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Phenomenological two–gap model for the specific heat of MgB_2

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Abstract. – We show that the specific heat of the superconductor MgB_2 in zero field, for which significant non–BCS features have been reported, can be fitted, essentially within experimental error, over the entire range of temperature to T_c by a phenomenological two–gap model. The resulting gap parameters agree with previous determinations from band–structure calculations, and from various spectroscopic experiments. The determination from specific heat, a bulk property, shows that the presence of two superconducting gaps in MgB_2 is a volume effect.

The discovery of superconductivity in MgB_2 [1] raised the questions of its nature and the origin of its relatively high transition temperature $T_\mathrm{c} \sim 40$ K. Specific heat (C) is a powerful tool to aid in answering these questions and, more generally, to provide information on the thermodynamics of the transition. Several groups have reported such measurements on MgB_2 [2–10]. It is now established that C significantly deviates from the standard BCS behaviour. First, a large excess in C is observed in the vicinity of $T_\mathrm{c}/4$ [2–6]. Second, an exponential fit of $C(T)$ in the region $T \ll T_\mathrm{c}$ indicates a gap ratio $2\Delta_0/\mathrm{k_B}T_\mathrm{c}$ only one–quarter to one–third of the isotropic BCS value [3, 4, 6]. This excess was interpreted as a possible sign of a second superconducting gap, whose existence is predicted by band–structure calculations [11–13]. The specific heat near T_c is puzzling also with the jump ΔC at T_c consistently smaller than the BCS weak–coupling lower bound. In this Letter, we present an empirical two–gap model that fits the experimental data over the whole range of temperature to T_c. This model resolves the apparent contradiction between different analyses of the specific heat, and relevant parameters show good agreement with determinations based on independent experiments.

We focus on two sets of specific–heat data obtained independently in two different laboratories. Experimental methods and results have been described elsewhere [2, 3, 5, 6]. The unusual excess specific heat at $\sim T_\mathrm{c}/4$, which denotes the presence of excitations within the main gap, is a consistent feature that is common to different samples and different techniques. These measurements also give similar values for the normal–state contribution, with a coefficient of the linear term $\gamma_n \sim 2.65(15)$ mJ mol^{-1} K^{-2}, and satisfy the criterion of the normal– and superconducting–state entropy being equal at T_c. However, detailed results, such as the height and the width of the jump ΔC at T_c, are sample–dependent. The sample of Ref. [3] was a powder of isotopically pure $\mathrm{Mg^{11}B_2}$ embedded in GE7031 varnish, whereas the sample of Ref. [2] was a sintered commercial powder. A third sample prepared from Mg and B by high–pressure techniques gave similar results [5]. The electronic part of the specific heat was determined by subtraction of the normal–state data, obtained either at fields of 14 or 16 T in Ref. [2], or with a short extrapolation of the 9 T data in Ref. [3]. We refer to the original articles for details.

Although the low–T behaviour of the specific heat data in the earlier studies [2,3] definitely pointed to the presence of excitations with a characteristic energy smaller than the BCS gap $\Delta_{BCS} = 3.53 \mathrm{k_B} T_c$, it was not clear whether this was due to a continuous, but extreme, distribution of the gap resulting from anisotropy, or two discrete values of the gap closing at the same temperature T_c, with possible anomalous temperature dependence at some intermediate temperature. Furthermore, it was not clear whether these models could account for the specific heat over the whole range of temperature to T_c. We present here a simple empirical model, based on the existence of two discrete gaps Δ_1 and Δ_2 at $T = 0$, both closing at T_c. In order to calculate their respective contributions, we first consider the case of a single gap Δ_0, following the method developed by Padamsee *et al.*, and generally referred to as the α–model [14]. The ratio $2\Delta_0/\mathrm{k_B}T_c$ (3.53 in the BCS theory) is not fixed, but is considered to be a fitting variable. The temperature dependence is taken to be the same as in the BCS theory, *i.e.* $\Delta(t) = \Delta_0 \delta(t)$, where $\delta(t)$ is the normalised BCS gap at the reduced temperature $t = T/T_c$ as tabulated by Mühlschlegel [15]. The thermodynamic properties, entropy (S) and C, can be calculated as appropriate for a system of independent fermion quasiparticles:

$$\frac{S}{\gamma_n T_c} = -\frac{6}{\pi^2}\frac{\Delta_0}{\mathrm{k_B}T_c}\int_0^\infty [f \ln f + (1-f)\ln(1-f)]\,\mathrm{d}y\,, \qquad \frac{C}{\gamma_n T_c} = t\frac{\mathrm{d}(S/\gamma_n T_c)}{\mathrm{d}t}\,, \qquad (1)$$

where $f = [\exp(\beta E) + 1]^{-1}$ and $\beta = (\mathrm{k_B}T)^{-1}$. The energy of the quasiparticles is given by $E = [\varepsilon^2 + \Delta^2(t)]^{0.5}$, where ε is the energy of the normal electrons relative to the Fermi surface. The integration variable is $y = \varepsilon/\Delta_0$.

