Optical studies of charge dynamics in c-axis oriented superconducting MgB$_2$ films

J.J. Tu,$^1$ G.L. Carr,$^2$ V. Perebeinos,$^1$ C.C. Homes,$^1$ M. Strongin,$^1$ P.B. Allen,$^3$ W.N. Kang,$^4$ Eun-Mi Choi,$^4$
Hyeong-Jin Kim,$^4$ and Sung-Ik Lee$^4$

$^1$Department of Physics, Brookhaven National Laboratory, Upton, New York 11973-5000
$^2$NSLS, Brookhaven National Laboratory, Upton, New York 11973-5000
$^3$Department of Physics and Astronomy, SUNY Stony Brook, Stony Brook NY 11794-3800
$^4$National Creative Research Initiative Center for Superconductivity, Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea

(Received November 11, 2018)

Temperature dependent optical conductivities and DC resistivity of c-axis oriented superconducting (T$_c$ = 39.6 K) MgB$_2$ films (~ 450 nm) have been measured. The normal state $ab$-plane optical conductivities can be described by the Drude model with a temperature independent Drude plasma frequency of $\omega_{p,D} = 13600 \pm 100 \text{ cm}^{-1}$ or $1.68 \pm 0.01 \text{ eV}$. The normal state resistivity is fitted by the Bloch-Grüneisen formula with an electron-phonon coupling constant $\lambda_{tr} = 0.13 \pm 0.02$. The optical conductivity spectra below T$_c$ of these films suggest that MgB$_2$ is a multi-gap superconductor.

PACS: 74.25.Gz, 74.76.Db, 74.25.Kc

The recent discovery of superconductivity in MgB$_2$ with T$_c$ of 39 K has generated much scientific interest [1]. As in the case of the high-T$_c$ cuprates, debate rages as to the mechanism of superconductivity in this material. Initial isotope effect measurements suggested electron-phonon coupling as the pairing mechanism for superconductivity in MgB$_2$ [2,3]. Many theoretical studies [4–7] have also been proposed, e.g. ‘dressing’ and ‘undressing’ of holes [8], acoustic plasmons [9] and the ‘filamentary’ theory [10]. This inconclusive state of affairs is mainly due to the lack of consensus on many important physical quantities in MgB$_2$. For example, the reported values for the superconducting gap 2$\Delta$ vary from 4 meV [11] to 15 meV [12]. Infrared spectroscopy is able to measure such quantities as the scattering rate $1/\tau$, the Drude plasma frequency $\omega_{p,D}$ and 2$\Delta$ [13]. In this work, we analyze the optical data of MgB$_2$ to determine the electron-phonon coupling constant, $\lambda_{tr}$, in a similar fashion as in the optical study [4] of Ba$_{0.5}$K$_{0.5}$BiO$_3$ (T$_c$ ~ 30 K), where $\lambda_{tr}$ ~ 0.2 was obtained experimentally.

There have been very few optical studies on MgB$_2$ to date. Gorshunov et al. [3] measured the reflectance of a polycrystalline pellet using the grazing angle method and set a lower limit of 2$\Delta$ to be 3 ~ 4 meV. Pronin et al. [11] examined the complex optical conductivity of a MgB$_2$ thin film in the frequency range of 0.5 ~ 4 meV. More recently, Jung et al. [14] carried out transmission measurements on a c-axis oriented MgB$_2$ film (~ 50 nm) with T$_c$ ~ 33 K and fitted the data with a gap value of 2$\Delta$(0) ~ 5.2 meV. However, to obtain the optical constants of bulk MgB$_2$ in a wide frequency region, reflectivity measurements are the preferred method.

In this Letter, temperature dependent optical conductivities and DC resistivity of c-axis oriented superconducting (T$_c$ = 39.6 K) MgB$_2$ films (~ 450 nm) are reported. The normal state $ab$-plane optical conductivities can be well described by the Drude model with $\omega_{p,D} = 13600 \pm 100 \text{ cm}^{-1}$. Using this plasma frequency $\lambda_{tr} = 0.13 \pm 0.02$ is determined by fitting the DC resistivity data. In addition, the optical conductivities in the superconducting state exhibit complex behavior suggesting that MgB$_2$ is a multi-gap superconductor.

