Time-Resolved Photoexcitation of the Superconducting Two-Gap State in MgB_2 Thin Films

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Femtosecond pump-probe studies show that carrier dynamics in MgB_2 films is governed by the sub-ps electron-phonon (*e*-ph) relaxation present at all temperatures, the few-ps *e*-ph process well pronounced below 70 K, and the sub-ns superconducting relaxation below T_c. The amplitude of the superconducting component versus temperature follows the superposition of the isotropic dirty gap and the three-dimensional π gap dependences, closing at two different T_c values. The time constant of the few-ps relaxation exhibits a double divergence at temperatures corresponding to the T_c's of the two gaps.

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The discovery of superconductivity near 40 K in magnesium diborides [1] has stimulated very intensive investigations intended to fully understand the superconducting mechanism and the physical properties of these materials. The phonon-mediated, Bardeen-Cooper-Schrieffer (BCS) pairing mechanism was identified by the boron isotope effect [2], as well as through other supporting experiments, including tunneling [3–5], photoemission spectroscopy [6,7], and nuclear magnetic resonance [8]. Recent theoretical work has predicted a two-band energy model for the MgB_2 superconductor, with two different BCS order parameters Δ [9], closing at the same critical temperature value T_c: the two-dimensional σ band gap Δ_σ with $2\Delta_\sigma/k_BT_c \approx 4$ and the three-dimensional π band gap Δ_π with $2\Delta_\pi/k_BT_c \approx 1.3$. It was stressed by Liu *et al.* [9] that these two different Δ's could be observed only in the clean limit, when the interband scattering is very weak. Indeed, the experimental data, obtained using the point-contact and scanning-tunneling spectroscopies, are in good agreement with the Δ_σ and Δ_π values predicted by the theory [3–5]. The anomalous behavior of the MgB_2 specific heat temperature dependence has also been explained within the two-gap model [10].

In the dirty limit, due to strong interband and intraband scattering, one can typically measure an isotropic energy gap Δ_{dirty} with the zero temperature value of about 4 meV [11]. The temperature dependence of Δ_{dirty} deviates considerably from the BCS $\Delta(T)$ curve [7,12], with a hump at temperatures below T_c [13]. Although the existence of the hump could be accounted for by introducing proximity-induced intergap coupling, the most natural explanation was presented using the two-gap model with two different T_c values: $T_{c,\text{dirty}}$ corresponding to the BCS $\Delta_{\text{dirty}}(T)$ dependence and the specimen's T_c, related to the closing of Δ_π [13]. The detailed correlation between the T_c's and the interband and intraband scattering mechanisms has been studied in the framework of the two-gap model by Mazin *et al.* [14], and this approach is most suitable for MgB_2 thin films fabricated using a postannealing process, since they exhibit both the crystalline and amorphous features.

In this Letter, we present time-resolved, pump-probe measurements of postannealed MgB_2 thin films with very smooth surface morphology. The Mg-B precursor films were prepared by coevaporation of Mg (purity 99.8%) and B (purity 99.9%) components on unheated *r*-cut sapphire and mica substrates. The deposited precursors were about 120 nm thick and were *ex situ* annealed in a vacuum chamber, using a computer-controlled halogen-lamp heater [15]. The annealing temperature was increased at the rate of 40 °C/s for mica and 60 °C/s for sapphire substrates and was leveled at 720 °C for 300 s. Next, the halogen lamps were switched off and the chamber was filled with Ar to quench the samples to room temperature in 30 s. The resultant MgB_2 films were amorphous with nanocrystal inclusions [16] and exhibited optically smooth surfaces. For both mica and sapphire substrates, the onset of the superconducting transition $T_{c,\text{on}}$ was ~35 K and the transition width was approximately 3 K. The critical current density j_c at 4.2 K was about 10^7 A cm^{-2}.

Optical pump-probe measurements of transient reflectivity change $\Delta R/R$ were performed on MgB_2 thin films in the temperature T range from 10 to 300 K. The samples were mounted on a cold finger in a T-controlled, liquid-helium continuous-flow optical cryostat. The light source was a commercial Ti:sapphire laser, which produced 100-fs-wide pulses at a repetition rate of 76 MHz. Since we did not observe any wavelength dependence of the $\Delta R/R$ signal within the tunable range (710 to 950 nm) of our laser, we chose an 800 nm wavelength (1.5 eV photon energy) to be our working optical radiation. The pump and probe beams were cross polarized to avoid the

coherent artifact, with an energy ratio of at least 10:1. The spot sizes on the samples were <100 μm in diameter. The probe beam reflected from the samples was collected by a photodetector and measured using a lock-in system. The pump energy was always smaller than 26 pJ per pulse ($\sim$2 mW average power) to avoid sample heating.

