CHAPTER 5

THERMODYNAMICS OF THE TRANSITION

IN PREVIOUS chapters we have from time to time made use of thermodynamic arguments to derive some of the properties of superconductors. In particular, we have been able to learn much about critical magnetic fields by considering how the free energy of a superconductor is altered by the application of a magnetic field. In this chapter we discuss a few further thermodynamic aspects not treated elsewhere in this book.

5.1. Entropy of the Superconducting State

We saw in Chapter 4 that though the free energy density g_n of a metal in the normal state is independent of the strength H_a of any applied magnetic field, the application of a magnetic field raises the free energy density g_s of the metal in the superconducting state by an amount $\frac{1}{2}\mu_0 H_a^2$. The critical field H_c is that field strength which would be required to raise the free energy of the superconducting state above that of the normal state. We have, therefore, in an applied magnetic field of strength H_a a difference in free energy between the normal and superconducting states,

$$g_n - g_s(H_a) = \tfrac{1}{2}\mu_0(H_c^2 - H_a^2). \tag{5.1}$$

As shown in Appendix B, the free energy of a magnetic body can be written

$$G = U - TS + pV - \mu_0 H_a M,$$

where U is the internal energy, S the entropy, p the pressure, V the volume, H_a the applied magnetic field and M the magnetic moment. If the pressure and applied field strength are kept constant but the temperature is varied by an amount dT there will be a change of free energy,

$$dG = dU - TdS - SdT + pdV - \mu_0 H_a dM.$$

But, by the first law of thermodynamics,

$$dU = TdS - pdV + \mu_0 H_a dM$$

so $$dG = -SdT \quad \text{and} \quad S = -\left(\frac{\partial G}{\partial T}\right)_{p, H_a}$$

The entropy per unit volume is given by

$$s = -\left(\frac{\partial g}{\partial T}\right)_{p, H_a}.$$

Substituting (5.1) into this we obtain for a superconductor,† since H_a does not depend on T,

$$s_n - s_s = -\mu_0 H_c \frac{dH_c}{dT}. \tag{5.2}$$

Now the critical magnetic field always decreases with increase of temperature, so dH_c/dT is always negative and the right-hand side of this equation must be positive. Hence, by simple thermodynamic reasoning applied to the known variation of critical field with temperature, we have been able to deduce that the entropy of the superconducting state is less than that of the normal state, i.e. that the superconducting state has a higher degree of order than the normal state. This is in agreement with the BCS microscopic description of superconductivity (Chapter 9) according to which the electrons in a superconductor "condense" into a highly correlated system of electron pairs.

The critical field H_c falls to zero as the temperature is raised towards T_c, therefore, according to (5.2), the entropy difference between the normal and superconducting states vanishes at this temperature. Furthermore, by the third law of thermodynamics, s_n' must also equal s_s at $T = 0$. An example of the temperature variation of the entropies is shown in Fig. 5.1.

From the fact that the entropies of the superconducting and normal states must be the same at $T = 0$ we can deduce from (5.2) that, since the critical field H_c is not zero, dH_c/dT must be zero at 0°K. This is in accordance with the experimental observation that, for all superconduc-

† H_a does not appear in (5.2) and, as we have assumed the normal state to be non-magnetic (i.e. properties independent of any applied field), this equation implies that the entropy of the superconducting state is independent of any applied magnetic field. This is only strictly true if we ignore the flux within the penetration depth. Equation (5.1), from which (5.2) is derived, did not take account of any flux penetration into the superconducting state. Equation (5.2) applies to bulk samples, i.e. those with dimensions greater than the penetration depth.

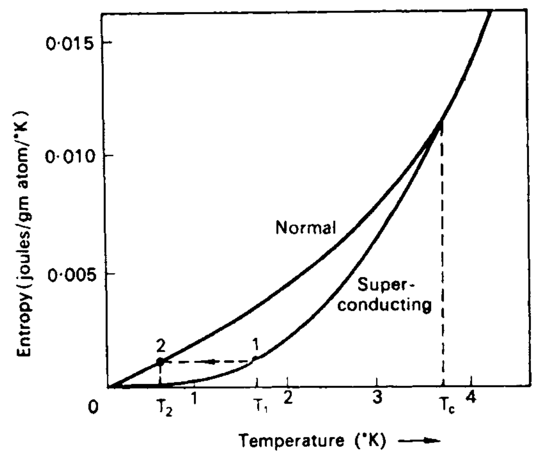

FIG. 5.1. Entropy of normal and superconducting tin (based on Keesom and van Laer). T_1 and T_2 refer to the adiabatic magnetization process described in § 5.2.2.

