Far-infrared transmission studies of c-axis oriented superconducting MgB$_2$ thin film

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We reported far-infrared transmission measurements on a c-axis oriented superconducting MgB$_2$ thin film in the frequency range of 30 $\sim$ 250 cm$^{-1}$. We found that these measurements were sensitive to values of scattering rate $1/\tau$ and superconducting gap $2\Delta$. By fitting the experimental transmission spectra at 40 K and below, we obtained $1/\tau = (700 \sim 1000)$ cm$^{-1}$ and $2\Delta(0) \approx 42$ cm$^{-1}$. These two quantities suggested that MgB$_2$ belong to the dirty limit.

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The surprising discovery of superconductivity in a known compound MgB$_2$ with a high $T_C$ of about 39 K has attracted lots of attention from solid state community and initiated a flurry of activities to understand its properties [1]. Most investigations on this binary compound yet indicate that MgB$_2$ behave as a phonon mediated superconductor [2]. However, there are still little consensus on its important physical quantities related to electrodynamic and superconducting responses. Near $T_C$, reported values of dc resistivity $\rho_{dc}$ are in the range from 0.38 [3] to 75 $\mu\Omega$cm [4], and those of carrier density $n$ vary from 6.7$\times$10$^{22}$ [4] to 1.5$\times$10$^{23}$/cm$^3$ [5]. Moreover, reported values of superconducting gap $2\Delta$ also vary from 3 [4] to 16 meV [6]. Since such physical quantities are closely related to the nature of the superconducting film, correct determination of their values cannot be over-emphasized.

It is well known that optical spectroscopy is a powerful method to measure such important parameters as scattering rate $1/\tau$, plasma frequency, $2\Delta$, and coherence effects [7]. Since the skin depth of light is about 1000 Å in the far-infrared (IR) region, this technique is able to provide information on $2\Delta$ complementary to other surface sensitive techniques, such as tunneling and photoemission measurements. However, there have been a few reports on the optical properties of MgB$_2$. Gorshunov et al. [6] measured grazing incident reflectivity of a polycrystalline pellet, and provided a lower estimate of $2\Delta$ to be 3 $\sim$ 4 meV. On the other hand, Pronin et al. [6] measured complex optical conductivity using a MgB$_2$ thin film in the frequency range of 4 $\sim$ 30 cm$^{-1}$. For MgB$_2$, its far-IR bulk reflectivity is very close to 1.0 due to the small value of $\rho_{dc}$, so the commonly used Kramers-Kronig analysis on the reflectivity is difficult to use and will result in large errors. A transmission measurement using a superconducting film is a superior method, since it is much more sensitive to small changes in optical constants. However, the measurements by Pronin et al. were limited below 30 cm$^{-1}$, so characteristic features of the gap temperature evolution could not be observed.

In this Letter, we investigated electrodynamics of a c-axis oriented MgB$_2$ thin film ($T_C$ $\sim$ 33 K) using transmission measurements in the frequency range of 30 $\sim$ 250 cm$^{-1}$. We found that the transmission spectra $T(\omega)$ were sensitive to changes in sheet resistance $R_s$ and $1/\tau$ of the ab-plane. Using the simple Drude model, we estimated $R_s = 10.3 \pm 0.2$ $\Omega$/d and $1/\tau = 700 \sim 1000$ cm$^{-1}$ at 40 K. Below $T_C$, a peak due to $2\Delta$ appeared and moved to a higher frequency with decreasing temperature. The ab-plane $2\Delta(T)$ seemed to follow the temperature dependence of the BCS theory and was estimated to be about 42 cm$^{-1}$ (5.2 meV) at 5 K. Comparing the values of $2\Delta(0)$ and $1/\tau$, we suggested that MgB$_2$ should belong to the dirty limit.

A high quality c-axis oriented MgB$_2$ film was deposited on a Al$_2$O$_3$ substrate using a pulsed laser deposition technique, as already reported elsewhere [9]. X-ray diffraction measurement showed that most of grains were oriented with their c-axes normal to the substrate. Using the four-probe method, its dc resistance was measured and showed a rather sharp $T_C$ near 33 K [11]. Temperature dependent $T(\omega)$ were measured with a resolution of 5 cm$^{-1}$ for the frequency range of 30 $\sim$ 250 cm$^{-1}$ using a Fourier transform spectrophotometer.

