Two-band Effects in the Angular Dependence of $H_{c2}$ of MgB$_2$ Single Crystals

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The angular dependence of the upper critical field $H_{c2}$ of MgB$_2$ single crystals is studied at various temperatures by means of specific heat and transport measurements in magnetic fields up to 17 T. Clear deviations from Ginzburg–Landau behavior are observed at all temperatures and are explained by two-band effects. The angular- and temperature dependence of the deviations are in qualitative agreement with theoretical predictions based on band-structure calculations. Quantitative agreement is obtained with an interband coupling slightly stronger than the calculated, enabling band-structure anisotropies and interband coupling strength to be experimentally estimated. This provides a new pathway to the study of disorder and doping effects in MgB$_2$.

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The emergence of new theoretical works with close experimental connections has significantly deepened the understanding of the properties of magnesium diboride (MgB$_2$). Despite the fact that the superconducting properties of MgB$_2$ with its fairly simple atomic structure were just recently discovered [1], this phonon mediated s-wave superconductor has already been the subject of intense and numerous studies [2] due to its exotic properties arising from a complex, disconnected, multi-band Fermi surface. Band-structure calculations have demonstrated that the Fermi surface is composed of pairs of three-dimensional $\pi$-bands and quasi-2D $\sigma$-bands [3]. This effective two-band structure has been confirmed by de Haas–van Alphen measurements [4] and angle-resolved photoemission spectroscopy [5].

The superconducting properties of the two sets of bands are quite different, due to the low overlap of the orthogonal $\sigma$- and $\pi$-band wave functions. The superconducting gap ranges from 1.5 to 3.5 meV on the $\pi$-bands and from 5.5 to 8 meV on the strongly superconducting $\sigma$-bands [6]. This double-gap nature has been verified by tunneling experiments [7], heat capacity measurements [8], and spectroscopy [9, 10, 11, 12].

Theoretically, two-band superconductivity has a history starting well before MgB$_2$ [13, 14, 15]. Through theoretical advances, a fairly unified picture has emerged with predictions that can be experimentally substantiated [3, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25]. One of the salient predictions associated with a pronounced two-band effect is a difference between the coherence length anisotropy $\gamma_{\xi} = \xi_{\theta}/\xi_{c}$ [18, 19, 20, 21] and the penetration depth anisotropy $\gamma_{\lambda} = \lambda_{\theta}/\lambda_{c}$ [22, 23], both of which become temperature dependent with opposite tendencies. For MgB$_2$, a strong decrease of $\gamma_{\xi} = H_{c2}^\theta/H_{c2}^{\pi}$ from $\gamma_{\xi}(0) \sim 5$ to $\gamma_{\xi}(T_c) \approx 2$ is found experimentally [24, 27, 28, 29, 30, 31], while controversy remains about the experimental temperature dependence of $\gamma_{\lambda}$ [32].

In this Letter we present evidence of clear deviations of the angular dependence of $H_{c2}$ from the anisotropic Ginzburg–Landau (GL) description. The $H_{c2}(T, \theta)$ transition of MgB$_2$ single crystals was determined from resistivity measurements and specific heat with excellent agreement between the two. With a slight adjustment of some of the parameters supplied by band-structure calculations, good quantitative agreement is found between theory [21] and experiment, yielding fundamental estimates of band-structure anisotropies and the interband coupling strength.

Several MgB$_2$ crystals with typical dimensions 50 – 250 $\mu$m were obtained through a high pressure heat treatment of a mixture of Mg and B in excess Mg as described elsewhere [33]. The crystals had $T_c$ values of 34 – 36 K and a $H_{c2}^{\theta}(0) \approx 3.5$ T. Transport measurements were performed using standard AC techniques at 23 Hz with a resolution better than 0.5 nV. For specific heat measurements, the crystals were mounted on top of flattened 12.7 $\mu$m chromel/constantan thermocouple junctions. Small temperature oscillations of the sample were induced by either a resistive heater wire (Sample 1, Argonne) or by modulating the temperature of the copper base [34] (Sample 2, Grenoble). The temperature
oscillation was measured through the AC voltage across the junction, the absolute base temperature monitored by a Cernox thermometer, and the sample temperature offset obtained from the DC voltage of the thermocouple.