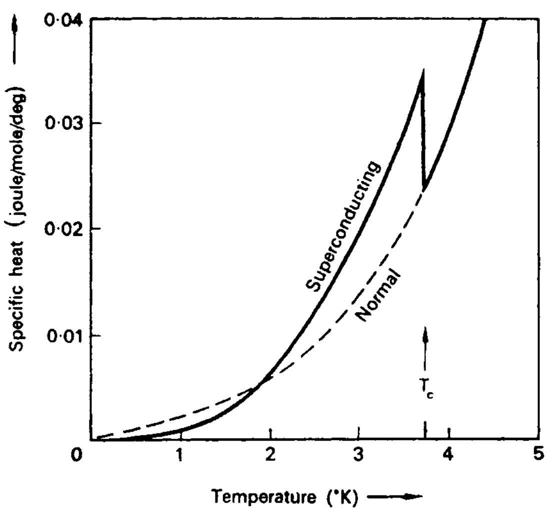

FIG. 5.2. Specific heat of tin in normal and superconducting states.

tors, the slope of the H_c versus T curve (Fig. 4.2) appears to become zero as the temperature approaches 0°K.

5.2. Specific Heat and Latent Heat

Much of the understanding of superconductors has been derived from measurements of their specific heat. The solid curve in Fig. 5.2 shows how the specific heat of a typical type-I superconductor varies with temperature in the absence of any applied magnetic field. We can draw several conclusions from the form of this curve, particularly if we compare it with the specific heat curve of the same metal in the normal state. The curve for the normal state can be obtained by making measurements in an applied magnetic field strong enough to drive the superconductor normal.

5.2.1. First-order and second-order transitions

The form of the specific heat curves can be predicted from thermodynamic arguments.

Since, at the transition temperature, $s_n = s_s$ and we have shown that $s = -(\partial g/\partial T)_{p,H_a}$, we have, for the superconducting-normal transition at T_c,

$$\left(\frac{\partial g}{\partial T}\right)_n = \left(\frac{\partial g}{\partial T}\right)_s.$$

A phase transition which satisfies this condition (i.e. not only is g continuous but $\partial g/\partial T$ is also continuous) is known as a *second-order phase transition.* A second-order transition has two important characteristics: at the transition there is no latent heat, and there is a jump in the specific heat.† The first characteristic follows immediately from the fact that $dQ = Tds$ and we have seen that at the transition temperature $s_n = s_s$. Hence when the transition occurs there is no change in entropy and therefore no latent heat. The second condition follows from the fact that the specific heat of a material is given by

$$C = vT\frac{\partial s}{\partial T}, \tag{5.3}$$

† For a discussion of second-order phase transitions, see Pippard, *Classical Thermodynamics*, Cambridge University Press, 1961, Ch. 9.

where v is the volume per unit mass, so the difference in the specific heats of the superconducting and normal states can be obtained from (5.2):

$$C_s - C_n = vT\mu_0 H_c \frac{d^2H_c}{dT^2} + vT\mu_0 \left(\frac{dH_c}{dT}\right)^2. \qquad (5.4)$$

In particular, at the transition temperature, $H_c = 0$ and so we have for the transition in the absence of an applied magnetic field

$$(C_s - C_n)_{T_c} = vT_c\mu_0 \left(\frac{dH_c}{dT}\right)^2_{T_c}. \qquad (5.4a)$$

This is known as Rutgers' formula, and it predicts the value of the discontinuity in the specific heat of a superconductor at the transition temperature. It should be emphasized that, though (5.4a) contains a term depending on H_c, it gives the specific heat difference in zero applied magnetic field. dH_c/dT is a property of the material whose value does not depend on whether or not a field is actually present. Equation (5.4), on the other hand, gives the specific heat difference in the presence of an applied magnetic field in which case the temperature of the transition is reduced from T_c to T. Expressions (5.4) and (5.4a) provide a useful link between the measured critical magnetic field curve and the thermodynamic properties. We can, for example, derive the magnitude of the specific heat jump at T_c from measurements of the slope of the critical field curve. Furthermore we can provide a check on experimentally measured quantities by seeing whether they satisfy these equations.