Figure 1 shows a set of three MgB_2 photoresponse $\Delta R/R$ signals, each typical for a different T range. In all cases, the $\Delta R/R$ rise time is limited by the width of the excitation pulses, while the relaxation processes change quite significantly with T. At high T's (300 K to approximately 70 K), the signal is dominated by a fast, single-exponential decay with a time constant $\tau_1 \approx$ 160 fs, as the electron system loses its high excess energy through the electron-phonon (e-ph) interaction [17]. This behavior is in good agreement with previous pump-probe measurements, performed on various metallic thin films at room temperature [18]. The sub-ps relaxation is followed by a component with a decay time τ_2 of the order of several picoseconds. As demonstrated in Fig. 1, the amplitude of this few-ps process is almost negligible at high temperatures. However, it becomes significant in the photoresponse below 70 K, so that the $\Delta R/R$ signal is biexponential, as a combination of τ_1 and τ_2 relaxations, with τ_2 strongly dependent on T. Finally, below T_c, a third process appears, in addition to the sub-ps and few-ps components existing above T_c. This third process is characterized by a T-dependent negative amplitude and a relaxation time τ_3 on the order of hundreds of picoseconds, as shown in the inset of Fig. 1. The decay time τ_3 is independent of the sample temperature, but it varies with different substrate materials.

To better understand the complex nature of the experimentally observed $\Delta R/R$ responses, we decomposed the total signals, using the nonlinear least squares fitting method into three separate single-exponential processes with different time constants of τ_1, τ_2, and τ_3. Figure 2(a) shows that the biexponential $\Delta R/R$ observed between T_c and 70 K (solid squares) can be fitted as the sum of two processes: the sub-ps e-ph process (dotted line), the same as observed at high T's (see top curve in Fig. 1) and is characterized by the same $\tau_1 \approx 160$ fs, and the few-ps e-ph process (dash-dotted line) with the T-dependent τ_2.

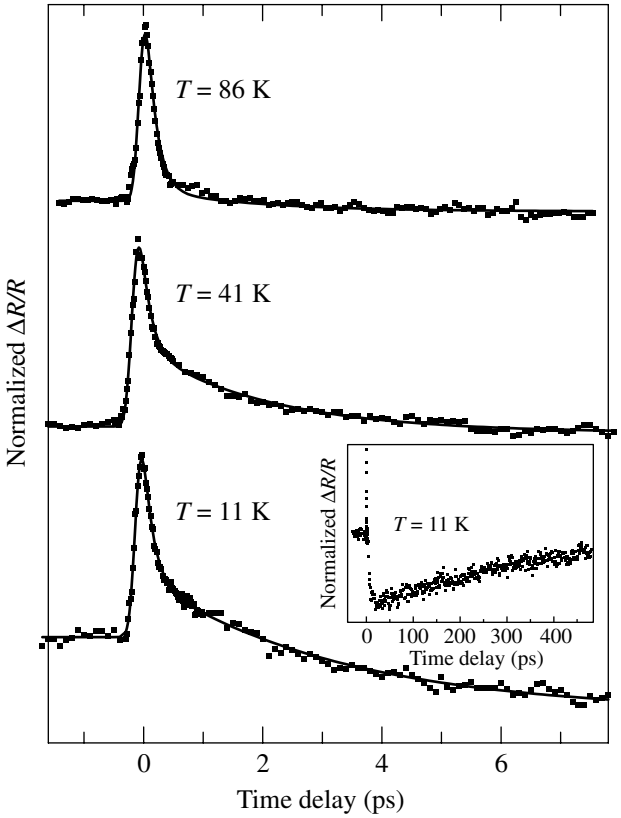

FIG. 1. Time resolved transient differential reflectivity $\Delta R/R$ of an MgB_2 thin film measured at three different temperatures. Both the pump and probe wavelengths were 800 nm and the average pump power was 1 mW. The inset shows the $\Delta R/R$ response below T_c in a much longer time window.

