Far-infrared optical conductivity gap in superconducting MgB$_2$ films

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We report the first study of the optical conductivity of MgB$_2$ covering the range of its superconducting energy gap. Terahertz time-domain spectroscopy is utilized to determine the complex, frequency-dependent conductivity $\sigma(\omega)$ of thin films. The imaginary part reveals an inductive response due to the emergence of the superconducting condensate. The real part exhibits a strong depletion of oscillator strength near 5 meV resulting from the opening of a superconducting energy gap. The gap ratio of $2\Delta_0/k_B T_C \approx 1.9$ is well below the weak-coupling value, pointing to complex behavior in this novel superconductor.

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The recent discovery of superconductivity in MgB$_2$ at 39 K has spawned intense research efforts, yet the nature of its remarkably high transition temperature remains to be understood [1]. While the isotope effect points to phonon-mediated mechanisms [2], its anomalous magnitude [3] and distinctly different values found for the superconducting energy gap $2\Delta_0$ [4,5,6,7,8] are puzzling. First-principle bandstructure calculations indicate that the dominant hole carriers in Boron p orbitals are split into two distinct sets of bands with quasi-2D and 3D character [9]. Among phonon-mediated mechanisms which attempt to explain the high $T_C$ are anisotropic two-gap scenarios where the quasi-2D holes couple preferentially [10], strong coupling Eliashberg calculations including low and high energy modes [11], and nonadiabatic superconductivity [12].

The prospect of unconventional coupling or an anisotropic order parameter motivates experiments which probe the density of states, governed foremost by the superconducting energy gap. Surface probes such as tunneling and photoemission found very different values for the gap $2\Delta_0$ ranging from 4 - 14 meV in polycrystalline MgB$_2$ [4,6,7,8]. Possible reasons for this large variation might include proximity effects or a distribution of surface composition that remains hidden in the bulk $T_C$ [5]. The results could also originate from a multigap mechanism, and indeed recent point contact experiments found regions where two distinct conductance peaks of different magnitude appear ($2\Delta_0 = 6$ and 14 meV) [8].

Optical probes offer important advantages since they penetrate deeply inside the bulk, where they probe the low-energy excitations including the superconducting energy gap [13]. In MgB$_2$, a first measurement of far infrared reflectivity in granular samples showed an increase below $h\omega \lesssim 9$ meV [14], while the transmission through films also increases in that range [15]. While this could stem from a gap in the real part of the optical conductivity, the necessary Kramers-Kronig transformations mandate measurements over a much broader spectral range and with high precision. Thus, direct measurements of the conductivity are crucial. First results at low photon energies (0.5 - 3.7 meV), however, found no characteristic signature of a BCS gap in that range [16].

In this Letter, we present the first measurement of the far-infrared conductivity of MgB$_2$ in a broad frequency range that spans excitations across its superconducting gap. The complex conductivity $\sigma(\omega)$, measured in transmission, reveals information about the fundamental low-energy excitations. Below $T_C$ the real part of the conductivity is dominated by the depletion of oscillator strength due to the opening of a superconducting gap, while the imaginary part displays the inductive response of the condensate. The normal state scattering rate exceeds the gap energy. We find a gap size of $2\Delta_0 \approx 5$ meV, which is only half the value expected for an isotropic BCS gap.

Highly crystalline, superconducting films of MgB$_2$ were grown in a two-step process. Deposition of B precursor films via electron-beam evaporation was followed by ex-situ post-annealing at 800 °C in the presence of bulk MgB$_2$ and Mg vapor [17]. For the optical measurements, we investigate films of 100 and 200 nm thickness on Al$_2$O$_3$ substrates, with corresponding $T_C$'s (zero resistance) of 30.5 K and 34 K (inset, Fig. 1) [18]. Scanning electron microscopy shows dense films with surface roughness below 5 nm for the 100 nm film, and a grain-like morphology similar to Ref. [17] was found for the thicker film.

In our experiment terahertz time-domain spectroscopy is used to determine the complex transmission function in the spectral range of interest without the need for Kramers-Kronig transformation [19]. Femtosecond near-infrared pulses from a 250 kHz Ti:sapphire amplifier are focussed onto 0.5 mm thick (110) oriented ZnTe crystals to generate and detect far-infrared pulses. This broad-
band far-infrared radiation (2-11 meV photon energy) is transmitted through the MgB$_2$ film mounted at normal incidence in a continuous-flow He cryostat equipped with Mylar windows.

Figure 1(a) shows the measured time-dependent electric field $E(t)$ of far-infrared pulses transmitted through the MgB$_2$ film in the superconducting and normal states. Below $T_C$ (solid line), the pulse exhibits an increase of its field amplitude along with an apparent phase shift. This reshaping is linked to the changes of the frequency-dependent conductivity in the superconducting state. Fourier transformation of the incident and transmitted fields, $E_i(t)$ and $E_t(t)$, yields spectral information via the complex transmission coefficient $t(\omega) = E_t(\omega)/E_i(\omega)$. The power transmission spectrum $T(\omega) = |t(\omega)|^2$, normalized to its 40 K normal state value, is shown in Figs. 1(b) and (c) for the 100 nm and 200 nm thick samples, respectively. Above $T_C$ (solid squares), the transmission remains unchanged, but below $T_C$ a transmission increase is observed in a broad spectral range. Its peak shifts to higher photon energies with decreasing temperature. At the lowest temperature (6 K, dots), a more than twofold increase is found for photon energies around 7 meV, concurrent with a strong decrease below 4.5 meV. The response of the two samples is similar and, most notably, the spectral features occur at an identical position.