Though there is no latent heat when, in the absence of a magnetic field, a metal undergoes the superconducting-normal transition, there is a latent heat *if a magnetic field is present.* The latent heat L for a transition between two phases a and b is given by $L = vT(s_a - s_b)$, so from (5.2) we have

$$L = -vT\mu_0 H_c \frac{dH_c}{dT}. \qquad (5.5)$$

In the absence of any magnetic field the transition occurs at the transition temperature and $H_c = 0$, but if there is a magnetic field the transition occurs at some lower temperature T where $H_c > 0$. This latent heat arises because at temperatures between T_c and 0°K the entropy of the normal state is greater than that of the superconducting state, so heat must be supplied if the transition is to take place at constant temperature. In the presence of an applied magnetic field, therefore, the superconducting-normal transition is of the *first-order*, i.e. although g is continuous, $\partial g/\partial T$ is not.

5.2.2. Adiabatic magnetization

The fact that at temperatures below T_c there is a latent heat and the entropy of the normal state is greater than that of the superconducting state has an interesting consequence. In an ordinary magnetic material application of a magnetic field decreases the entropy because the atomic dipoles become aligned in the field. This decrease in entropy with magnetic field strength is the basis of the well-known method of lowering temperature by "adiabatic demagnetization", where the temperature of a thermally isolated specimen falls as the applied magnetic field is reduced. However, the application of a sufficiently strong magnetic field to a superconducting metal will drive it into the normal state and at a given temperature this has a *greater* entropy than the superconducting state. If the specimen is thermally isolated no heat can enter and the latent heat of the transition must come from the thermal energy of the crystal lattice. Hence the temperature falls. Thus, in contrast to a paramagnetic material, a superconductor is cooled by adiabatic *magnetization*. The temperature drop to be expected can be deduced from an entropy diagram such as Fig. 5.1. If the superconductor is initially at temperature T_1, adiabatic destruction of the superconductivity by the magnetic field will take the material from point 1 to 2 and the temperature will fall to T_2.

Although Mendelssohn and his co-workers have demonstrated that a lowering of temperature can be obtained by this method, it is not used in practice to obtain very low temperatures because there are several practical disadvantages compared to other methods of cooling.

5.2.3. Lattice and electronic specific heats

There are two contributions to the specific heat of a metal. Heat raises the temperature both of the crystal lattice and of the conduction electrons. We may therefore write the specific heat of a metal as

$$C = C_{\text{latt}} + C_{\text{el}}.$$

However, as will be pointed out in Chapter 9, the properties of the lattice (crystal structure, Debye temperature, etc.) do not change when a metal becomes superconducting, and so C_{latt} must be the same in both the superconducting and normal states. Hence the difference between the specific heat values in the superconducting and normal states arises only from a change in the electronic specific heat, i.e.

$$C_s - C_n = (C_{el})_s - (C_{el})_n.$$

The fact that just below the transition temperature the specific heat is greater in the superconducting state than in the normal state implies that, when a metal in the superconducting state is cooled through this region, the entropy of its conduction electrons decreases more rapidly with temperature than if it were in the normal state [see (5.3)]. Hence on cooling a superconductor some extra form of electron order must begin to set in at the transition temperature in addition to the usual decrease in entropy of the conduction electrons which occurs when a normal metal is cooled. This additional order increases as the temperature is lowered and so gives an extra contribution to dS/dT and therefore increases the specific heat. As we have seen, the transition in zero field is second order with no latent heat and no sudden change of entropy at the transition temperature. There is at the transition temperature only a change in the *rate* at which the entropy decreases as the temperature is reduced. The two-fluid model was based on the above considerations, it being supposed that at the transition temperature some conduction electrons begin to become highly ordered superelectrons, the fraction approaching 100% as the temperature is lowered towards 0°K. The nature of this more ordered state of the electrons in a superconducting metal is discussed in Chapter 9.

Figure 5.2 shows that at temperatures well below the transition temperature the specific heat of the superconducting metal falls to a very small value, becoming even less than that of the normal metal. We have seen that the difference in the specific heats of the superconducting and normal states is the result of a change in the electronic specific heat. In order to understand the difference in specific heats we need, therefore, to be able to deduce the value of the electronic specific heat from the experimentally measured values of the total specific heat. This may be done as follows: for a *normal* metal at low temperatures the specific heat has the form

$$C_n = C_{latt} + (C_{el})_n = A\left(\frac{T}{\theta}\right)^3 + \gamma T, \tag{5.6}$$