Figure 1 shows the transitions from resistivity (top) and specific heat (bottom) as a function of angle at $T = 27.5$ K and $T = 25.0$ K, respectively. The resistive transitions were measured at a relatively high current density to suppress the effects of surface superconductivity at the well-shaped crystal surfaces, as discussed in [35]. The value of $H_{c2}(\theta)$ was determined through a linear extrapolation of the steep drop to zero resistivity as shown by the nearly vertical dashed lines in the top panel. The appearance of the peak effect just below $H_{c2}$ for some angles is evident in the figure. The thermodynamic signature of $H_{c2}$ was defined from the midpoint of the specific heat transitions, as illustrated in the bottom panel. The choice of definition was checked not to be significant. It is interesting to note that the specific heat step height is fairly independent of the field direction. This is in agreement with GL theory, where the step height should scale with $T(dH_c/dT)^2$, where $H_c$ is the (isotropic) thermodynamic critical field. Possible deviations from a constant step height arising from two-band effects are too small to be resolved in the current data due to uncertainties in the experimental method.

Clear deviations from an anisotropic GL description are, however, seen in the angular dependence of $H_{c2}$. In Fig. 2 the $H_{c2}(\theta)$ curves are shown for two selected temperatures together with corresponding fits to the effective mass description $H_{c2}^{GL}(\theta) = H_{c2}^0/(\cos^2\theta + \gamma_2^2 \sin^2\theta)^{1/2}$. The relative deviations are fairly small at $12.1$ K as compared to $25.0$ K. They are nevertheless clearly discernible at all temperatures and are reproducible between different measuring setups, samples, and methods. Resistive measurements by Eltsev et al. displayed similar deviations but were not analyzed in detail [36]. Deviations were also reported at $33$ K using torque measurements [37]. The latter, however, suffer from the inability to measure $H_{c2}$ along the symmetry axes.

The deviations from GL behavior are illuminated by plotting the ratio $A = [H_{c2}(\theta)/H_{c2}^{GL}(\theta)]^2$ as a function of $\cos^2\theta$ as shown in Fig. 3. When the field is directed along the $c$ axis or within the basal plane there are no deviations, since the experimental $H_{c2}^0$ and $H_{c2}^{GL}$ were used as parameters for the GL-fit ($A = 1$) at each temperature. The shape of the deviations as a function of angle is similar for all temperatures, with a maximum amplitude at around $\theta = 20^\circ - 30^\circ$, i.e., for $\cos^2\theta \sim 0.9$. The theoretical curves are discussed below.

To investigate the temperature dependence of the deviations in more detail, the maximum amplitude of $A(\theta)$ is plotted as a function of temperature in Fig. 4 (top). Good agreement is found between the transport and specific heat data from Argonne (Sample 1, measured on the same crystal, $T_c = 35.5$ K) and specific heat measurements taken at Grenoble (Sample 2, $T_c \approx 34$ K), illustrating the fundamental and consistent nature of the deviations. The amplitude is relatively small at low tem-
temperatures and reaches a maximum slightly below $T_c$. By comparing the temperature dependence of $A_{\text{max}}$ with that of $\gamma_\ell$ (bottom panel) one can see that the maximum of $A_{\text{max}}(T)$ occurs at intermediate values of $\gamma_\ell$.

The general experimental features of $H_\Delta(T, \theta)$ can be excellently described by the recent theory of the angular dependence of dirty two-band superconductors \[21\]. The two-band theory requires as input (i) the matrix of effective coupling constants $\Lambda_{\alpha\beta} = \lambda_{\alpha\beta} - \mu^*_{\alpha\beta}$, where $\lambda_{\alpha\beta}$ are the electron-phonon coupling constants and $\mu^*_{\alpha\beta}$ are the Coulomb pseudopotentials ($\alpha$ and $\beta$ are indices for the $\sigma$- and $\pi$-bands), (ii) band anisotropies $\gamma_\sigma$ and $\gamma_\pi$, and (iii) a ratio of the diffusion constants in the two bands, e.g., $r_z = D_{\pi,z}/D_{\sigma,z}$. The theoretical dependencies of $A(T)$ and $\gamma_\ell(T)$ obtained by using coupling constants and anisotropies supplied by band-structure calculations \[17, 24\] are illustrated by the dashed curves in Fig. \[3\]. It is clear that, while qualitatively similar, the theoretical curves are displaced closer to $T_c$ and the predicted anisotropy is higher than the experimental one.

The shapes of the theoretical curves are sensitive to mainly two parameters, the interband coupling strength, expressed through the reduced parameter $S_{12} \approx \Lambda_{\sigma\pi} / [\lambda_{\sigma\sigma} - \lambda_{\pi\pi}]^2$ \[21\], and the ratio $r_z$. In particular, the overall change of anisotropy can be estimated as $\gamma_\ell(T_c)/\gamma_\ell(0) \approx 1/\sqrt{1 + S_{12}r_z}$. We found that a quantitative description of the experimental data requires (i) a significantly increased relative interband coupling $S_{12}$, (ii) a somewhat decreased anisotropy $\gamma_\sigma$ of the $\sigma$-band, and (iii) an almost isotropic $\pi$-band. $S_{12}$ was increased by augmenting the two off-diagonal coupling constants by a factor 1.9 from the values provided in Ref. \[21\]. The set of parameters that gives the best description of the experimental data is listed in Table \[I\] together with the original parameters. The resulting fits are shown as solid curves in Figs. \[3\] and \[4\]. We note that the fits in Fig. \[3\] allow for an independent determination of $D_{\sigma,z}/D_{\pi,z} \equiv (\gamma_\sigma/\gamma_\pi)^2/r_z \approx 0.23$, in good agreement with the observation of an enlarged vortex core \[25, 38\].