In the thin-film geometry, an approximate form of $T(\omega)$ is well known for $\lambda \gg \lambda_p \gg d$, where $\lambda$ is the wavelength of light, $\lambda_p$ is the skin depth, and $d$ is the film thickness. Taking into account of multiple reflections inside the substrate, $T(\omega)$ can be approximated as

$$ T(\omega) = \frac{4n}{|1 + \tilde{N} + y|} \times \frac{T_s \exp(-\alpha x)}{1 - R_s R_f \exp(-2\alpha x)}, $$

where $\tilde{N} = (n + ik)$, $\alpha = 4\pi\omega\kappa$, and $x$ are complex refractive index, absorption coefficient, and thickness of the substrate, respectively. $T_s = 4n/|1 + \tilde{N}|^2$ and $R_s = |1 - \tilde{N}^2/|1 + \tilde{N}|^2$ are transmission and reflec-
tivity of the substrate-vacuum boundary, and \( R_f = |\tilde{N} - 1 + \tilde{y}|^2 / |\tilde{N} + 1 + \tilde{y}|^2 \) is reflectivity of the substrate-film boundary with \( \tilde{y} = 4\pi \tilde{\sigma}_0 / c \), where \( \tilde{\sigma}_0 = \sigma_1 + i\sigma_2 \) is complex sheet conductance of the film. Using transmission and reflectivity spectra of \( \text{Al}_2\text{O}_3 \), we could obtain \( \tilde{N} \) values independently and used these to calculate the theoretical \( T(\omega) \).

Fig. 1. \( T(\omega)/T_{\text{Sub}}(\omega) \) at normal state. (a), the dashed, the solid, and the dotted lines represent fitting lines for \( R_\| = 10.8, 10.3, \) and \( 9.6 \, \Omega/\square \), respectively. And in (b), the dashed, the solid, and the dotted lines represent fitting lines for \( 1/\tau = 400, 800, \) and \( 4000 \, \text{cm}^{-1} \), respectively.

Far-IR transmission measurements can determine \( R_\| \) and \( 1/\tau \) of the film quite exactly. Figures 1(a) and 1(b) show the ratio of transmission spectra between the MgB\(_2\) film and the \( \text{Al}_2\text{O}_3 \) substrate, i.e., \( T(\omega)/T_{\text{Sub}}(\omega) \) at 40 K. To understand effects of \( R_\| \), we calculated \( T(\omega)/T_{\text{Sub}}(\omega) \) using Eq. (1) with the simple Drude model. Figure 1(a) shows variations of \( T(\omega)/T_{\text{Sub}}(\omega) \) with changing \( R_\| \) when the value of \( 1/\tau \) is fixed to be 800 cm\(^{-1} \): the dashed, the solid, and the dotted lines represent the calculated \( T(\omega)/T_{\text{Sub}}(\omega) \) at \( R_\| = 10.8, 10.3, \) and \( 9.6 \, \Omega/\square \), respectively. It is clear that \( T(\omega)/T_{\text{Sub}}(\omega) \) are quite sensitive to \( R_\| \). It was found that \( R_\| \) of our film was 10.3\( \pm 0.2 \) \( \Omega/\square \) at 40 K.

The frequency dependence of \( T(\omega) \) should be dependent on \( 1/\tau \). At 40 K, \( T(\omega)/T_{\text{Sub}}(\omega) \) gradually increase as frequency increases, due to the finite value of \( 1/\tau \). Figure 1(b) shows variations of \( T(\omega)/T_{\text{Sub}}(\omega) \) with changing \( 1/\tau \) when the value of \( R_\| \) is fixed to be 10.3 \( \Omega/\square \): the dashed, the solid, and the dotted lines represent the calculated \( T(\omega)/T_{\text{Sub}}(\omega) \) at \( 1/\tau = 400, 800, \) and \( 4000 \, \text{cm}^{-1} \), respectively. It was found that \( 1/\tau \) of our film was \( 800^{+200}_{-100} \, \text{cm}^{-1} \).

![Figure 1](image1.png)

FIG. 1. \( T(\omega)/T_{\text{Sub}}(\omega) \) at normal state. (a), the dashed, the solid, and the dotted lines represent fitting lines for \( R_\| = 10.8, 10.3, \) and \( 9.6 \, \Omega/\square \), respectively. And in (b), the dashed, the solid, and the dotted lines represent fitting lines for \( 1/\tau = 400, 800, \) and \( 4000 \, \text{cm}^{-1} \), respectively.

![Figure 2](image2.png)

FIG. 2. Experimental and theoretical results of \( T(\omega) \) at superconducting states. In the inset, the open circles and the open triangles represent \( \omega_P \) obtained from the experimental and the theoretical data, respectively. For comparison, \( 2\Delta(T) \) is also shown as a solid line.