where A is a constant with the same value for all metals. The Debye temperature of the lattice θ, and the Sommerfeld constant γ, which is a measure of the density of the electron states at the Fermi surface, both vary from metal to metal. We can determine the lattice contribution, C_{latt}, as follows. Equation (5.6) may be re-written as

$$\frac{C_n}{T} = \left(\frac{A}{\theta^3}\right)T^2 + \gamma,$$

so a plot of the experimentally determined values of C_n/T against T^2 should give a straight line whose slope is A/θ^3 and whose intercept is γ. Hence, from measurements on the superconductor in the normal state, i.e. by applying a magnetic field greater than H_c, we can determine the lattice specific heat, $C_{latt} = A(T/\theta)^3$. The specific heat of the lattice is the same in both the superconducting and normal states, so, by subtracting the value of C_{latt} from the total specific heat C_s of the superconducting state, we can obtain the electronic contribution $(C_{el})_s$.

It is difficult to obtain accurate experimental values of the specific heats of superconductors, because at low temperatures the specific heats become very small. However, careful measurements have revealed that at temperatures well below the transition temperature the electronic specific heat of a metal in the superconducting state varies with temperature in an exponential manner,

$$(C_{el})_s = ae^{-b/kT},$$

where a and b are constants. Such an exponential variation suggests that as the temperature is raised electrons are excited across an energy gap above their ground state. The number of electrons excited across such a gap would vary exponentially as the temperature. We shall see in Chapter 9 that the BCS theory of superconductivity predicts just such a gap in the energy levels of the electrons.

The BCS theory also shows that, though the energy gap is substantially constant at very low temperatures, it decreases if the temperature is raised towards the transition temperature, falling to zero at T_c. This rapid decrease in the energy gap just below T_c accounts for the rapid increase in the specific heat of a superconducting metal as the temperature approaches T_c.

5.3. Mechanical Effects

Both the transition temperature and the critical magnetic field of a superconductor are found experimentally to be slightly altered if the material is mechanically stressed. Many of the mechanical properties of the superconducting and normal states are thermodynamically related to the free energies of these states, and we have seen that the critical magnetic field strength depends on the difference in the free energies of the two states. Hence, once it is known that the critical field changes slightly when the material is under stress, thermodynamic arguments show that the mechanical properties must be slightly different in the normal and superconducting states. For example, there is an extremely small change in volume when a normal material becomes superconducting, and the thermal expansion coefficient and bulk modulus of elasticity must also be slightly different in the superconducting and normal states. It is possible to derive expressions for these effects by straightforward thermodynamic manipulation,† but the effects are extremely small and we shall not consider them further in this book.

5.4. Thermal Conductivity

The thermal conductivity of a metal is affected if it goes into the superconducting state. Most of the heat flow along a normal metal in a temperature gradient is carried by the conduction electrons. In the superconducting state, however, the superelectrons no longer interact with the lattice in such a way that they can exchange energy, and so they cannot pick up heat from one part of a specimen and deliver it to another. Consequently, if a metal goes into the superconducting state, its thermal conductivity is reduced. This effect can be very marked at temperatures well below the critical temperature, where there are very few normal electrons left to transport the heat. For example, at 1°K the thermal conductivity of lead in the superconducting state is about 100 times less than that of the metal in the normal state.

If, however, the superconductor is driven normal by the application of a magnetic field, the thermal conductivity is restored to the higher value of the normal state. Hence the thermal conductivity of a superconductor can be controlled by means of a magnetic field, and this effect has been used in "thermal switches" at low temperatures to make and break heat contact between specimens connected by a link of superconducting metal.

† See, for example, E. A. Lynton, *Superconductivity*, Methuen, London, 1964.

5.5. Thermoelectric Effects

It is found, both from theory and experiment, that thermoelectric effects do not occur in a superconducting metal. For example, no current is set up around a circuit consisting of two different superconductors, if the two junctions are held at different temperatures below their transition temperatures. If a thermal e.m.f. were produced there would be a strange situation in which the current would increase to the critical value, no matter how small the temperature difference. It follows from the Thomson relations that, if there is no thermal e.m.f. in superconducting circuits, the Peltier and Thomson coefficients must be the same for all superconducting metals, and they are in fact zero.

Because all superconducting metals have identical thermoelectric constants they may, in principle, be used as a standard against which to measure other metals. The absolute values of the thermoelectric coefficients of a normal metal can be measured in a circuit comprising the metal and any superconductor.

The absence of thermoelectric effects only applies to the superconductors considered in Part I of this book. Thermoelectric effects may appear in the "Type-II" superconductors considered in Part II.