Specific heat of single crystal MgB$_2$: a two-band superconductor with two different anisotropies

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Heat-capacity measurements of a 39 µg MgB$_2$ single crystal in fields up to 14 T and below 3 K allow the determination of the low-temperature linear term of the specific heat, its field dependence and its anisotropy. Our results are compatible with two-band superconductivity, the band carrying the smaller gap being isotropic, that carrying the larger gap having an anisotropy of $\sim 5$. Three different upper critical fields are thus needed to describe the superconducting state of MgB$_2$.

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Shortly after the discovery of 40-K superconductivity in MgB$_2$ [1], its nature was intensively studied. The isotope effect soon indicated phonon-mediated pairing [2]. However, MgB$_2$ cannot be considered as a classic conventional superconductor; indeed several studies point to the existence of a gap much smaller than the expected BCS value: band-structure calculations [3, 4], STM [5, 6], specific heat [7, 8, 9, 10, 11], penetration depth [12], and various spectroscopic experiments [13, 14, 15, 16, 17, 18].

The so-called “two-band” model [19, 20], which considers two different s-wave superconducting gaps (a larger and a smaller gap, $\Delta_{\sigma}$ and $\Delta_{\pi}$) on separate sheets of the Fermi surface (the $\sigma$- and $\pi$-band, respectively), now seems widely accepted and explains most experimental results [19, 20], with few exceptions [21]. The theory of two-band superconductivity was suggested soon after the development of the BCS theory [22], and some s-d metals have shown hints of this phenomenon, generally in the form of small deviations from BCS predictions, e.g. in C experiments [23]. In contrast, MgB$_2$ shows such clear signatures that it might serve as a textbook example. For instance, the electronic specific heat of MgB$_2$ shows an excess by an order of magnitude at $\sim T_c$ /5, and presents an exponential dependence at low temperature $T$ indicating the existence of a small gap on a large fraction ($\sim 50\%$) of the Fermi surface [8, 9, 10, 11]. At low $T$ the effect of a small magnetic field $H$ on the coefficient of the linear C-term, $\gamma(H) \equiv \lim_{T \to 0} C(H)/T$, is dramatic. Classically, $\gamma(H)$, a thermodynamic probe of the electronic density of states at low-energy, is expected to be linear in $H$ up to $H_{c2}$ [23]. However, for MgB$_2$ an extreme non-linearity was observed, which was assigned to the existence of an additional, smaller gap [8, 9, 10].

The only specific heat experiment on single crystal reported so far was focused on the superconducting transition [23, 24]. Such experiments are delicate since the mass of MgB$_2$ crystals is usually smaller than 100 µg, but are required to study the anisotropy. Previous studies showed that the anisotropy of superconducting properties depends on both field and temperature [23, 24]. This puzzling behavior motivated the present study.

We measured the low-temperature specific heat of a MgB$_2$ single crystal with the field parallel and perpendicular to the boron planes. The results clearly show that the extreme non-linearity of $\gamma(H)$, first observed in polycrystals [8, 9, 10], is an intrinsic property of MgB$_2$, related to the existence of two superconducting gaps. Moreover, these measurements reveal a dramatic variation of the effective anisotropy with the field, from 1 to $\sim 5$. We interpret these results as a manifestation of the two-band nature of superconductivity in MgB$_2$, plus the dimensionality of the $\pi$-band (isotropic) and $\sigma$-band (anisotropic).

The single crystal of MgB$_2$ is similar to those described in Ref. [23]. Its mass, 39 µg, is small for a quantitative study of specific heat. For this purpose, we developed a miniaturized version of the relaxation calorimeter described in Ref. [1]. A commercial Cernox bare chip [30] was thinned down to 1 mg mass and used simultaneously as sample platform, heater and thermometer. Two 10 µm phosphor-bronze wires soldered onto the chip acted as mechanical support, thermal links and electrical leads. Only low-$T$ studies were possible, since the heat capacity...
of the platform, essentially of phononic origin (sapphire), increases rapidly with $T$. We thus restrained our study to the range 2 to 3 K. Previous experiments have shown that this range of temperature lies sufficiently above the domain of possible parasitic magnetic contributions, but low enough ($\sim T_c/15$) to allow reliable determination of $\gamma(H)$ (see e.g. Ref. [8]). Owing to the small value of $C$ at these temperatures, the relaxation time was short (0.1–0.5 s), necessitating aperture times shorter than one power line cycle for the digitization of voltages. In order to suppress the 50 Hz noise, the signal was averaged over 50 to 200 relaxations. The field dependence of the adenda represents at most 13% of the normal electronic linear term of the MgB$_2$ crystal, and was calibrated by measuring a 196 µg Ag reference sample.

