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1 Phenomenology

1.1 Basic Properties

1.1.1 Infinite Conductivity

Superconductivity was discovered in 1911 by H. Kamerlingh Onnes [1] in Leiden. Kamerlingh Onnes was a pioneer in reaching experimentally low temperatures and exploring physics in this by then new realm. He was the first in 1908 to liquify helium gas (he got the Nobel Prize for this in 1913), which provided him a powerful cooling agent at these temperatures.

Kamerlingh Onnes was interested in the variation of the conductivity of metals at low temperature, which was at the time a controversial matter. He chose to work on mercury because it is much easier to purify by distillation than other metals, since it is liquid at room temperature. In this way, he could get rid of impurities, which contribute to the electrical resistivity of metals, and study the intrinsic low-temperature behavior. Upon cooling his solid mercury wire, he observed a slow decrease of its resistance, corresponding to his expectations, and then around the temperature of 4.2 K, a sudden drop to a value so low that he could not actually measure it, as seen in Fig. (1.1). This experimental disappearance of the resistance implies a vanishing resistivity ρ for mercury below the "critical temperature" of $T_c = 4.2$ K,

$$\rho = 0 \tag{1.1}$$

Kamerlingh Onnes called "superconductivity" this property of a metal to have in effect an infinite conductivity $\sigma = 1/\rho$. The year after his discovery, he found that tin and lead were superconductors with critical temperatures of 3.7 K and 7.2 K, respectively.

Naturally it is meaningless to claim that Eq. (1.1) is an experimental result; it is only a logical extrapolation of the experimental result. An experiment always has a limited accuracy and can only claim that the resistivity is extremely small. Nevertheless experimentalists have pushed as far as they could to determine how small the resistivity of a superconductor is. A clever and striking way to do this indirectly is to observe persistent currents. Indeed one can generate currents by induction in a metal having the shape of a ring. For a standard metal with a nonzero resistivity, these currents decay rapidly by dissipation due to Joule heating. However, for a superconductor, Eq. (1.1) holds and no dissipation occurs, so the induced currents can persist indefinitely. These currents can be observed by the magnetic field they generate. Kamerlingh Onnes performed first such an

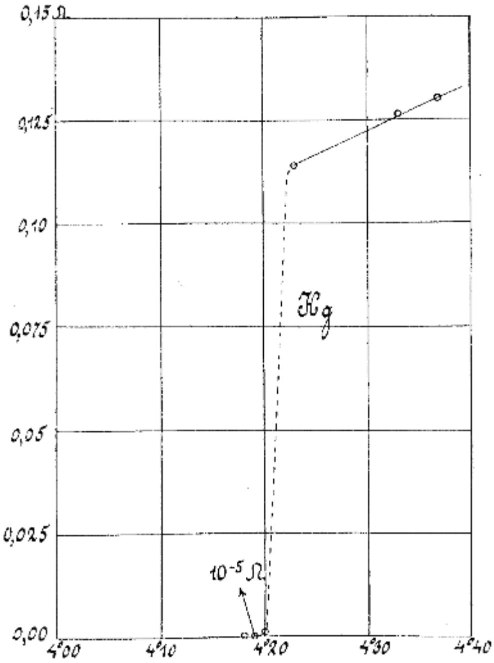

Fig. 1.1 The resistance of mercury as a function of temperature as measured by H. Kamerlingh Onnes [1].

experiment in 1914, and observed persistent currents for hours. This kind of experiment has been repeated; persistent currents have been observed for several years, and the decay time for the persistent current has been evaluated to $\sim 10^5$ years. This comes quite close to an experimental proof of Eq. (1.1).