For this study, several c-axis oriented MgB$_2$ films are used: one very thin film (~ 50 nm) similar to the film studied by Jung et al. [14] and two thicker films (~ 450 nm). These high-quality c-axis oriented films were deposited on c-cut Al$_2$O$_3$ substrates using a pulsed laser deposition method as described previously [18]. X-ray measurements showed that the MgB$_2$ grains were highly oriented with their c-axes normal to the substrate. These MgB$_2$ films have a tan appearance, similar to the high purity MgB$_2$ polycrystalline samples [18]. The thick MgB$_2$ films (~ 450 nm) are opaque in the visible region.

The Al$_2$O$_3$ substrates with the MgB$_2$ films are mounted on an optically-black cone, and the temperature dependent reflectance is measured in a near-normal-incidence arrangement from ~ 30 to over 22 000 cm$^{-1}$, with the electric field parallel to the ab-plane on Bruker IFS 66v/S and 113v spectrometers. The absolute reflectance is determined by evaporating a gold film in situ in ultra-high vacuum (~ 10$^{-8}$ Torr). The details of this technique have been described previously [19].

In Fig. 1(a), the temperature dependent DC sheet resistance, R$_{ab}$, measured by a standard four-probe technique of a MgB$_2$ film (~ 450 nm) is shown. The residual resistance ratio (RRR) of R$_{ab}$ at 295 K and at 40 K is 2.2. The low temperature region near T$_c$ is given in the insert of Fig. 1(a). The superconducting transition in this film is extremely sharp with a transition region of $\delta T_c < 0.1$ K and a T$_c$ of 39.6 K indicating that these...
thick MgB$_2$ films are of excellent quality [18].

The raw data of the optical measurements on these MgB$_2$ films ($\sim$ 450 nm) are summarized in Fig. 2. The absolute reflectance is quite high as shown in Fig. 2(a), however, several sharp phonon features can be clearly identified. As a comparison, the reflectance of the thin MgB$_2$ film ($\sim$ 50 nm) is also measured. The two strong infrared active TO-phonons of $c$-cut Al$_2$O$_3$ crystals at 440 and 570 cm$^{-1}$ [20] can be easily observed for the thin MgB$_2$ film but completely absent in the reflectance data of the thick films ($\sim$ 450 nm), indicating that the thick films are totally opaque. Therefore, the $ab$-plane optical properties measured for these MgB$_2$ films ($\sim$ 450 nm) are intrinsic. In the insert, the reflectance data at 295 K is given for the entire frequency region: from 30 to 22 000 cm$^{-1}$. The largest possible frequency interval is needed to carry out a reliable Kramers-Kronig analysis. The results of such an analysis are shown as temperature dependent $\sigma_1(\omega)$ in Fig. 2(b) and $\sigma_2(\omega)$ in Fig. 2(c). Superconducting behavior can be easily identified as a drop in $\sigma_1(\omega)$ at low frequencies below $T_c$.

The normal state optical conductivities of these MgB$_2$ films are analyzed in Fig. 3. In Fig. 3(a), $\sigma_1(\omega)$ and $\sigma_2(\omega)$ at 295 K are shown. Both the real and imaginary parts of the optical conductivities at low frequencies can be well described by the simple Drude model of the form:

$$\sigma(\omega) = \sigma_1 + i\sigma_2 = \frac{\omega_p D}{4\pi} \frac{\omega^2 + \omega^2_D \tau}{1 + \omega^2 \tau}, \quad \omega_p^2 = \frac{4\pi n e^2}{m^*}$$