Figure [3] shows the specific heat for both orientations. It is impossible to compensate exactly for the small but unknown quantity of GE-varnish used to attach the sample. Instead, in order to calculate $\gamma(H)$, we used the zero-field curve as a reference. It was shown on polycrystals that the electronic specific heat of MgB$_2$ is negligible in zero field in this temperature range [9, 10]: the parallel shift of the $C/T$ curves in Fig. [3] is thus a direct measurement of $\gamma(H)$. This shift was precisely determined by fitting each curve with a linear electronic term $\gamma(H)T$ plus a $\beta T^2$ lattice term, imposing the same β coefficient for all fields. The result for $\gamma(H)$ is plotted in Fig. [2] for both orientations. With the field perpendicular to the boron planes, $\gamma(H)$ saturates above 3–4 T, indicating that the sample has entered the normal state. This value is consistent with previous reports giving $\mu_0 H_{c2}^a(c) \approx 3$ T for the upper critical field along the $c$-axis [25, 26, 27, 31]. This also determines the normal electronic linear term $\gamma_n = 0.76 \pm 0.03$ mJK$^{-2}$gat$^{-1}$, comparable with literature values [8, 9, 10, 11]. The normal state is not fully established when the field is parallel to the $(ab)$-planes, indicating that $H_{c2}^{(ab)}$ is higher than the maximum applied field of 14 T. An extrapolation suggests $\mu_0 H_{c2}^{(ab)} \approx 18–22$ T, in agreement with reported values [12]. Therefore, the anisotropy of the upper critical field at $T \ll T_c$ is established in bulk.

The anisotropy of $H_{c2}$ in MgB$_2$ has long been debated [22, but was finally assessed by experiments using clean single crystals [23, 24, 25, 26, 27]. Two kinds of anisotropy can be considered: the anisotropy of the superconducting gap, and that of the Fermi surface. To model the former, some $k$-dependence of the gap has to be assumed. Such an approach was attempted using a one-band model for MgB$_2$ [23]. The two-band model is an extreme case of such an anisotropy: depending on which Fermi sheet is considered, the superconducting gap may be either large or small. The effect of an anisotropic Fermi surface on superconducting properties can be modeled by renormalizing the isotropic results by a function of the ratio of the effective masses, a method that was successfully applied to cuprate superconductors [23]. Angst et al. used this approach for MgB$_2$ [23, but showed that the shape of the torque curves did not follow this simple one-band, anisotropic model over the whole range of field orientations.

From Fig. [2] it is clear that it is not possible to normalize the effect of the field by using a constant anisotropy factor. For $H \leq 0.5$ T, the values of $\gamma(H)$ are almost indistinguishable, irrespective of the field direction, showing the absence of anisotropy (see inset of Fig. [2]). However, a field scaling factor of $\approx 5$ is needed to superpose the $\gamma(H)$ curves just below saturation, i.e. near $H_{c2}$. An effective anisotropy $\Gamma_{eff}$ can be defined as the scaling factor by which the field along the $c$-axis must be multiplied in order to merge both $\gamma(H)$ curves. Figure [3] presents $\Gamma_{eff}$ versus $H/|ab|$. At low field, $\Gamma_{eff} \approx 1$, since the effect of $H$ does not measurably depend on the orientation; $\Gamma_{eff}$ rapidly increases with $H$, and tends toward the anisotropy of $H_{c2} \sim 5$. Such an $H$-dependent anisotropy was also deduced from torque measurements [27]. The present analysis shows that the change of $\Gamma_{eff}$ with $H$ (and possibly with $T$) is an intrinsic property of MgB$_2$, having a bulk thermodynamic signature, even though the amplitude of this variation may depend on the physical quantity by which it is determined. We will argue in the following that, to explain specific heat measurements, both kinds of anisotropy are required: the band dependence of the gap, plus a renormalization by the effective masses on the $\sigma$-band.

Let us first focus on the shape of the $\gamma(H)$ curves. Similarly to previous data on polycrystals, $\gamma(H)$ increases sharply at low fields. The present data show that this effect does not depend on the orientation of the field, and point to the existence of a large fraction of normal electrons in the mixed state already at very low $H$. In a typical s-wave, dirty type-II superconductor, $\gamma(H)$ mainly originates from the vortex cores and should be approxi-
Irrespective of the field direction. The effect is particu-
larly proportional to $H$ (i.e., the number of vortices). The strong non-linearity of $\gamma(H)$ for MgB$_2$ is atypical: for $\mu_0 H = 1$ T, approximatively half of $\gamma_n$ is recovered, irrespective of the field direction. The effect is particularly striking for $H//(ab)$: about 5% of $H_{c2}^{\text{ab}}$ drives $\sim 50\%$ of the electrons into the normal state.