Figure 2 shows the temperature dependent \( T(\omega) \) of the MgB\(_2\) film in its superconducting state, i.e., at temperatures below 33 K. Note that there is little temperature dependence of \( \tilde{N} \) below 40 K, so \( T_{\text{Sub}}(\omega) \) are nearly flat and independent of temperature. In its superconducting state, \( T(\omega) \) show a peak-like structure near 50 cm\(^{-1} \). As frequency increases, \( T(\omega) \) at 5 K gradually increase up to around 52 cm\(^{-1} \) and then approach to those at the normal state. As temperature increases, the peak height gradually decreases and the peak position \( \omega_P \) gradually moves to lower frequencies.

Similar peak structures have been observed for numerous superconducting thin films, and their \( 2\Delta \) values have been found to be close to \( \omega_P \). Such a peak structure can be understood from the complex optical conductivity spectra \( \tilde{\sigma}(\omega) \). In the normal state, \( \sigma_1(\omega) \) at \( \omega < 1/\tau \) become nearly frequency independent. In the superconducting state, \( \sigma_1(\omega) \) below \( 2\Delta \) become suppressed and the missing spectral weight moves to the zero frequency to form a delta function, representing a superconducting condensate. Due to the delta function, \( \sigma_2(\omega) \) will have a \( 1/\omega \) dependence. For \( \omega \ll 2\Delta \), \( T(\omega) \propto \omega^2 \), which can be easily seen in Eq. (1). On the other hand, for \( \omega \gg 2\Delta \), \( T(\omega) \) in the superconducting state should be almost the same as those in the normal state. Near \( 2\Delta \), \( \sigma_1(\omega) \) are nearly zero and \( \sigma_2(\omega) \) drastically decrease, resulting in a minimum value of the denominator in Eq. (1). So, there is a peak in transmission.

One of important physical quantities in a superconductor is the ratio between \( 1/\tau \) and \( 2\Delta(0) \), which will determine electrodynamic responses. For most metal
superconductors, such as Al and Pb, \((1/\tau)/2\Delta(0) \gtrsim 100\). For such BCS superconductors in the extremely dirty limit, their optical responses can be explained by the Mattis-Bardeen theory [1, 17]. However, in high temperature superconductors, their \(2\Delta(0)\) values are much larger than those of metal superconductors, and they are believed to belong to the clean limit, where \((1/\tau)/2\Delta(0) \sim 1\) [17]. Optical properties of superconductors in the clean limit are different from those in the dirty limit: for example, \(\sigma^1_\omega/\sigma^2_\omega\) in the clean limit has a steeper rise near \(2\Delta\) [13], where \(\sigma^1_\omega\) and \(\sigma^2_\omega\) represent \(\sigma_\omega\) at superconducting and normal states, respectively. Zimmerman et al. calculated optical conductivity of a homogeneous BCS superconductor with arbitrary purity [17].

In order to explain the temperature dependent \(T(\omega)\), we applied the formula developed by Zimmerman et al. [17] with the measured values of \(1/\tau\) and \(R_0\) at 40 K, i.e., 800 cm\(^{-1}\) and 10.3 \(\Omega\)/\(\Omega\), respectively. As shown in Fig. 2, \(\omega_p\) of the 5 K data could be fitted quite well with \(2\Delta(0) \cong 42\) cm\(^{-1}\). Note that the \(2\Delta(0)\) value is smaller than the \(\omega_p\) value by about 10 cm\(^{-1}\). Assuming that the temperature dependence of \(2\Delta(T)\) follow the BCS prediction, we calculated \(T(\omega)\). The solid circles (solid line), the solid triangles (dashed line), the solid stars (dot-dashed line), and solid squares (dotted line) represent the experimental (calculated) \(T(\omega)\) at 5, 13, 23, and 33 K, respectively. The predicted temperature dependences of \(\omega_p\) and \(2\Delta(T)\) are shown in the inset as the open triangles and the solid line, respectively. Within the experimental error bars, \(2\Delta(T)\) seems to follow the prediction of the BCS theory quite well.

Although many experimental studies have been performed on the \(2\Delta(0)\) value of MgB\(_2\), there is little consensus on its magnitude and symmetry. In specific heat measurements, a couple of groups reported that \(2\Delta(0)/k_BT_C \sim 2.4\) [18] or 4.2 [19], both of which were explained in terms of the conventional \(s\)-wave type BCS model. Using the same technique, Wang et al. [20] reported that the values of \(2\Delta(0)/k_BT_C\) were varied form 1.2 to 4.2 and suggested a \(d\)-wave superconductor with nodes in the gap. In photoemission measurements, Takahashi et al. [21] found that the superconducting gap was \(s\)-like with \(2\Delta(0)/k_BT_C \sim 3.0\), but Tsuda et al. [22] reported a spectroscopic evidence for two gaps with \(2\Delta(0)\) = 3.4 and 11.2 meV. More seriously, in tunneling experiments, the values of \(2\Delta(0)\) were varied from 4 to 16 meV, and both isotropic and anisotropic gap symmetries were suggested [23]. To explain the large variations of \(2\Delta(0)\) values, Hass and Maki [24] recently proposed a model of anisotropic \(s\)-wave superconductivity.