where $\omega_p D$ is the Drude plasma frequency, $1/\tau$ is the scattering rate, $n$ is the number of free-carriers per unit volume and $m^*$ is the average effective mass of the occupied carrier states. The Drude model describes the experimental data surprisingly well at 295 K. The fitting parameters have the values $\omega_p D = 13 600 \pm 100$ cm$^{-1}$, and $1/\tau = 170 \pm 5$ cm$^{-1}$. This Drude plasma frequency of 13 600 cm$^{-1}$ is quite consistent with the value obtained from an optical study of a polycrystalline MgB$_2$ sample [21]. However, in addition to the Drude peak, some other contributions to $\sigma_1(\omega)$ are also observed in that optical study [21]. Using the optical data, one can determine the DC resistivity $\rho = 1/\sigma_0$ to be $53 \pm 2 \mu\Omega$-cm at 295 K. Thus, the averaged thickness of this MgB$_2$ film is derived as $t = \rho / \sigma_0 = 450 \pm 20$ nm which agrees very well with the typical thickness of 400 nm of these films [18]. The DC resistivity can now be plotted as shown in Fig. 1(b). It is interesting that the experimental Drude plasma frequency of 1.68 eV is much smaller than the value of $\sim$ 7 eV predicted by calculations of the electronic structure in MgB$_2$ [12]. These calculations usually give values of Drude plasma frequencies that are reasonably close to experimental values, even in highly correlated systems like high $T_c$ cuprates [22].

Keeping $\omega_{p,D}$ the same, the optical conductivities at 45 K are fitted with Eq. (1). The results are given in Fig. 3(b). Both $\sigma_1(\omega)$ and $\sigma_2(\omega)$ again fit well with the Drude model with a scattering rate of $1/\tau = 75 \pm 5$ cm$^{-1}$. In addition, the DC resistivity at 45 K is in good agreement with the zero frequency extrapolation of $\sigma_1(\omega)$. Therefore, the DC conductivity and real part the optical
conductivity are in excellent agreement.

From the $ab$-plane optical data, one can calculate the frequency dependent electron-phonon coupling constant $\lambda(\omega)$ in the extended Drude formalism:

$$
\frac{m^*_{eff}(\omega)}{m^*} = 1 + \lambda(\omega) = \frac{1}{4\pi} \frac{\omega_p^2}{\omega} \frac{1}{\sigma(\omega)} \Im \left[ \frac{1}{\sigma(\omega)} \right], \quad (2)
$$

where $\omega_p$ is the total plasma frequency of free $ab$-plane carriers. The purpose of casting the optical data in the extended Drude form is to account for the small deviations from the simple Drude model by using a frequency dependent scattering rate $1/\tau(\omega)$. The result of this analysis is shown in Fig. 3(c). The value of $\lambda(\omega)$ derived optically varies from 0 to about 0.2 in the optical phonon region, where $\omega_p = 14750 \pm 150$ cm$^{-1}$ is derived from the conductivity sum rule. The value of $\omega_p$ is slightly larger than $\omega_{p,D}$ due to the fact that the sum rule captures additional spectral weight in the high frequency region.

The electron-phonon coupling constant $\lambda_{tr}$ is traditionally determined from the temperature dependent DC resistivity using the Bloch-Grüneisen formula

$$
\rho(T) = \rho_0 + \lambda_{tr} \frac{4\pi}{3\omega_{p,D}^2} \frac{128\pi(k_BT)^5}{(k_B\Theta_D)^3} \int_0^{\frac{\Theta_D}{k_B}} \frac{x^5}{\sin^2 x} dx, \quad (3)
$$

with three parameters: $\rho_0$ - the residual resistivity at $T = 0$; $\Theta_D$ - the Debye temperature and $\lambda_{tr}$. A nonlinear least squares fit to the resistivity data with the

Eq. (3) is given in Fig. 1(b) using $\omega_{p,D} = 1.68 \pm 0.01$ eV. The experimental curve and the theoretical fit agree quite well with the fitting parameters: $\rho_0 = 24.3 \pm 0.3 \mu\Omega \cdot $cm; $\Theta_D = 950 \pm 100$ K and $\lambda_{tr} = 0.13 \pm 0.02$. The value $\Theta_D = 950 \pm 100$ K is consistent with the experimentally measured value that varies from 800 K [24] to 1050 K [25]. However, $\lambda_{tr} = 0.13 \pm 0.02$ is significantly smaller than most theoretical predictions of $\lambda \sim 1$ [4] in MgB$_2$.

