c-axis Raman Scattering in MgB$_2$: Observation of a Dirty-Limit Gap in the $\pi$-bands

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MgB$_2$ exhibits a rich multiple-band structure which has been observed by a number of experimental techniques including angle-resolved photoemission spectroscopy, de Haas-van Alphen effect and Hall resistivity [1, 2, 3]. These results confirm band structure calculations [4, 5] and reveal strongly two-dimensional (2D) $sp_xp_y$ ($\sigma$) bands and three-dimensional (3D) $p_z$ ($\pi$) bands. The existence of different superconducting gaps associated with the different band systems has, in the time since its theoretical proposal [4, 7], become the foremost topic of discussion surrounding MgB$_2$. While observations of two gaps in polycrystal samples have been reported (see Ref. 8 for a review), it is extremely difficult to distinguish between a strongly anisotropic single gap and two distinct gaps from polycrystal measurements. Moreover, none of the reports could conclusively associate the gaps with particular band systems because they could not distinguish the $\sigma$ and $\pi$ bands.

Raman scattering, which has the benefits of excellent energy resolution, a relatively large penetration depth and the ability to selectively measure different portions of the Fermi surface(s), has been somewhat inconsistent on the subject of multiple gaps in MgB$_2$. Recent single crystal measurements restricted to $ab$-plane polarised spectra showed only a single superconducting gap [8], while data from polycrystalline MgB$_2$ were interpreted in terms of two superconducting gaps both residing on the $\sigma$-bands [10]. It was suggested that the second gap feature might appear only in out-of-plane polarisations [9] and a complete set of polarisation data would permit superconductivity on the $\sigma$ and $\pi$ Fermi surfaces to be discerned [11]. Thus, to resolve the inconsistency between Raman measurements and to clarify the multiple gap issue in MgB$_2$, out-of-plane measurements of single crystals are crucial.

In this letter we report $ac$-face Raman scattering measurements from thick MgB$_2$ single crystals with $ac$-face dimensions 100–150 by 100–150 $\mu$m and superconducting transition temperatures of 38.0–38.4 K. Raman measurements were performed in near-backscattering configuration with polarisation geometries $zz(A_{1g})$, $xx(A_{1g} + E_{2g})$ and $xz(E_{1g})$; details of crystal fabrication and experimental setup are reported elsewhere [8, 11, 12]. The Raman vertex $\gamma(k)$, which weights the electronic Raman scattering cross section [13, 14, 15], is a function of the band energies; the anisotropy of the $\sigma$ and $\pi$ bands gives $\gamma_\pi(k) \neq 0$ in $zz$ and $xx$ polarisations while $\gamma_\sigma(k) \approx 0$ for $xz$. Thus $zz$ polarised spectra isolate the $\pi$ band response while both $\sigma$ and $\pi$ bands contribute to $xx$ polarisation.

Raman spectra taken at 40 and 15 K from one of the single crystals studied are shown in Fig. 1 for three different polarisation conditions in the $ac$-face. All spectra have been corrected for the Bose thermal contribution.
The polarisation dependence of the the $E_{2g}$ symmetry phonon, seen at around 620 cm$^{-1}$ in the $xx$ spectrum, confirms both the crystal alignment in our experiment and, incidentally, micro-Raman results on single crystals [16].

A strong electronic continuum is present in all spectra, constituting the principal component of the $zz$ and $xx$ spectra and always showing greater intensity in $zz$ polarisation. Notably, the superconductivity-induced renormalization of the continuum seen at low frequencies in all polarisations has markedly different character in $zz$ and $xx$ compared to $xx$ polarisation. As expected, the $xx$ continuum at 15 K exhibits the sharp pair-breaking peak at around 100 cm$^{-1}$ seen in the same polarisation measured in-plane [9]. Meanwhile the $zz$ and $xx$ renormalizations are very similar in character, showing a shoulder around 25–40 cm$^{-1}$ accompanied by an increase in intensity above the threshold relative to the normal-state continuum. Despite the formation of a threshold, no sharp coherence peak due to the breaking of Cooper pairs is seen in the $zz$ (or $xz$) polarised continua — neither directly above the threshold edge nor in the vicinity of 100 cm$^{-1}$. Similar temperature dependence of the low-frequency continuum was also seen in spectra from another six crystals (not shown here). Indeed, we have been unable to find a sharp coherence peak anywhere in the $zz$ (or $xz$) spectra of any single crystals studied. Since the $zz$ and $xx$ polarisations are similar, the following results and discussion will focus on the $zz$ continuum.

Figure 2 shows the temperature dependence of the $zz$ polarised electronic Raman continuum in the range 40–15 K. As the temperature is reduced below $T_c$ a threshold forms in the continuum, gaining a maximum extent at 15 K of around 29 cm$^{-1}$. As best as can be discerned, the onset temperature appears to coincide with $T_c$ and the temperature dependence appears to be BCS-like [11].