The fit of experimental data for $\mathrm{MgB_2}$ leads to very low values of $2\Delta_0/\mathrm{k_B}T_c$ for one of the gaps, substantially less than 3.53 (see below). The α–model was devised for simulation of strong–coupling effects [14], and has usually been applied to strong–coupling superconductors, leading to values > 3.53. In that case, the temperature at which the gap closes *is lowered* relative to the normal BCS closing temperature by retardation effects. Since the BCS ratio, $2\Delta_0/\mathrm{k_B}T_c = 3.53$, is the weak–coupling lower limit, smaller values can have no physical meaning as measures of the strength of the coupling. (However, anisotropy, both as theoretically studied [16] and experimentally observed [17], does lead to values < 3.5.) In the present case, as applied to a two–gap superconductor, a small value of $2\Delta_0/\mathrm{k_B}T_c$ has no bearing on the strength of the coupling , but means only that the temperature at which the small gap closes *is raised* relative to the normal BCS closing temperature by coupling to a larger gap.

Figure 1 shows the calculated $C/t\gamma_n T_c$ for $1 \leq 2\Delta_0/\mathrm{k_B}T_c \leq 5$. We checked the numerical results by comparing the data for $2\Delta_0/\mathrm{k_B}T_c = 3.53$ with Mühlschlegel's tables [15], and by verifying that the entropy at T_c is equal to that of the normal state. The curves for $2\Delta_0/\mathrm{k_B}T_c \geq 3.5$ are similar to those reported in Ref. [14]. The unusual shape of the curves for low values of $2\Delta_0/\mathrm{k_B}T_c$ may be understood by considering two characteristic temperatures,

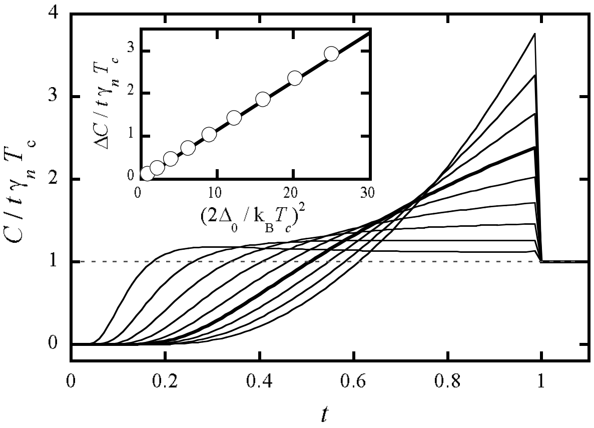

Fig. 1 – $C/t\gamma_{\rm n}T_{\rm c}$ *vs.* t according to the α–model for $2\Delta_0/{\rm k_B}T_{\rm c} = 1, 1.5, 2, 2.5, 3, 3.5$ (BCS), $4, 4.5, 5$. Inset: specific–heat jump at $T_{\rm c}$ *vs.* $(2\Delta_0/{\rm k_B}T_{\rm c})^2$.

$T_\Delta = \Delta_0/(1.76{\rm k_B})$, and $T_{\rm c}$, which are equal in the BCS limit, but which are independent in the present model:

- For $T \ll T_\Delta$, the thermal energy is too small for many quasiparticles to be excited across the gap. Only the tail of the statistical distribution contributes, so that the electronic specific heat follows an exponential behaviour approximately, similar to that of a semiconductor.

- Above $T \approx T_\Delta < T_{\rm c}$, the temperature is high enough to excite most of the quasiparticles across the gap. The specific heat approaches that of the normal state, although the system is still superconducting.

- At $T = T_{\rm c}$, the gap closes. If $T_{\rm c} \gg T_\Delta$, *i.e.* if the gap is small compared to the thermal energy at $T_{\rm c}$, only a small change occurs in the number of excited quasiparticles. The BCS ground state is essentially empty. As a consequence, the specific–heat jump is small.