1.1.2 Critical Temperature

Kammerlingh Onnes realized naturally that in principle, superconductivity could allow one to generate very large electric currents and, as a result, very large magnetic fields. Obviously the very low temperature at which the phenomenon occurs makes it in practice quite inconvenient to set up such a device. Hence the value of the critical temperature is not only an important quantity to characterize superconductivity, but it is also of utmost practical interest. This has led to the exploration of a number of materials for their possible superconducting properties. Among the elements of the periodic table, 33 are superconductors at atmospheric pressure (with an additional 24 which become superconductors under pressure). The one with the highest critical temperature is niobium, with $T_c = 9.26$ K.

More generally, it has been progressively realized that, far from being an exceptional phenomenon, superconductivity appears quite frequently at low temperature. Its absence may be due to the competing appearance of another kind of transition, for example toward magnetic order. It should be noted that superconducting transitions may be found at very low temperature, which while not being practically useful may be of fundamental interest. There is no lower bound for T_c. In particular copper, the best standard conductor,

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does not display a superconducting transition at the lowest temperatures presently reached. Similarly gold and silver are not superconductors.

Coming back to the more practically interesting purpose of finding high T_c, a number of metallic alloys have also been explored. In this search, the one with highest critical temperature has been Nb_3Ge with $T_c = 23.2$ K. This is already above the boiling point of liquid hydrogen, which is at 20 K under atmospheric pressure, but not enough to be of practical interest. Hence, although it has a slightly lower $T_c = 18.3$ K, Nb_3Sn is rather used industrially because it can withstand high currents and magnetic fields. Nevertheless it is NbTi that is presently the industrially preferred compound for practical reasons, although its T_c is only 10 K. It is this alloy that is mostly used for the production of the high magnetic fields required in magnetic resonance imaging (MRI) in standard medical devices. Similarly this is the alloy used in large high-energy particle accelerators, although the need for higher fields induces a switch to Nb_3Sn. In all cases, the required low temperature is obtained through liquid Helium cryogenics, which has seen much development to large scale for this purpose.

Despite many efforts, progress in increasing T_c had become so slow in the fifties and sixties that researchers in the field of superconductivity tended to believe that there was some kind of intrinsic upper bound for T_c and that in practice its increase was near saturation. Hence it has been a great shock to this community when in 1986 Georg Bednorz and Alex Müller found that a perovskite[1] in "the La-Ba-Cu-O system" (more precisely with chemical composition $Ba_xLa_{1-x}CuO_{3-y}$) is a superconductor with T_c around 35 K. They received the Nobel Prize the next year for this breakthrough. Then things progressed very rapidly, essentially guided by chemical reasoning that leads one to replace an element with a chemically similar one. The following year, $T_c = 93$ K was reached in $YBa_2Cu_3O_7$. More generally, the critical temperature of $YBa_2Cu_3O_{7-x}$ is very sensitive to the "doping" x since $YBa_2Cu_3O_6$ is an antiferromagnetic insulator. It reaches $T_c = 95$ K for $x \simeq 0.07$. Such critical temperatures have represented an essential step in the increase of T_c since they are above the boiling point of liquid nitrogen, which is at 77 K under atmospheric pressure. Liquid nitrogen is routinely obtained in the gas industry, with a typical annual world production of 8 million tons. Hence cooling such a superconductor below its critical temperature is a considerably simpler matter than when helium has to be used.

Further progress with these kinds of compounds has led to the discovery of bismuth compounds of general formula $Bi_2Sr_2Ca_nCu_{n+1}O_{2n+6-\delta}$ with T_c ranging from 95 K to 107 K depending on n, thallium compounds $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2+\delta}$ with a highest T_c reaching 127 K, and finally mercury compounds $HgBa_2Ca_2Cu_3O_{8+\delta}$ with a highest critical temperature of 135 K found in 1993. The highest critical temperature reported to date in these cuprates superconductors has been 166 K in $HgBa_2Ca_2Cu_3O_{8+\delta}$ at a pressure of 23 GPa. A remarkable feature of all these compounds is that above the critical temperature, they are fairly bad metals with poor conductivity, in contrast with the earlier superconductors discussed at the beginning of this section. They are also quasi-bidimensional materials since they are essentially stacks of CuO_2 planes, which are their conducting part, with a fairly weak electronic coupling between the planes.