The peculiar shape of $\gamma(H)$ can be understood by considering the meaning of a vortex within a two-band model. Both bands supply the carriers and currents that define one vortex, and both bands contribute to the local density-of-states (LDOS) in one vortex core. Simulations and STM studies suggest that a core results from the superposition of two peaks in the LDOS with different diameters defined as usual by the coherence length $\xi_\sigma$ or $\xi_\pi$ associated with each band. The sharper peaks with diameter $\xi_\sigma$ lead to a conventional core contribution for the $\sigma$-band, and overlap at $H_{c2}$. In contrast, the large coherence length of the $\pi$-band gives rise to broad LDOS peaks, with a diameter much larger than $(\Phi_0/2\pi H_{c2})^{\frac{1}{2}}$. These giant cores, which have been observed by STM [3], contribute heavily to the total low-$T$ DOS, as measured by $\gamma(H)$, until they start to overlap much below $H_{c2}$. At this point, the contribution of the $\pi$-band to $\gamma(H)$ saturates. At higher fields, superconductivity in the $\pi$-band is maintained up to $H_{c2}$ by coupling to the $\sigma$-band, but the variation of $\gamma(H)$ now comes from the $\sigma$-band contribution. The $\gamma(H)$ curves of Fig. 2 correspond qualitatively well with these predictions. Note that the analysis of previous measurements on polycrystalline samples [2, 6, 10] was complicated by angular averaging of $\gamma(H//c)$ and $\gamma(H//ab)$, leading to a flattening above 8 T.

Within the present scheme, the data of Fig. 2 can be used to determine the anisotropy $\Gamma_\pi$ and $\Gamma_\sigma$ of each subsystem separately. The abnormally fast initial increase of $\gamma(H)$ at low $H$ is attributed to the giant vortex cores associated with $\pi$-band carriers, and, as shown by the inset of Fig. 2, is isotropic; therefore $\Gamma_\pi = 1$. On the other hand, the $\sigma$-band contribution is responsible for the anisotropy of $H_{c2}$, which we determined when describing Fig. 2; therefore $\Gamma_\sigma \approx 6$. This is consistent with the 3D and quasi-2D character of the $\pi$- and $\sigma$-band, respectively, found in band-structure calculations [4, 19, 20], and with the experimental determination by torque magnetometry at low $T$ [23]. The effective anisotropy shown in Fig. 2 is a weighted average which depends on the relative contribution of each band to the condensate for a given $H$ and $T$: it varies smoothly from $\Gamma_\pi$ at low fields to $\Gamma_\sigma$ at high fields.

Besides the anisotropy of each subsystem, we can attempt to determine the full shape of the unusual contribution of the $\pi$-band, $\gamma^\pi(H)$. For this purpose, we assume that the $\sigma$-band contribution, $\gamma^\sigma(H)$, follows a classical behavior [23], increasing linearly from 0 to $\gamma^\sigma_0$ as the field goes from 0 to $H_{c2}^{\text{ab}}$ or $H_{c2}^{\text{c}}$, depending on the field orientation. The linear sections above 1 T in Fig. 2 correspond to this contribution of the $\sigma$-band; their extrapolation to $H = 0$ points to the normal-state value $\gamma_n^\sigma$ of the $\pi$-band contribution ($\gamma_n^\sigma + \gamma_n^\pi = \gamma_n$). By subtracting $\gamma^\sigma(H)$ from $\gamma(H)$, we isolate $\gamma^\pi(H)$ (Fig. 3).

The parameters $H_{c2}^{\text{c}}$, $H_{c2}^{\text{ab}}$, $\gamma_n^\pi$, and $\gamma_n^\sigma$ are determined from Fig. 3. By requiring that the saturation value of $\gamma^\pi(H)$ is isotropic, we find that the parameters cannot depart by more than $\pm 15\%$ from the average fitted values $\mu_0 H_{c2}^{\text{c}} = 3.5$ T; $\mu_0 H_{c2}^{\text{ab}} = 19$ T, $\gamma_n^\pi = 0.42$ mJ K$^{-2}$ nm$^{-2}$, and $\gamma_n^\sigma = 0.34$ mJ K$^{-2}$ nm$^{-2}$. The $\gamma_n^\pi/\gamma_n^\sigma$ ratio $\approx 55/45 \approx 1$, is consistent with independent fits of the zero-field specific heat [1] and penetration depth [12], and with band-structure calculations [4, 19, 20]. Furthermore, $\gamma^\pi(H)$ appears to follow quantitatively numerical simulations [2, 23]. This shows that a model consisting of two superfluids of nearly equal weight, having different gaps and different anisotropy, gives a consistent description of various properties of MgB$_2$.