A possible source of the discrepancy between the theoretical calculations and the experiments is a theoretical overestimation of the off-diagonal Coulomb pseudopotentials (see discussion in Ref. \[39\]) resulting in too low values of $\Lambda_{\sigma\pi}$ and $\Lambda_{\sigma\sigma}$. Unfortunately, no direct experimental probe of the off-diagonal coupling constants is available at present. On the other hand, the $T_c$ values of our single crystals are somewhat lower than for polycrystalline samples. Thus, it is also possible that the discrepancy is due to a slightly modified band-structure arising from a non-stoichiometric composition of the crystals. Another origin of $T_c$ suppression in single crystals could be interband impurity scattering. A natural question is how interband scattering affects the anisotropic properties. By analyzing the theoretical corrections to the components of the upper critical fields from the in-
TABLE I: Parameters used in the theoretical computations.

| Parameter | Predicted Params. | Best Experimental Fit |
|-----------|------------------|-----------------------|
| $\gamma_\pi$ | 0.82 | 1.02 |
| $\gamma_\sigma$ | 6.3 | 5.4 |
| $S_12$ | 0.034 | 0.105 |
| $(\Delta_{\sigma x}, \Delta_{\pi x})$ | (0.81, 0.115) | (0.81, 0.216) |
| $(\Delta_{\pi x}, \zeta_{\pi x})$ | (0.091, 0.278) | (0.171, 0.278) |
| $r_z = D_{\pi \sigma}/D_{\pi,\pi}$ | 300 | 120 |

*As predicted by band-structure calculations. $\Lambda$-values are taken from Ref. [24] and $\gamma$-values are obtained from Ref. [17]. The parameter $r_z = 300$ was not calculated but estimated, and corresponds to $D_{\pi,\pi}/D_{\pi,\pi} = (\gamma_\pi/\gamma_\sigma)^2/\gamma_z = 0.2$ [28].

In conclusion, when the data is analyzed with respect to the interband scattering parameter $T_{\alpha\beta}$, it is found that the interband impurity scattering acts as a pair breaker, homogeneously suppressing $T_c$ and both components of $H_2$ without modifying the anisotropy. The leading corrections to the anisotropy have the origin of weak interband scattering, we conclude that it is unlikely that this scattering is responsible for discrepancies between the calculated band-structure and experiment (e.g., for the lower value of $\gamma_\sigma$) [11].

MgB$_2$ single crystals are usually described as fairly clean, with the $\sigma$-band probably in the clean limit [1, 38, 40]. This is supported by the low, reproducible value of $H_{c2}(0) \approx 3.5$ T. The temperature dependence of $\gamma_\xi$ has also been described successfully within the clean-limit formalism [24]. However, this still requires similar modifications of coupling and band anisotropies from the predicted values. To our knowledge, a clean-limit calculation of the angular dependence of $H_{c2}$ has not yet been presented. One could expect deviations from the anisotropic GL dependence of $H_{c2}$ at low temperatures even for a clean $\sigma$-band due to Fermi surface effects. On the other hand, the theory [21] for $H_{c2}(\theta)$ should remain valid even for a clean $\sigma$-band in the vicinity of $T_c$, where this band is described by GL theory and only the contribution from the $\pi$-band requires a microscopic approach.

In summary, we have studied the angular and temperature dependence of the upper critical field of MgB$_2$ single crystals by means of heat capacity (specific heat) and transport measurements. Clear two-band effects are found in both $H_{c2}(\theta)$ and the temperature dependence of the upper critical field anisotropy $\gamma_\xi(T)$. The experiments are well explained by the theory [21], providing a deep understanding of the microscopic parameters describing the system. This work thus points out a new pathway to the study of disorder and doping effects in MgB$_2$, with great implications for future applications.

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der $\Gamma_{xx}/\Lambda_{ss}$ meaning that the relative change of anisotropy due to the interband scattering at any temperature has to be significantly smaller than the relative change of $T_c$. In addition, the correction to the basal-plane upper critical field has an extra small factor $1/\sqrt{\tau}$. 