The smaller the gap, the closer the $C/t\gamma_{\rm n}T_{\rm c}$ curve approaches the normal–state line, and the smaller the ΔC at the transition. We verify numerically the relation between the gap and the jump, $\Delta C = {\rm k_B}N(0)/({\rm k_B}T_{\rm c})^2({\rm d}\Delta^2/{\rm d}\beta) \propto \Delta_0^2$ (inset of Fig. 1) [18]. This quadratic dependence holds only because the variation of the normalised gap with t is common to all curves.

In a two–band, two–gap model, the total specific heat can be considered as the sum of the contributions of each band calculated independently according to eq. (1) if interband transitions due to scattering by impurities or phonons can be neglected. Each band is characterised by a partial Sommerfeld constant γ_i, with $\gamma_1 + \gamma_2 = \gamma_{\rm n}$. C data are fitted with three free parameters, the gap widths Δ_1 and Δ_2, and the relative weights $\gamma_1/\gamma_{\rm n} \equiv x$ and $\gamma_2/\gamma_{\rm n} \equiv 1-x$. Figure 2 shows the data (circles) and the fit (thick line), compared to the BCS specific heat (thin line). Insets show the gap functions, and the various contributions to the total electronic specific heat. The latter curves show evidence of weak correlation between the fitting parameters; the low–temperature excess is related to Δ_2, whereas the jump at $T_{\rm c}$ is due essentially to the Δ_1 component. Numerical results are given in Table I.

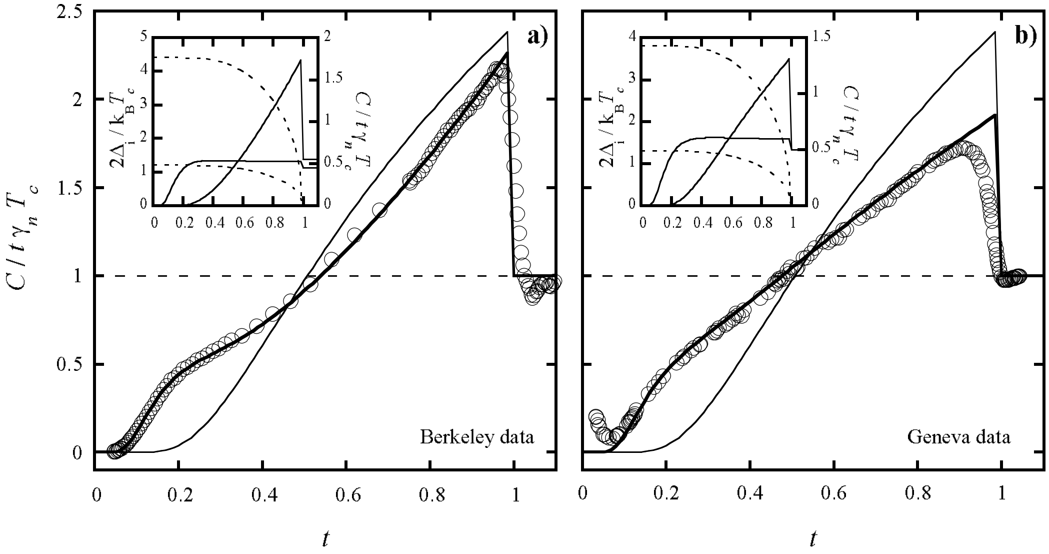

Fig. 2 – BCS normalized specific heat (thin line), experimental data (∘), and two–gap fits (thick lines), versus the reduced temperature t. (a) data from Ref. [3]; (b) data from Ref. [2]. Insets: gaps $2\Delta_1/\mathrm{k_B}T_\mathrm{c}$ and $2\Delta_2/\mathrm{k_B}T_\mathrm{c}$ versus t (dotted lines), and partial specific heat of both bands (full lines). Parameters obtained from the fits are given in Table I.