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[1] This is a material with the same crystal structure as $CaTiO_3$.

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The cuprate discovery clearly showed that there was no barrier around 20 K for T_c. Hence this produced an incentive to check the low-temperature properties of various materials. As early as 1988, superconductivity was found in $Ba_{0.6}K_{0.4}BiO_3$ around 30 K. Like the cuprates, this compound is a perovskite, but it does not contain CuO_2 planes and it is tridimensional. Hence, it is in a somewhat different class of materials.

Markedly different are the "doped" fullerenes, with the main ingredient being the fullerene molecule C_{60}, which has the shape of a soccer ball. It can be doped with various alkali, with Cs_3C_{60} reaching in 1995 a surprising $T_c = 40$ K under pressure. These materials could almost be considered as organic superconductors, with other organic compounds having much lower T_c.

A surprising result was then found in 2001, where MgB_2 was discovered to have a critical temperature of 39 K. This compound is similar to the alloys investigated earlier with the hope of finding higher critical temperature, and its late discovery looks like a miss of earlier searches.

More interesting is the discovery of superconductivity in iron-based compounds. Indeed, starting in 2006, superconductivity in these compounds was investigated because they have fairly high T_c, considering that the magnetic properties of Fe were believed to be detrimental to superconductivity. In 2008, a T_c of 26 K was reported in $LaO_{1-x}F_xFeAs$ (called an "oxypnictide"[2]) with $x = 0.05 - 0.12$, followed the same year by the finding of $T_c = 55$ K in $SmO_{1-x}F_xFeAs$. These iron-based materials form a rich family with several parent compounds.

Finally the quite recent last step in this progress in T_c has been the evidence for superconductivity in various hydrides around 200 K, under high pressure. A first result of $T_c = 203$ K in H_3S at 155 GPa has appeared in 2015. Then, in 2018, $T_c = 215$ K was reached in LaH_{10} (although the stoichiometry in H may be somewhat uncertain in these compounds), followed by a claim for superconductivity at $T_c = 260$ K around 200 GPa in the same compound. Clearly the search for superconductivity in these hydrides is not over. It is already quite close to the long-lasting dream of finding superconductivity at room temperature.

1.1.3 Meissner Effect

We now come to the second defining property of a superconductor. Although it has been found by Meissner and Ochsenfeld [2] in 1933, a fairly long time after the discovery by Kamerlingh Onnes, it turned out to be a fundamental feature of the superconducting state. Meissner and Ochsenfeld cooled a sample of tin in the presence of an applied magnetic field **H**. They expected no change of the field when the temperature was going below the critical temperature T_c for tin. Instead, when measuring the field in the vicinity of the superconducting tin, they found strong changes, as if tin behaved as a magnetic material. These modifications were consistent with the magnetic induction **B** going to zero inside the superconducting tin sample. As a result the field lines are pushed away from the superconductor, as shown in Fig. (1.2). The field is "expelled" from the superconductor.

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[2] A pnictide element is an element belonging to the nitrogen column in the periodic table: N, P, As, Sb, Bi.

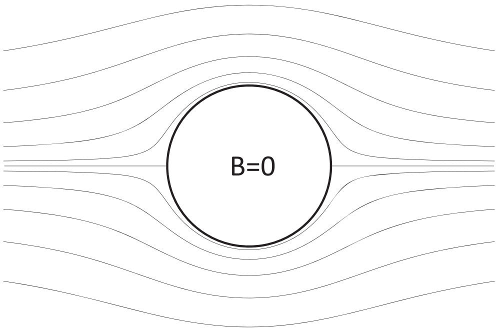

Fig. 1.2 Schematic view of the magnetic field lines for a spherical superconductor, in the presence of an applied magnetic field. Without the superconductor or for a normal metal, the magnetic field lines would just be horizontal parallel lines.