Recalling that $zz$ polarisation selects Raman scattering from the $\pi$ Fermi surface only, this superconductivity-induced renormalisation must be directly related to the superconducting gap on the $\pi$ sheets. The residual intensity below the shoulder edge varies between crystals and it is likely that specular scattering from surface defects is the predominant contribution.

In order to properly evaluate the superconductivity-induced spectral change seen in Fig. 2, we must first examine the normal state electronic Raman continuum. As shown in Fig. 3, the $zz$ continuum is well described over the entire frequency and temperature range by a relaxation response due to impurity scattering [14]

$$I(\omega) = \frac{A \omega \Gamma}{\omega^2 + \beta^2 T^2},$$

where $A$ is an arbitrary intensity factor, $\Gamma$ is the impurity scattering rate for each scattering channel, and the Raman vertex has been absorbed into $A$. Anisotropy of the impurity scattering rate will be revealed in the polarisation-dependence of the Raman continua [14]. To accommodate the nearly flat continuum at higher frequencies a frequency-dependent impurity scattering rate $\Gamma(\omega, T) = \sqrt{\alpha \omega^2 + (\beta T)^2}$ is introduced, were $\alpha$ and $\beta$ are constants of the order of unity. An example fit to the 40 K spectrum is shown in Fig. 3 and the $\alpha$ and $\beta$ parameters are plotted against temperature (inset). Below 90 K the static-limit impurity scattering rate $\Gamma_0(\omega \to 0)$ is around 110 cm$^{-1}$. These results indicate that the increase in intensity above the threshold in the superconducting state $zz$ and $xx$ continua is at least partly attributable to the trend of increasing spectral weight seen in the normal state, and does not represent a broad pair-breaking peak. The peakless threshold in the superconducting state continuum remains to be explained.

A threshold $sans$ peak may be seen in the Raman
spectrum of some clean superconductors when the optical penetration depth $\delta$ is less than the superconducting coherence length $\xi$. To examine this possibility in MgB$_2$, we use $\delta = \sqrt{2/\mu_0 \sigma \omega}$ and take $\sigma = 0.18 \times 10^6 \ \Omega^{-1}\text{m}^{-1}$ at $\omega = 514.5 \ \text{nm}$ to obtain $\delta \approx 500 \ \text{Å}$. In comparison, estimates of $\xi_c$ range from 23 Å – 50 Å to $\xi_c \approx 500 \ \text{Å}$, giving $\delta > \xi$. A sharp pair-breaking peak is thus expected to appear in the absence of significant impurity scattering. The analysis of the normal-state spectra indicates, however, that the $zz$ continuum arises from relatively strong impurity scattering.

Devereaux has developed a theory of Raman scattering in dirty superconductors for the case of non-magnetic impurity scattering. The channel-dependent Raman intensity is expressed as

$$ I(\omega) = \frac{A\omega}{\omega^2 + \Gamma^2} \Theta(\omega - 2\Delta) \left( \frac{\omega - 2\Delta}{\omega + 2\Delta} \right)^2 E(a) + \frac{\omega^2 + \Gamma^2 + 4\Delta}{\omega^2 + \Gamma^2 + 2\Delta} K(a) + \frac{2(2\Delta\omega)^2}{(\omega^2 + \Gamma^2)^2 - (2\Delta)^2} \Pi(n, a), \quad (2) $$

where $\Theta(x)$ is the theta function ($0$ for $x < 0$; $1$ for $x > 0$), $\Delta$ is the magnitude of the superconducting gap and $K$, $E$ and $\Pi$ are complete elliptic integrals of the first, second and third kind. The arguments of the elliptic integrals are

$$ a = \frac{\omega - 2\Delta}{\omega + 2\Delta}, $$

$$ n = \frac{(\omega - 2\Delta)^2 + (a\Gamma)^2 (1 - \frac{2\Delta}{\omega})^2}{(\omega - 2\Delta)^2 + \Gamma^2 (1 - \frac{2\Delta}{\omega})^2}. $$

In the limit $\Gamma \to 0$ Eq. (2) yields a spectral line shape analogous to that for clean superconductors [13]. Note that this model neglects corrections to the Raman vertex (such as final state interactions) and assumes an isotropic $s$-wave gap [14]. Despite indications that the gaps which form on the $\sigma$ and $\pi$ Fermi surfaces will be anisotropic in clean MgB$_2$ [21], the use of an isotropic gap function is justified by the expectation that gap anisotropy will be strongly suppressed by impurity scattering [22].

Figure 4 shows the $zz$ polarised Raman spectrum at 15 K. Using Eq. (2) with the frequency-dependent impurity scattering rate defined above, and convolving with a Gaussian to account for broadening effects [13, 14], the fit shown as the solid line in Fig. 4 is obtained. The agreement between the fit and spectrum is adequate. The scattering rate obtained from the fit $\Gamma_\sigma(\omega \to 0, 15 \text{K}) = 100 \text{ cm}^{-1}$ is large enough to suppress the pair-breaking peak, leaving only a threshold at $2\Delta_\sigma = 29 \text{ cm}^{-1}$, consistent with the observed spectra. The smearing Gaussian half-width was 3.5 cm$^{-1}$. We mention in passing that the $\sigma$ and $\pi$ parameters from this fit at 15 K agree reasonably well with extrapolated values from the normal state fits (including in the inset to Fig. 8 as open circles).