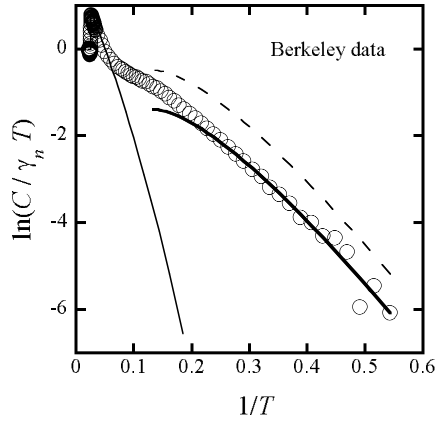

Fig. 3

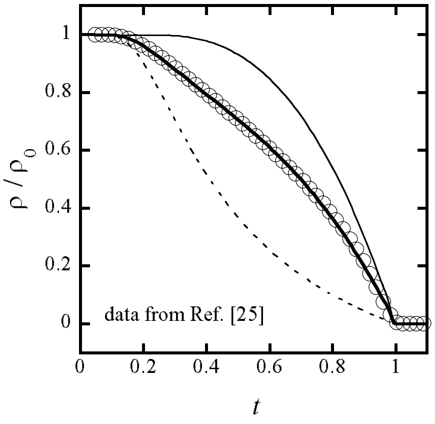

Fig. 4

Fig. 3 – Semi–logarithmic plot of the electronic specific heat versus $1/T$. Dashed line: asymptotic curve, eq. (2) with $\gamma = \gamma_\mathrm{n}$; thick line: eq. (2) with $\gamma = 0.4\gamma_\mathrm{n}$ (see text); thin line: standard BCS curve, also shown in Fig. 2; (∘), data from Ref. [3].

Fig. 4 – Superfluid fraction versus reduced temperature. Thin line: contribution of Δ_1; dotted line: contribution of Δ_2; thick line: full two–gap fit; (∘): data obtained from measurements of the penetration depth presented in Ref. [25]. Fitted parameters are given in Table I.

TABLE I – *Gap ratios* $2\Delta_1/k_BT_c$, $2\Delta_2/k_BT_c$ *and weights* x *as determined by the two–gap model (lines 1–4) and by different techniques (lines 5–10).*

Ref.	Technique	$2\Delta_1/k_BT_c$	$2\Delta_2/k_BT_c$	$x : (1-x)$
[3]	specific heat	4.4	1.2	55% : 45%
[2]	specific heat	3.8	1.3	50% : 50%
[5]	specific heat	3.9	1.3	50% : 50%
[25]	penetration depth	4.6	1.6	60% : 40%
[19]	Raman	3.7	1.6	
[20]	photoemission	3.6	1.1	
[21]	tunneling	4.5	1.9	
[22]	point–contact spectroscopy	4.1	1.7	
[23]	point–contact spectroscopy	4.2	1.0	
[13]	band structure	4.0	1.3	53% : 47%

In spite of its limitations, this empirical model fits the measured specific heat well over the whole range of T to T_c. The sample dependence of the results is reasonably low, and may reflect metallurgical differences. The larger value of Δ_1 for the sample of Fig. 2a (isotopically pure $Mg^{11}B_2$ powder [3]) reflects a sharper jump and a steeper slope just below T_c compared to the sample of Fig. 2b (MgB_2 sinter [2]). On average, $2\Delta_1/k_BT_c \sim 4.0$ and $2\Delta_2/k_BT_c \sim 1.2$, with approximately equal weights.

Moreover, the fitted parameters are qualitatively and quantitatively comparable with independent determinations from other sources. They are consistent with band–structure calculations [13] and spectroscopic measurements [19–23], which report the presence of two gaps, the smaller gap having approximately one–third the BCS value and the larger gap being slightly greater than the BCS value (Table I). We emphasise that C, a thermodynamic property, probes the whole volume, whereas spectroscopic measurements are more sensitive to surface conditions.

The relative weights (1:1, *i.e.* $x \sim 0.5$) are consistent with the calculations of Ref. [13]. Liu *et al.* attribute the larger gap Δ_1 to particular 2D sheets of the Fermi surface, whereas the smaller gap Δ_2 is associated with 3D sheets. Using partial densities of states and de Haas–van Alphen mass renormalizations, the weight of the smaller gap is evaluated as $x \sim 0.47$, and $1-x \sim 0.53$ for the larger one. The agreement with the two–gap model fits is remarkable.

The present two–gap model reconciles the apparently conflicting results of Ref. [9] and [3,4]. By fitting their specific heat data close to T_c, Kremer *et al.* [9] concluded that their data was consistent with a medium– to strong–coupling $2\Delta_0/k_BT_c \sim 4.2$. However, the fitted value of γ_n at T_c was 1.1 mJ $mol^{-1}K^{-2}$, less than half of γ_n measured in the normal state. Alternatively, Yang *et al.* [4] and Bouquet *et al.* [3] fitted the exponential decrease of the low–T data and concluded that $2\Delta_0/k_BT_c \sim 0.9$. However, the fitted value of γ_n at low T was too small also, 0.7 mJ $mol^{-1}K^{-2}$ in Ref. [3]. In the framework of the two–gap model, the main contribution just below T_c is that of the larger gap Δ_1, with a break in the slope characteristic of medium– to strong–coupling, and an amplitude of ΔC determined by $\gamma_1 = x\gamma_n \sim \gamma_n/2$ (insets of Fig. 2), in qualitative agreement with Kremer's analysis. The main contribution at $T \ll T_c$ is that of the smaller gap Δ_2, with the exponential decrease determined by Δ_2, and the amplitude by $\gamma_2 = (1-x)\gamma_n \sim \gamma_n/2$ (insets of Fig. 2), again in qualitative agreement with the analysis of Ref. [3]. The latter data are presented below in a slightly different approach. Rather than the usual empirical interpolation $C \propto \exp(-1.44 T_c/T)$, we use the low–$T$ asymptotic formula [24]:

$$\lim_{T\to 0} \frac{C}{\gamma T} = 3.15 \left(\frac{\Delta_0}{1.76 \mathrm{k_B} T}\right)^{5/2} \exp\left(-\frac{\Delta_0}{\mathrm{k_B} T}\right) . \tag{2}$$

In Fig. 3, we plot data in the form $\ln(C/\gamma_n T)$ versus $1/T$, together with the limit given by eq. (2). With $2\Delta_0/\mathrm{k_B}T_c = 0.9$ and $\gamma = \gamma_n$, eq. (2) overestimates the data, although the slope determined by Δ_0 is correct. With $\gamma \cong 0.4\gamma_n$, the fit is good in the domain where eq. (2) holds.

The same two–gap model can be applied to the superfluid density ρ, which is given, for a single gap, by $\rho = 1 - 2\Delta_0/\mathrm{k_B}T \int_0^\infty f(1-f)\,\mathrm{d}y$. The penetration depth $\lambda \propto \rho^{-1/2}$ is given in Ref. [25] and is plotted in Fig. 4, together with a two–gap fit (thick line) and its components (full and dotted lines). These data are not strictly bulk measurements, but probe the sample to a typical depth of $\lambda \cong 1800$ Å [2]. Nevertheless, λ is large compared to the typical sampling depth of many spectroscopic experiments, which is on the scale of the coherence length $\xi \cong 50$ Å [2]. The fitted parameters $2\Delta_i/\mathrm{k_B}T_c$ and x are consistent with other determinations (Table I).

The empirical α–model allows a quantitative comparison to be made between different experiments and theory within a general framework. The results are numerically consistent, and confirm the coexistence of two gaps for the bulk sample. This situation holds the promise of interesting single–crystals properties. Our two–gap model is phenomenological since we *postulate* the existence of the gaps, without specifying their origin. Any theoretical approach leading to a similar average electronic density of states would be compatible with the present results, so that specific–heat measurements alone cannot settle in favour of any particular microscopic model [11, 13].

Some limitations exist. First, the α–model assumes a BCS–like T–dependence of the gap. However, if the variation of the smaller gap is reasonably smooth, the results should not depend critically on its exact shape, since the main effect on the specific heat occurs below T_Δ where $\Delta_2(T)$ is expected to be essentially constant. Self–consistent calculations of $\Delta(T)$ might lead to corrections, and more elaborate simulations are currently under way [26]. Second, we calculate each contribution of the gaps independently and assume that they are additive. Some coupling is present, but within the present model, its sole effect amounts to bringing the natural closing temperature of the smaller gap, *i.e.* ≈ 10 K, up to ≈ 40 K.

Our two–gap model describes only the zero–field specific heat. As data in $H > 0$ suggest a different field dependence for each gap, a theory of the mixed–state specific heat for a two–gap superconductor would be most useful in extracting quantitative information from $C(T,H)$. Indeed, the field dependence of the electronic contribution at low temperature is unusual. The coefficient of the linear term in the mixed–state, $\gamma(H)$, dramatically increases in small fields [2–6], in a quasi–logarithmic way [5], and saturates for fields much below H_{c2}, in fact near $H_{c2}/2$. Moreover, the characteristic dip in C/T for $0 < T < 10$ K associated with the gap Δ_2 in one of the bands vanishes by ≈ 0.5 T. Qualitatively, these results would seem to indicate that a small field is able to quench the smaller gap, in agreement with spectroscopic measurements [22]. The saturation of $\gamma(H)$ much below H_{c2} suggests that a major part of the electrons are either normal or in a gapless state, possibly by virtue of inter–band scattering in the presence of a normal sheet on the Fermi surface. Forthcoming models may have to embody the different dimensionality of the gaps. Interesting developments are expected for the physics of the vortex state for superconductors with such an unusual k–dependent gap.

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