Our measured value of \(2\Delta(0)\), i.e., about 42 cm\(^{-1}\) (5.2 meV) is quite smaller than the BCS prediction for the isotropic \(s\)-wave superconductor. Since our \(c\)-axis oriented film has \(T_C \sim 33\) K, \(2\Delta(0)/k_BT_C\) can be evaluated to be about 1.8. There are at least three possibilities to explain the small value of \(2\Delta(0)/k_BT_C\). The first possibility is an existence of dead layers at the film surface and the film/substrate interface. We found that the reflectivity spectra in the visible region for numerous thick films varied from film to film, indicating possible existence of dead layers. Since our film used in this transmission study is only 500±70 A thick [25], effects of the dead layers could be important. However, the temperature dependent changes in \(T(\omega)\) are quite large and agree well with the predictions of the BCS theory, so the dead layer effect cannot be very large. And the dead layer effect will be less effective for transmission measurements than reflectivity measurements. The second possibility is inhomogeneities of our films, especially in \(T_C\) and/or \(2\Delta(0)\). However, our \(T(\omega)\) could not be explained by introducing a distribution of \(2\Delta(0)\) at a higher frequency region in our calculation. The last possibility is the anisotropic gap symmetry. Since our measurements were made on the \(c\)-axis oriented film, our \(2\Delta(0)/k_BT_C\) value represents the \(ab\)-plane property. The anisotropic \(s\)-wave superconductivity, suggested by Hass and Maki [24], is consistent with the small \(ab\)-plane value of \(2\Delta(0)\). In order to prove this gap symmetry, it would be useful to perform polarization dependent optical measurements on a single crystal or an epitaxial film with its \(c\)-axis parallel to a substrate.

![FIG. 3. Calculated \(T(\omega)\) at 5 K with changing \(1/\tau\). The solid circles represent the experimental data. The dot-dashed, the dashed, the solid, and the dotted lines represent \(T(\omega)\) at \(1/\tau = 42, 100, 800,\) and \(\infty\) cm\(^{-1}\), respectively.](image-url)
of $1/\tau \simeq 42$ cm$^{-1}$. However, our experimental data in the normal state as well as the superconducting states showed that $1/\tau \approx 800$ cm$^{-1}$ \cite{27}. We calculated $T(\omega)$ at 5 K with various values of $1/\tau$, shown in Fig. 3. Note that the calculated $T(\omega)$ with $1/\tau \approx 42$ cm$^{-1}$ predict a very sharp peak structure near $2\Delta(0)$ and a steep increase of $T(\omega)$ at the high frequency region, which do not agree with our experimental observations. Our experimental $T(\omega)$ seem to be quite close to predictions of the Mattis-Bardeen theory in the extremely dirty limit, i.e., $1/\tau = \infty$ cm$^{-1}$. Although the Mattis-Bardeen theory is slightly better to explain the 5 K data than the Zimmerman’s formula with $1/\tau = 800$ cm$^{-1}$, the temperature dependence of the peak can be explained better by the latter method. Moreover, our 40 K transmission data suggested that $1/\tau \approx 800$ cm$^{-1}$.

In literature, there is a large variation of $\rho_{dc}$ value. Our measured value of $1/\tau \approx 800$ cm$^{-1}$ provides a certain limitation to electrodynamic quantities. Using the reported values of $v_p = 4.8 \times 10^7$ cm/s and $n = 6.7 \times 10^{22}$ /cm$^3$ \cite{28}, we estimated values of $I$ and $\rho_{dc}$ were 32 Å and 24 $\mu$Ωcm, respectively. Note that, the estimated value of $I$ is somewhat smaller than $\xi_0 \approx 52$ Å and that of $\rho_{dc}$ is much larger than 0.38 $\mu$Ωcm reported for MgB$_2$ wire \cite{29}. It is clear that more investigations are necessary to determine even simple physical quantities, such as $\rho_{dc}$.

In summary, we investigated the c-axis oriented superconducting MgB$_2$ thin film using transmission measurements. By fitting transmission spectra at normal and superconducting states, we found that the scattering rate was (700 $\sim$ 1000) cm$^{-1}$ at 40 K and zero temperature superconducting gap was about 42 cm$^{-1}$. These electrodynamics quantities suggested that MgB$_2$ should belong to the dirty limit.

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[28] If we used the values of $\rho_{dc}$ = 0.38 $\mu$Ωcm, we found that $d$ should be less than 4 Å to fit the experimental $T(\omega)$. 