If the temperature was first lowered below the critical temperature T_c with a zero applied magnetic field (zero-field-cooling), and then the magnetic field would be raised at fixed temperature, this experimental result could easily be understood as resulting from the infinite conductivity of the superconductor. Indeed, in this case, raising the magnetic field gives rise to induced currents in the superconductor, and from Lenz's law, they oppose the variation of the induction inside the superconductor. For a standard metal, these induced currents decay by dissipation due to the metal resistivity. However, with the infinite conductivity of the superconductor there is no such dissipation; these currents run forever, and Lenz's law can reach its full effect of maintaining the magnetic induction at its initial value $\mathbf{B} = \mathbf{0}$.

This "freezing" of the induction lines is, for example, well known in plasma physics, where very large conductivity (although not infinite) can be found. Basically the infinite conductivity σ forces the electric field $\mathbf{E} = \mathbf{j}/\sigma$ to be zero inside the superconductor regardless of the current $\mathbf{j}$. Then for $\mathbf{E} = \mathbf{0}$, Maxwell's equation $\mathbf{curl}\,\mathbf{E} = -\partial \mathbf{B}/\partial t$ implies that the magnetic induction cannot change. However, in this zero-field-cooled case, we would have reached an out-of-equilibrium situation lasting forever.

By contrast, the Meissner effect cannot be explained by Lenz's law, since it is obtained by merely changing the temperature at a fixed field, so that no induced currents can arise. Rather, one comes to the conclusion that the situation depicted by Fig. (1.2) corresponds to a thermodynamical equilibrium situation for the superconductor since, for given temperature and field, it is the one that is found regardless of the order in which the temperature is lowered and the magnetic field is raised.

Nevertheless, although infinite conductivity cannot fully explain by itself the Meissner effect, it is an essential ingredient of the effect. Indeed the fact that the induction is zero inside the superconductor is physically due to the existence of permanent currents in the superconductor which screen the external field, and they can persist only because conductivity is infinite.

If one does not look for a microscopic understanding of the superconductor and stays only at a macroscopic level, one can summarize the Meissner effect by the fact that it is a magnetic material with the property $\mathbf{B} = \mathbf{0}$ in the superconductor in the presence of an applied magnetic field **H**. By definition of the magnetic susceptibility χ of the material, we have

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) = \mu_0(1 + \chi)\mathbf{H} \tag{1.2}$$

since the magnetization **M** is related to the field by $\mathbf{M} = \chi\mathbf{H}$. Here μ_0 is the vacuum permeability. Hence we have for a superconductor

$$\chi = -1 \tag{1.3}$$

In other words, a superconductor is perfect diamagnet. In general, diamagnets tend to weaken the external magnetic field. A superconductor does it perfectly by reducing the magnetic induction to zero.

Let us conclude by stressing that the standard procedure for identifying a metallic compound as a superconductor is to show experimentally that it has zero resistivity and displays the Meissner effect. “Zero” resistivity only may just correspond to a very good conductor with a resistivity below the experimental resolution. The Meissner effect is usually checked both when the compound is cooled in a zero field (and then a field is applied) and when it is cooled through the critical temperature in the presence of a magnetic field, to check that the field is properly expelled from the superconductor below the critical temperature. A practical complication is that the Meissner effect may not be complete: some parts of the superconductor may actually stay in the normal state due to inhomogeneities, impurities, and other kinds of defects. As a result, the measured susceptibility may not be as strong as it should be, which may bring some ambiguity in the identification of the compound as a superconductor.

1.1.4 Critical Field

The Meissner effect makes it clear physically that there must be a critical field, beyond which the superconductor no longer exists at a given temperature. Indeed there is clearly a magnetic energy cost to the distortion of the field from its value in the absence of the superconductor. This will be quantified below in the next subsection. This is compensated by the lowering in energy associated with the spontaneous transition from the normal to the superconducting state. However, this gain in energy is a fixed amount, independent of the field, whereas the magnetic energy cost increases indefinitely with the field. Obviously, if the field is too high, the total energy for going into the superconducting state will be positive and this state will no longer be stable with respect to the normal state of the metal. Hence, for a given temperature T, there is a critical field $H_c(T)$ beyond which superconductivity disappears.