A more detailed understanding can be derived from the frequency dependent complex conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ of the film, which is obtained from the measured transmission function at normal incidence in the thin-film limit via $\sigma = ((1+n_s) t_f / t_s - n_s - 1) / (Z_0 d)$ [13]. Here, $Z_0$ is the impedance of free space, $d$ the film thickness, $n_s$ the substrate refractive index, and $t_f$ and $t_s$ the complex transmission coefficients of film + substrate, and substrate, respectively. The thin-film approximation ($n_{film}\omega d/e \ll 1$) is fulfilled well for the 100 nm film (transmission coefficient $|t(\omega)| \approx 0.1$), but the 200 nm film is optically too thick and thus was not evaluated quantitatively in this manner.

Absolute values of the normal state conductivity are shown in the inset of Fig. 2 for both the real part (circles) and imaginary part (squares). In the simplest case, the results can be compared to a single-component Drude conductivity $\sigma(\omega) = \epsilon_0 \omega_p^2 / (\tau^{-1} - i\omega)$. The parameters are constrained by fitting the real and imaginary part simultaneously (solid lines), which yields a plasma frequency $\omega_p = 12000$ cm$^{-1}$ (1.5 eV) and scattering rate $\tau^{-1} = 300$ cm$^{-1}$ (37 meV). Even for a strong coupling gap of $\approx 10$ meV this corresponds to the so-called dirty limit $h/\tau \gg 2\Delta$ in which absorption should set in for photon energies exceeding the gap energy $2\Delta$ since elastic scattering enables momentum conservation to the final state.

The ratio of the experimentally determined real part of the conductivity $\sigma_1(\omega)$ to its normal state value is plotted in Fig. 2 for different temperatures. As expected, the changes are small above $T_C$ (diamonds), yielding a ratio close to one. As the temperature falls below $T_C$ a strong depletion of $\sigma_1$ is observed: the conductivity is smallest around 4.5 meV and then increases monotonically at higher photon energies. The steepest slope is obtained at the lowest temperature (6 K, dots) revealing a strong absorption onset around $\approx 5$ meV. Results for the corresponding imaginary part of the conductivity $\sigma_2(\omega)$ are given in Fig. 3(a) [symbols]. In the superconducting state $\sigma_2(\omega)$ shows the typical shape indicative of the supercurrent’s high-frequency electromagnetic response, falling off strongly with photon energy and decreasing with temperature.

We now discuss the spectral shape and temperature dependence of the observed far-infrared conductivity. For comparison, calculations were performed using the theory of Mattis and Bardeen for an isotropic s-wave gap [20]. In view of the lower energy threshold of the observed absorption onset, an artificially small gap value of $2\Delta_0 = 5$ meV was chosen. The results of such calculations at different temperatures are shown in Fig. 2 (dashed lines) where the gap $\Delta(T)$ was assumed to follow the usual BCS temperature dependence. The calculated absorption sets in above $2\Delta_0$ and converges to the normal state conductivity at higher photon energies. In addition, a low-frequency Drude-like component due to thermally activated normal carriers gains weight with increasing temperature. We emphasize that the experimental data follow this overall trend in frequency and temperature dependence. A slower rise with photon energy is observed in the experiment, however, and some low-frequency residual conductivity remains at the lowest temperature which could also result from a slightly larger film thickness (dotted line, Fig. 2). Most strikingly, the value of the absorption onset is almost a factor of two smaller than even the value $2\Delta_0 = 3.5 k_B T_C \approx 9$ meV expected in a weak-coupling scenario.

The calculated imaginary part of the conductivity shown in Fig. 3(a) (solid line) for the lowest temperature of 6 K comes close to the experimentally observed frequency dependence. Whereas Pronin et al. found $\sigma_2(\omega) \sim \omega^{-1}$ at much lower frequencies [16], we observe here that $\sigma_2(\omega) \sim \omega^{-2}$ yields a more faithful representation of the data for larger photon energies $h\omega \geq 5$ meV. This is in agreement with the Mattis-Bardeen calculation, and is microscopically explained by the onset of dissipative excitations across the gap. The penetration depth $\lambda$ can be obtained from the optical conductivity at frequencies sufficiently below the gap, where $\lambda^{-2}(T) = \mu_0 \omega \cdot \sigma_2(\omega,T)$. We estimate $\lambda(0) \approx 3000$ Å from our data at the lowest available temperature and photon energy. Further insight is obtained from the temperature dependence of $\sigma_2$, which at low frequencies should follow the square of the penetration depth. Figure 3(b) displays the measured temperature dependent conductivity at 3 meV (dots). Within the experimental accuracy,
and in contrast to Ref. \[14\], satisfactory agreement is found with the Mattis-Bardeen calculation at the given frequency (solid line). The data thus indicate that despite the lowered gap size the penetration depth follows the BCS behaviour quite well.