The optical conductivities of these MgB$_2$ films in the superconducting state are examined in Fig. 4. The superfluid plasma frequency is found to be $\omega_{p,S} = 7300 \pm 50$ cm$^{-1}$ at 6 K from the Ferrel-Glover-Tinkham sum rule. However, the optical spectra below $T_c$ cannot be fitted by the BCS model using a single isotropic gap. Theoretical curves at 30 K and 6 K generated with a BCS model [26] are shown in Figs. 4(a) and 4(b). The parameters used are: $2\Delta = 65$ cm$^{-1}$ and $1/\tau = 75$ cm$^{-1}$. There are significant deviations between the experimental data and the BCS calculations. However, from our optical data the upper and lower limits of the superconducting gap can be estimated: $5$ meV $< 2\Delta_x < 15$ meV. The complex gap behavior observed in our optical conductivity data in the superconducting state adds support to the suggestion that MgB$_2$ is a multi-gap superconductor [8,22,23].

Four sharp phonon peaks can be identified in $\sigma_1(\omega)$ as shown in Fig. 4(c) that can be assigned to $\Gamma$-point optical phonons in MgB$_2$ [4]. The two strong phonon...
peaks marked as A and B are the two infrared active lattice modes: at 380 cm$^{-1}$ ($E_{1u}$) and at 480 cm$^{-1}$ ($A_{2u}$). Their relatively large oscillator strengths are the consequence of the low plasma frequency in MgB$_2$. Two weak phonon peaks marked as C and D at 510 cm$^{-1}$ and 630 cm$^{-1}$ are tentatively assigned as the Raman active $E_{2g}$ mode and the silent $B_{1g}$ mode according to the phonon calculations [1]. These two phonons with even symmetry become infrared active because of the lattice imperfections in the films. Alternatively, several Raman studies [27] on MgB$_2$ have assigned a very broad band centered at 620 cm$^{-1}$ as the $E_{2g}$ mode. In addition, three broad features are also observed at 160, 880 and 1240 cm$^{-1}$ in $\sigma_1(\omega)$. The resolution of this optical study is 4 cm$^{-1}$ in the phonon region, and none of the four sharp phonon modes exhibit detectable changes in either their intensities, peak positions, or line-widths going through $T_c$.

The surprising aspect of our results is the small value of $\lambda_{tr} = 0.13$ derived from both the DC resistivity and optical conductivity measurements. A simple application of McMillan formula [28] with $\lambda \approx \lambda_{tr} = 0.13$ will give $T_c < 1$ K. However, there are several reasons why the BCS theory should not be abandoned right way for MgB$_2$: 1) the superconducting gap in MgB$_2$ has unusual properties. Gap anisotropy including dimensional effects [29] modifies $T_c$ relative to the McMillan formula; 2) the $\lambda$ value that goes into the McMillan formula can differ somewhat with respect to $\lambda_{tr}$ [30]; 3) c-axis optical and transport properties should be experimentally studied. On the other hand, given the small value of $\lambda_{tr} = 0.13$ alternative mechanisms of superconductivity in MgB$_2$ should be examined both experimentally and theoretically. It is interesting to note that many of the optical constants in MgB$_2$ are quite similar to those in Ba$_{0.6}$K$_{0.4}$BiO$_3$ [3], e.g. the scattering rate, the Drude plasma frequency, and particularly the small value of $\lambda_{tr}$. A common mechanism might be responsible for superconductivity in both systems. In addition, having a small free-carrier plasma frequency ($< 3$ eV) seems to be an universal characteristic shared by almost all superconductors with a $T_c > 30$ K.

In conclusion, we have measured optical conductivities and DC resistivity of c-axis oriented superconducting MgB$_2$ films. With a Drude plasma frequency of $\omega_{p,D} = 13,600 \pm 1$00 cm$^{-1}$, $\lambda_{tr} = 0.13 \pm 0.02$ is determined from DC resistivity data. The small measured $\lambda_{tr}$ value poses a serious problem to the strong electron-phonon coupling picture. Other theoretical models need to be explored to account both for the complex behavior of the superconducting gap and possible different pairing mechanism in MgB$_2$.