The existence of this critical field was actually discovered experimentally by Kamerlingh Onnes in 1914, not much after his initial discovery of superconductivity, and much earlier than the Meissner effect. Indeed, soon after his discovery, Kamerlingh Onnes was interested in the possibility of producing high magnetic fields by electromagnets with superconducting wires, in which huge currents could in principle be fed. The existence of a critical field puts a fundamental limit to the production of such high currents, since

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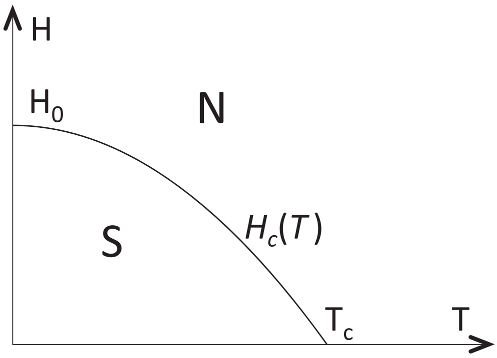

Fig. 1.3 Phase diagram of a type I superconducting metal in the presence of a magnetic field H. In the domain below the critical field curve $H_c(T)$, the metal is in the superconducting state (S), while above this curve it is in the normal state (N).

the magnetic field produced by the current itself destroys superconductivity when it goes beyond the critical field. Hence there is an upper limit for the supercurrent carried by the superconductor, which is called the critical current.

Experimentally the critical field $H_c(T)$ decreases with increasing temperature and goes smoothly to zero at the critical temperature. The resulting phase diagram is pictured in Fig. (1.3). The experimental results turn out to be very close to a parabolic law:

$$H_c(T) = H_0 \left[1 - \left(\frac{T}{T_c} \right)^2 \right] \tag{1.4}$$

Actually this simple situation holds only for one class of superconductors, called type I superconductors, which have been the first to be discovered and studied. A second class of superconductors, called type II superconductors, was discovered by Shubnikov in 1933. In these type II superconductors, instead of having a sudden transition from the superconducting state to the normal state upon increasing the magnetic field, the transition is progressive. More precisely, below a first critical field $H_{c1}(T)$ the situation is exactly the same as in type I superconductors and one has a complete exclusion of the field from the bulk of the superconductor. However, above $H_{c1}(T)$, there is a progressive admission of the field in the bulk of the superconductor, until an upper critical field $H_{c2}(T)$ is reached where superconductivity disappears completely and the metal is in the normal state. The state between $H_{c1}(T)$ and $H_{c2}(T)$ is called the "mixed state." This more complex situation is depicted in Fig. (1.4).

Since there is a partial admission of the field in the mixed state, it is intuitively clear that the magnetic energy cost is lowered, compared to the situation of full exclusion we have seen for type I superconductors. Hence, in this case, superconductivity can survive to higher magnetic fields than for type I. Indeed type II superconductors are the only ones of interest for applications where superconductivity has to survive very high fields or very high currents.

Finally it is important to stress that if we want to directly apply the above considerations to a real superconducting sample, we have to take it with a shape infinitely elongated in the

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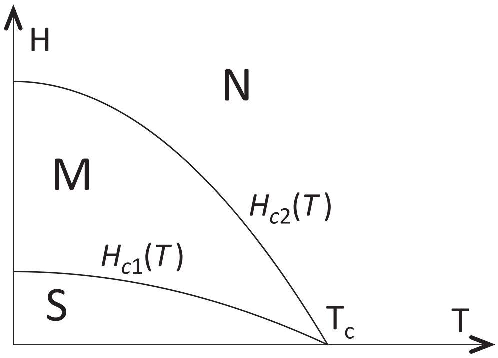

