_c}\left(\frac{-d\Delta^2(T)}{dT}\right)_{T_c} . \tag{12}$$

With $\Delta(T) = 1.7366\,\Delta(0)\,[1-(T/T_c)]^{1/2}$ for $T \simeq T_c$, this results in

$$\frac{\Delta c_p}{c_{p,n}} = \frac{3\cdot 1.7366^2}{2\pi^2}\left(\frac{\Delta(0)}{k_\mathrm{B}T_c}\right)^2 = 0.45837\left(\frac{\Delta(0)}{k_\mathrm{B}T_c}\right)^2 = 1.4261\ldots . \tag{13}$$

The smaller value is caused by the fact that BCS theory yields a temperature dependence $B_\mathrm{cth}(T)$ which slightly deviates from the empirical approximation $B_\mathrm{cth}(T) \propto [1 - (T/T_c)^2]$. If we use the values given for $\Delta(0)$ and T_c in Table 1 we obtain the values for $\Delta c_p/c_{p,n}$ listed in Table 3.

(d) The ratio $\Delta(0)/k_\mathrm{B}T_c$ is a measure for the coupling strength between the conduction electrons in superconductors. In the limit of weak coupling (BCS theory), $\Delta(0)/k_\mathrm{B}T_c = \pi/\mathrm{e}^\gamma = 1.7638\ldots$ in the isotropic case ($\gamma = 0.5772\ldots$ is Euler's constant) and hence $\Delta c_p/c_{p,n} = 12/7\zeta(3) = 1.4261\ldots$ (with Riemann's ζ-function). In contrast, we obtain $\Delta c_p/c_{p,n} = 1.8913\ldots$, if we use eq. (10), and $\Delta c_p/c_{p,n} = 2$, if we use the thermodynamic low temperature limit. In this context it is important to note that besides the BCS result the numbers are not relevant. They only should show that one can approach the correct value by simple considerations.

The jump $\Delta c_p/c_{p,n}$ increases with increasing coupling strength. Particularly interesting is the fact that the macroscopic and microscopic parameters can be measured and/or calculated independent of each other. Therefore, we can use simple thermodynamic considerations to derive qualitative relations between them, thereby performing a consistency check. The achieved consistency is astonishingly good in view of the simplicity of the assumptions made in deriving the BCS expressions.