We thank P.C. Canfield, V.J. Emery, J.E.Hirsch, P.D. Johnson, S.A. Kivelson, G. Schneider, T. Valla, T. Vogt, and Z. Yusof for helpful discussions. Part of the work was supported by the U.S. Department of Energy under Contract No. DE-AC02-98CH10886 and the other part by the Ministry of Science and Technology of Korea through the Creative Research Initiative Program. Research undertaken at NSLS was supported by the U.S. DOE, Division of Materials and Chemical Sciences.

* Electronic address: jtu@bnl.gov

[1] J. Nagamatsu et al., Nature (London) 410, 63 (2001).
[2] S.L. Bud’ko et al., Phys. Rev. Lett. 86, 1877 (2001).
[3] D.G. Hinks, H. Claus, and J.D. Jorgensen, cond-mat/0104242.
[4] J. Kortus et al., Phys. Rev. Lett. 86, 4656 (2001).
[5] A.V. Liu, I.I. Mazin, and J. Kortus, cond-mat/0103570.
[6] Y. Kong, O.V. Dolgov, O. Jepsen, and O.K. Anderson, Phys. Rev. B 64, 020501(R) (2001).
[7] J.M. An and W.E. Pickett, Phys. Rev. Lett. 86, 4366 (2001).
[8] J.E. Hirsh and F. Marsiglio, cond-mat/0102479.
[9] K. Voelker, V.I. Anisimov, and T.M. Rice, cond-mat/0103089.
[10] J.C. Phillips and J. Jung, cond-mat/0102261.
[11] G. Rubio-Bollinger, H. Suderow, and S. Vieira, Phys. Rev. Lett. 86, 5582 (2001).
[12] F. Giubileo et al., cond-mat/0104516.
[13] M. Tinkham, Introduction to Superconductivity (Krieger, Malabar, 1975); B. Farnworth and T. Timusk, Phys. Rev. B 10, 5119 (1976); F. Gao et al., Phys. Rev. B 54, 700 (1996).
[14] A.V. Puchkov, T. Timusk, W.D. Mosley, and R.N. Shelton, Phys. Rev. B 50, 4144 (1994).
[15] B. Gorshunov et al., cond-mat/0103164.
[16] A.V. Pronin, A. Pimenov, A. Loidl, and S.I. Kransnosvobodtsev, cond-mat/0104291.
[17] J.H. Jung et al., cond-mat/0105188.
[18] W.N. Kang et al., Science 292, 1521 (2001).
[19] C.C. Homes, M. Reedyk, D. Crandles, and T. Timusk, Appl. Opt. 32, 2972 (1993).
[20] A.S. Barker, Phys. Rev. 132, 1474 (1963).
[21] A.B. Kuz’menko et al., in Sixth International Conference on Spectroscopy of Novel Superconductors, edited by A. Bansil (Elsevier, Chicago, 2001), p. 51 (poster P28).
[22] W.E. Pickett, P.B. Allen, and H. Krakauer, Phys. Rev. B 37, 7482 (1988).
[23] A.V. Puchkov, D.N. Basov, and T. Timusk, J. Phys. C 8, 10049 (1996).
[24] R.K. Kremer, B.J. Gibson, and K. Ahn, cond-mat/0102432.
[25] F. Bouquet et al., cond-mat/0104206.
[26] W. Zimmermann et al., Physica C 183, 99 (1991).
[27] X. K. Chen et al., cond-mat/0104009; A.F. Goncharov et al., cond-mat/0104041; J. Hinka et al., cond-mat/0105275.
[28] W.L. McMillan, Phys. Rev. 167, 331 (1968); P.B. Allen and R.C. Dynes, Phys. Rev. B 12, 905 (1975).
[29] P.B. Allen, Z. Phys. B 47, 45 (1982) (and references therein).
[30] P.B. Allen, in Handbook of Superconductivity, edited by C.P. Poole (Academic, San Diego, 2000), p. 478.