Fig. 1.4 Phase diagram of a type II superconducting metal in the presence of a magnetic field H. In the domain below the critical field curve $H_{c1}(T)$, the metal is in the superconducting state (S); between $H_{c1}(T)$ and $H_{c2}(T)$, it is in the mixed state (M); and above $H_{c2}(T)$, it is in the normal state (N).

direction of the field – for example, a very long cylinder parallel to the field. Otherwise, as for any magnetic material, we have to take into account the demagnetizing field created by the sample itself, which is naturally inhomogeneous and depends on the sample shape. As a result, the strength of the actual field depends on the spatial position. For example, in the situation depicted qualitatively in Fig. (1.2), the field at the equator of the sphere will be stronger than at the poles.

If we take the case of a type I superconductor, this may result in the fact that if the applied field is strong enough, some parts of the metal will have a field larger than the critical field and will accordingly be in the normal state, while some other parts will have a field smaller than the critical field and be superconducting. Naturally the field distribution itself depends on which parts of the sample are normal and which parts are superconducting. Hence one finds a situation where there is a mixture of normal and superconducting domains in the metallic sample. This is called the "intermediate state." Finding the distribution of domains that minimizes the energy is quite a complicated problem, and the result may be a fairly complex structure. Correspondingly, it is also quite difficult to experimentally determine this structure with good precision.

1.1.5 Thermodynamics

The interpretation of the Meissner effect in magnetic terms, leading to the conclusion that a superconductor can be considered as a perfect diamagnet, allows one to relate in a simple way the thermodynamic properties of a superconductor and its magnetic properties. Actually this holds only for type I superconductors, to which we here restrict ourselves, the case of type II superconductors being somewhat more involved.

Thermodynamics tells us that the appropriate thermodynamical potential, to investigate the properties of a system as a function of its temperature T and its volume V, is its free energy $F(T,V) = E - TS$, rather than its energy E. Indeed the differential of the free energy, in terms of the entropy S and the pressure p of the system, is

$$dF = -SdT - p\,dV \tag{1.5}$$

whereas we have for the energy $dE = TdS - pdV$. Note that here, since we deal with a system with a fixed number of particles N, we do not have to include a contribution $\mu\, dN$, where μ is the chemical potential, in contrast with situations we will deal with later on.

When a magnetic field is present, this has to be generalized to take into account the magnetic variables. In terms of the magnetic field H and the magnetic induction B, electromagnetism tells us that the energy increase dE, due to a change dB in magnetic induction, is given by $dE = HdB$. Actually, in standard electromagnetism, one deals usually with space-dependent field $H(\mathbf{r})$ and induction $B(\mathbf{r})$, and the local change in energy $H(\mathbf{r})dB(\mathbf{r})$ has to be summed over all space to give the total energy change $\int d\mathbf{r}\, H(\mathbf{r})dB(\mathbf{r})$. However, we consider here a homogeneous system, so we do not need to take into account space dependence.

To take into account the change in energy due to magnetic variables, this electromagnetic contribution has to be added to the above energy variation, and similarly to the free energy variation, to give

$$dF = -SdT - pdV + HdB \tag{1.6}$$

However, by analogy with the case of a temperature T imposed by an external source, we rather want to consider the superconductor submitted to an external magnetic field H, produced, for example, by external currents in a coil. For this purpose, it is more convenient to perform a Legendre transform and consider the thermodynamical potential $G = F - HB$, which has a differential

$$dG = -SdT - pdV - BdH \tag{1.7}$$

Actually the effects associated with the volume variation of a superconductor, at the low temperature we are interested in, are in practice extremely small, and hence we will disregard them. We will assume that the superconductor has a fixed volume, which we take for convenience equal to the unit volume. Hence, we may omit the pdV term in Eq. (1.7), which reduces merely to

$$dG = -SdT - BdH \tag{1.8}$$

Consider first the compound in its normal state, for which we assume that there are no magnetic properties at all, so that $B = \mu_0 H$ where μ_0 is again the vacuum permeability. Hence $BdH = \mu_0 HdH$. Integrating Eq. (1.8) at fixed temperature with the magnetic field going from 0 to H, we obtain the normal state potential $G_n(T,H)$ in terms of $G_n(T,0)$ as

$$G_n(T,H) - G_n(T,0) = \int_0^H dG = -\mu_0 \int_0^H HdH = -\frac{1}{2}\mu_0 H^2 \tag{1.9}$$