The $xx$ polarised spectrum may also be fitted with Eq. (2). Taking the simplest approach, decomposing the electronic continuum into $\sigma$ and $\pi$ components and using Eq. (2) to describe each, a satisfactory fit is obtained as shown in the inset to Fig. 8. The phonon was represented by a Fano lineshape and a linear term added to accommodate the weak luminescence background. Additionally, $2\Delta_\pi$ was fixed at 29 cm$^{-1}$ and the smearing Gaussian width fixed at 3.5 cm$^{-1}$ during the fits. Since contributions from the different scattering channels have been ignored, the fit results are channel-averaged. We obtain $2\Delta_\sigma \sim 100 \text{ cm}^{-1}$, $\Gamma_\sigma \sim 30 \text{ cm}^{-1}$ and $\Gamma_\pi \sim 120 \text{ cm}^{-1}$ from the $ac$-face $xx$ spectra of this and another [22] crystal. Fits to the $xx$ and $xy$ polarised spectra measured in-plane [8] give $\Gamma_\sigma \sim 20 \text{ cm}^{-1}$ and $\Gamma_\pi \sim 190 \text{ cm}^{-1}$ in both polarisations. These results strongly suggest that anisotropy in the $\sigma$ and $\pi$ impurity scattering rates, if present, is not pronounced.

Our analysis thus indicates that below $T_c$ a dirty-limit gap forms on the $\pi$ sheets and a clean-limit gap forms on the $\sigma$ sheets in MgB$_2$. Different impurity scattering rates in the $\sigma$ and $\pi$ bands have been reported in other experiments [17] and calculations [24], and our measurements of the static-limit $\Gamma_\sigma$ and $\Gamma_\pi$ agree within a factor.

![Figure 4: The $zz$ polarised Raman spectrum at 15 K. The solid line shows the result of fitting to a single gap model in the presence of impurity scattering. Inset: The $xx$ polarised Raman spectrum at 15 K, fitted with a two gap model.](image-url)
of two with those deduced from $ab$-plane and $c$-axis resistance measurements of similar crystals [8]. We note that the theoretical expectation for this two-band system is that $\sigma$-$\pi$ interband scattering will be much smaller than intraband scattering [24, 25]. Based on the presence of a single pair-breaking peak and clean-limit superconductivity in MgB$_2$, we previously noted only a single gap in $xx$ and $xy$ spectra [11]. Here we find that two gaps can be observed in the $xx$ and $xy$ polarised spectra and that the residual scattering below the $2\Delta_\sigma$ peak is due, at least in part, to an intrinsic $\pi$ band contribution with a dirty-limit gap [11]. Nonetheless, the residual scattering seen in $ab$-plane measurements varies in both strength and character between both polarisations and crystals [6], hindering a precise determination of the $\pi$ band contribution to $xx$ and $xy$ spectra.

The measurements confirm two gap model calculations [6, 7], which indicate a gap on the $\pi$ sheets with a magnitude approximately one third that of the $\sigma$ sheets. Furthermore, the gap magnitudes determined here fall within the range of values measured by other experimental techniques [8]. Neither $\Delta_\sigma$ nor $\Delta_\pi$ show evidence of strong anisotropy; the measured anisotropy is of the order of $5\,\text{cm}^{-1}$ at most [11], consistent with the idea that impurity scattering will strongly suppress gap anisotropy in MgB$_2$ [22]. Despite the satisfactory agreement between our fits and the data (Fig. 1), some discrepancies remain. It is possible that a more complex description of the continuum, which accounts for effects such as a long coherence length in the $\pi$ bands [21], interband scattering effects, and Raman vertex corrections, would resolve these discrepancies.

In conclusion, Raman scattering from the $ac$-face of thick MgB$_2$ single crystals allows Raman scattering from the $\pi$ and $\sigma$ Fermi surfaces to be discerned. In the superconducting state a sharp pair-breaking peak at just over $100\,\text{cm}^{-1}$ is seen only in $xx$ polarisation and we conclude that this feature is associated with clean-limit superconductivity on the $\sigma$ bands. In contrast, a threshold accompanied by a sharp peak appears at around $29\,\text{cm}^{-1}$ in the $zz$ and $xz$ continuum which we determine to be a strongly damped superconductivity-induced renormalization on the $\pi$ bands. The Raman spectra thus successfully distinguish two gaps in MgB$_2$, a larger gap on the $\sigma$-bands and a smaller dirty-limit gap on the $\pi$-bands, with relatively strong impurity scattering restricted to the $\pi$ band system. These observations are unusual even if we take into account the multiple-band structure of MgB$_2$. A dirty-limit gap on the $\pi$-band might arise if the dominant cause of carrier scattering is defects in the magnesium layers, affecting only the $\pi$-band electrons [24].

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