One particularly intriguing result of this study is the persistently small size of the conductivity gap as compared to the transition temperature. Here, we find a ratio of only $2\Delta_0/k_BT_C = 1.9$, which is far below the usual weak or strong coupling BCS values. Our experiment shows that the dramatic transmission changes observed in this spectral range (Fig. 1b) are ultimately linked to the emergence of this conductivity gap as in conventional metals \[13\]. The identical spectral position of such transmission changes for both samples investigated here, as well as that from a different study \[15\], point to a more robust nature of this observation.

We emphasize that this reduced ratio cannot be due to a sample inhomogeneity in which percolative paths through regions with increased gap would yield the transport $T_C$, whereas the bulk fraction of the sample would become superconducting at a much lower temperature linked to the smaller gap via the usual BCS ratio. This scenario is not possible since our optically measured imaginary part of the conductivity, which probes the complete volume of the film, shows directly that the major fraction of the condensate persists up to the large transport-derived $T_C$.

Different mechanisms might explain the observed small gap. First, it is interesting to ask to what extent the two-gap scenario might apply \[10\], where our observed conductivity gap would correspond to the smaller order parameter, whereas the larger one lies outside our optically accessible range. We observe that $\sigma_1(\omega)$ rises slower with photon energy than predicted by the isotropic calculations, which might support this contention. Yet, we also note that extended strong-coupling calculations including a modified phonon spectral density allow a smaller gap ratio to emerge even in an isotropic Eliashberg formalism \[11\]. However, a calculation of the optical conductivity in these models for MgB$_2$ has not been carried out so far.

Anderson’s theory of superconductors in the dirty-limit shows that for an isotropic order parameter neither the gap size nor $T_C$ are affected by the nonmagnetic impurity scattering events that prevail in our films \[21\-22\]. Nevertheless, a more general anisotropic gap could be averaged out in this case, evoking a gap ratio that approaches the usual weak or strong coupling values. However, the two-gap state should persist for predominantly intra-band nonmagnetic scattering \[23\], e.g. for small-angle impurity scattering which lacks the momentum to scatter holes between the quasi-2D and 3D Fermi surfaces well separated in momentum space. Comprehensive theoretical calculations of the optical and other fundamental physical properties are imperative to achieve a full understanding of the low-energy excitations in MgB$_2$.

In summary, we have studied the far-infrared conductivity of thin MgB$_2$ films using terahertz time-domain spectroscopy in a broad spectral range. The complex conductivity exhibits the characteristic electrodynamic response of a dirty-limit metal in the normal state. An inductive response in the imaginary part appears below $T_C$ due to the emergence of the superconducting condensate. A strong depletion of the real part of the conductivity corresponds to the opening of the superconducting gap, yet its energy threshold $2\Delta \approx 5$ meV is only half that expected in an isotropic, weak-coupling theory.

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FIG. 1. (a) Electric field transients transmitted through the 100 nm MgB$_2$ film at $T = 6$ K (solid line) and 40 K (dashed line). Inset: resistance of the 200 nm (dots) and 100 nm film (open squares) corresponding to $\rho(40$ K $) \approx 10$ and 100 $\mu\Omega$cm, respectively. (b) Transmission $T$ normalized to $T(40$ K $)$ as obtained from the transients for the 100 nm thick film at $T = 6$ K (dots), 20 K (open circles), 27 K (solid diamonds), 30 K (open diamonds), and 33 K (solid squares). (c) results for the 200 nm thick film at $T = 6$ K (dots), 20 K (open circles), 25 K (solid diamonds), 30 K (open diamonds), and 36 K (solid squares).

FIG. 2. Real part of conductivity $\sigma_1(\omega)$ for the 100 nm film normalized to its normal state value $\sigma_{1N}(40$ K $)$ for $T = 6$ K (dots), 17.5 K (open circles), 24 K (solid squares), 27 K (open squares), 30 K (solid diamonds), 50 K (open diamonds). Mattis-Bardeen calculations for $2\Delta_0 = 5$ meV, $T_C = 30$ K are shown for (dashed and dotted lines, bottom to top) 6 K, 12 K, 17.5 K, 24 K, and 27 K. Inset: real (circles) and imaginary part (squares) of normal state conductivity along with a Drude calculation (lines) explained in the text.
FIG. 3. (a) Imaginary part of the conductivity, $\sigma_2(\omega)$, normalized to the normal state value $\sigma_{1N}$ at $T = 40$ K. Results are shown for $T = 6$ K (solid squares), 17.5 K (open squares), 24 K (dots), 27 K (open circles), 30 K (solid triangles), 33 K (open triangles). Solid line: Mattis-Bardeen calculation for $T = 6$ K (parameters see Fig. 2). (b) Normalized temperature dependence of $\sigma_2(3$ meV) [solid circles], compared to the Mattis-Bardeen result at this frequency (solid line) and the BCS penetration depth (dashed line).