The recent measurements of the thermal conductivity of single crystals by Sologubenko et al. [21] were interpreted in a similar way. At low fields, the heat conduc-

![FIG. 3: Effective anisotropy, defined as the ratio of magnetic fields applied in the $(ab)$-planes and along the $c$-axis yielding the same $\gamma$-value. Note that the choice of the abscissa is arbitrary: we chose $H//\sigma$, but we could just as well plot it versus $H//c$ or versus $\gamma(H)$.](image)

![FIG. 4: Separation of both contributions to $\gamma(H)$: $\gamma^\pi(H)$ (straight lines) and $\gamma^\sigma(H)$ for the field applied along the $c$-axis (●) and in the $(ab)$-planes (□). The dashed line is a guide to the eyes for $\gamma^\pi(H)$.](image)
tivity increases sharply, for all field directions. As discussed for $\gamma(H)$, this is attributed to the contribution of normal 3D $\pi$-band carriers in the anomalously large vortex cores. At higher field, this effect saturates and the anisotropy rises, due to the increasing contribution of the quasi 2D $\sigma$-band. A similar approach may explain not only why the anisotropy obtained from magnetic torque experiment changes with $H$ and $T$, but also why a single-anisotropy model does not fit the angular dependence of $H_c2$ [27, 28]. We emphasize, however, that this view is simplified and phenomenological. A more elaborate description for the interaction between the two bands was proposed [29] for the anisotropy of penetration depth and its temperature dependence (which can be understood as a consequence of the rapid thermal depletions of the isotropic $\pi$-band condensate).

The phenomenological two-band model of Ref. [11] also uses two independent superfluids to explain the zero-field $C$ of MgB$_2$. Inter-band coupling was introduced by considering that the “virtual” $T_c$ of the $\pi$-band ($\Delta n/1.76kb \sim 13K$) is brought up to that of the $\sigma$-band; the peculiar features in $C_T$ of MgB$_2$ are then dominated by this superconductivity “above $T_c$.” Here a similar situation arises: a “virtual” upper critical field can be defined for the $\pi$-band, $H_c2^\pi \sim (\Phi_0\Delta_2^\pi)/(\hbar^2v_2^\pi)$ [35]; superconductivity persists up to $H_c2^\pi$ or $H_c2^{(ab)}$, depending on the field orientation, but above $H_c2$ the overlap of huge vortex cores drives the majority of the $\pi$-band electrons normal (superconductivity “above $H_c2$”). Three characteristic fields are thus needed to describe the physics of MgB$_2$: the two upper-critical fields $H_c2^\sigma$ and $H_c2^{(ab)}$ associated with the anisotropic $\sigma$-band, and a cross-over field $H_c2^{\pi}$ associated with the $\pi$-band. We estimate the latter one by linearly extrapolating the low field $\gamma(H)$ to the partial normal-state $\gamma$ for this band ($\sim 0.55\gamma_c$), by analogy with classic superconductors. The inset of Fig. 2 shows this construction: we find $\mu_0H_c2^\pi \sim 0.3-0.4T$. These fields determine the values of the three coherence lengths of the system: for the anisotropic $\sigma$-band $\xi_\sigma^{(ab)} \sim 10$ nm and $\xi_\sigma^{(c)} \sim 2$ nm; for the isotropic $\pi$-band $\xi_\pi \sim 30$ nm. The latter value compares favorably with a direct measurement by STM giving 50 nm for the vortex-core diameter in the $\pi$-band [3]. All three fields are needed to give a phenomenological description of the superconducting properties of MgB$_2$. Note that the ratio between $H_c2^{(ab)}$ and $H_c2^{(c)}$ is driven by $\Gamma_\sigma$, i.e. the anisotropy of the effective masses of the $\sigma$-band, whereas the ratio between $H_c2^{(c)} \sim (\Phi_0\Delta_2^\pi)/(\hbar^2v_2^\pi)$ and $H_c2^{(ab)}$ is given by $\sim \Delta_\pi^2/\Delta_\sigma^2$, since the Fermi velocities are comparable on both bands. The experimental ratio $H_c2^{(c)}/H_c2^{\pi} \sim 10$ reported here agrees with various estimations of $\Delta_\sigma/\Delta_\pi \sim 3-3.5$ [1, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38].

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