In the superconducting state, we may perform the same calculation, which gets even simpler since from the Meissner effect we merely have $B = 0$ in the superconductor. This leads to

$$G_s(T,H) - G_s(T,0) = \int_0^H dG = -\int_0^H BdH = 0 \tag{1.10}$$

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Let us now, for a given temperature T, take the magnetic field equal to $H_c(T)$, which is the field corresponding to the transition line from the superconducting to the normal state. On this line, there is a thermodynamical equilibrium between the superconducting and the normal states, which implies that the corresponding potential G for these two phases are equal:

$$G_s(T, H_c(T)) = G_n(T, H_c(T)) \tag{1.11}$$

Making use of Eq. (1.9) and Eq. (1.10), this leads to

$$G_n(T, 0) - G_s(T, 0) = \frac{1}{2}\mu_0 H_c^2(T) \tag{1.12}$$

Hence we have just to measure the magnetic field corresponding to the normal-superconducting phase transition, and we know the thermodynamic potential $G_s(T, 0)$ in the zero field in the superconducting state as soon as we know the corresponding thermodynamic potential $G_n(T, 0)$ in the normal state. And from Eq. (1.9) and Eq. (1.10), we have the same information for any magnetic field.

We make use of Eq. (1.12) to investigate the order of the normal-superconducting phase transition. From Eq. (1.8), the entropy of any phase is given by $S = -\partial G/\partial T|_H$. Having the entropy of the two phases, the latent heat L is obtained from $L = T(S_n - S_s)$, to be evaluated on the transition line. From Eq. (1.9), Eq. (1.10), and Eq. (1.12), we obtain

$$\begin{aligned} S_n - S_s &= -\frac{\partial(G_n(T,H) - G_s(T,H))}{\partial T}\Big|_H \\ &= -\frac{\partial(G_n(T,0) - G_s(T,0))}{\partial T} = -\mu_0 H_c(T)\frac{dH_c(T)}{dT} \end{aligned} \tag{1.13}$$

and the latent heat is given by

$$L = -\mu_0 T H_c(T)\frac{dH_c(T)}{dT} \tag{1.14}$$

We see from Fig. (1.3) that experimentally the transition field $H_c(T)$ decreases with increasing temperature, so that $dH_c(T)/dT < 0$ and the latent heat Eq. (1.14) is positive. This means that the transition from superconducting to normal state is first order. The only exception is at the zero field, where $H_c(T) = 0$, so that $L = 0$ and the transition is second order at the standard critical temperature T_c of the superconductor.

For this second-order phase transition at zero field, we can obtain the specific heat jump $C_s - C_n$ from the experimental knowledge of $H_c(T)$. Since $C = T\,\partial S/\partial T$, we have at temperature T

$$C_s - C_n = T\,\frac{d(S_s - S_n)}{dT} = \frac{1}{2}\,\mu_0 T\,\frac{d^2 H_c^2(T)}{dT^2}\Big|_{T_c} \tag{1.15}$$

At $T = T_c$ where $H_c(T) = 0$, this quantity reduces to $\mu_0 T_c (dH_c(T)/dT)^2$, which is positive. But without further microscopic knowledge, there is nothing more to be said about this. However, it is interesting to try to go further by introducing some phenomenological considerations.

We first take the very good parabolic approximation for the critical field $H_c(T) = H_0[1 - (T/T_c)^2]$ and insert it in Eq. (1.15). Furthermore, we assume the temperature to