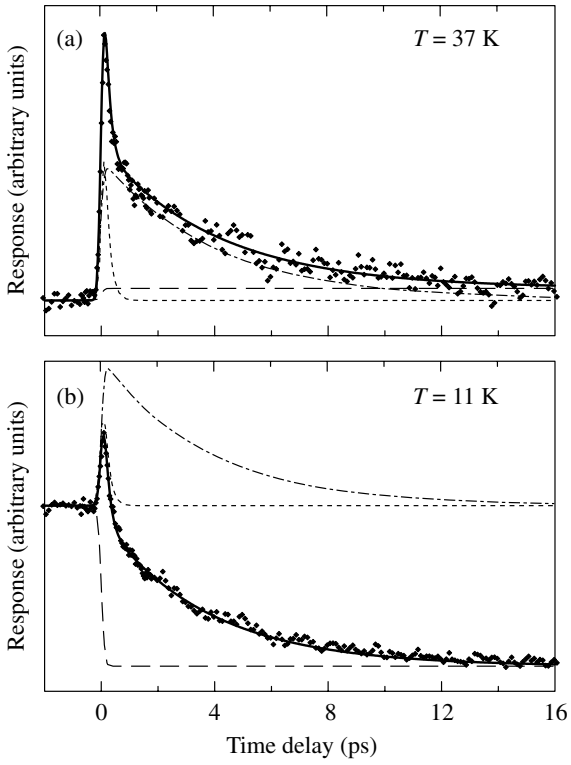

FIG. 2. The $\Delta R/R$ signals (solid squares) measured above (a) and below (b) T_c and decomposed into constituting single-exponential relaxation processes. The dotted line represents the sub-ps e-ph process, the dash-dotted line the few-ps e-ph process, and the dashed line the phonon relaxation either in the form of bolometric cooling (a), or the phonon escape from the superconducting film (b). Note that since τ_3 of the phonon process is much longer than the time window shown, it appears to be a step function. The solid lines are the superpositions of the single-exponential processes.

For the completeness of simulations, we also added a small, very slow offset (dashed line), which is a signature of a long-lasting phonon cooling process and is not studied here [18]. Figure 2(b) demonstrates that the experimental $\Delta R/R$ at temperature far below T_c (solid squares) consists of the two e-ph relaxation processes (dotted and dash-dotted lines) observed above T_c, and the third process with a negative amplitude and a subnanosecond time constant τ_3. The solid lines shown in Figs. 2(a) and 2(b) are superpositions of the three individual, single-exponential relaxation fittings and reproduce the experimental data extremely well.

In this Letter, we focus on the relaxation processes characterized by the τ_2 and τ_3 time constants, as the fast (τ_1) e-ph process represents the initial cooling of very hot electrons and, as we stressed before, its nature is well understood [17,18]. The slowest (τ_3) process with the negative amplitude is clearly related to superconductivity in MgB_2 since it exists only below T_c and represents the decrease in the total number of excited electrons as they annihilate, forming Cooper pairs. The time evolution of the negative $\Delta R/R$ component is T independent and is characterized by $\tau_3 = 400$ ps for ~100-nm-thick MgB_2-on-sapphire films, and by a somewhat shorter τ_3 value for the MgB_2-on-mica films. Thus, we can identify τ_3 as the phonon escape time τ_{es} [19]. We must stress that the negative $\Delta R/R$ component in the superconducting state was reported earlier in a number of publications devoted to pump-probe studies of high-temperature superconductors (HTS) [20,21]. In our MgB_2 films, this superconducting component could be seen only under a very weak pump perturbation. With high incident pump power (e.g., 5 mW of average power), the $\Delta R/R$ signal below T_c contained only the positive components [22] [analogous to Fig. 2(a)], as the optical energy transferred from the electron system to phonons was large enough to drive the phonon temperature above T_c during the early relaxation stage. The negative component was also absent at $T < T_c$ when our MgB_2 films were driven into their resistive state by a dc bias [22].

The T dependence of the amplitude of the negative $\Delta R/R$ component (closed squares) is shown in Fig. 3. The most striking is a humplike behavior just below T_c [13,19]. As the negative component reflects the superconducting state of the material, one can expect that it should follow the $\Delta(T)$ dependence. The dashed line in Fig. 3 represents the BCS $\Delta(T)$ best fit. We note that at higher temperatures, our experimental data points deviate quite significantly from the BCS dependence. Fits based on the strong coupling formalism and the formula $\Delta(T) = \Delta(0)[1 - (T/T_c)^p]^{1/2}$ derived by Choi *et al.* [10] also failed to fit the experimental data.

The alternative approach is to fit the data with a combination of two BCS $\Delta(T)$ dependences (solid lines): one representing the isotropic $\Delta_{\text{dirty}}(T)$, closing at $T_{c,\text{dirty}} = 30.5$ K, and the other corresponding to the three-dimensional $\Delta_\pi(T)$, closing at $T_c = 34.7$ K, equal to $T_{c,\text{on}}$ earlier obtained from the resistance versus temperature measurement. The above model should be applicable for the mixed clean/dirty case and is consistent with the fabrication procedure of our MgB_2 films [13,14,19]. Our films are definitively not in the clean regime, as is reflected by their relatively high normal-state resistivity [$\rho_{\text{DC}}(T = 40\ \text{K}) > 10\ \mu\Omega\,\text{cm}$] [14], and there must exist an enhanced intraband π scattering. The "dirtiness" of our films result in appearance of the isotropic Δ_{dirty}. On the other hand, $T_{c,\text{dirty}}$ is significantly larger than the 22 K value, predicted for the 100% dirty case [9]. Thus, we also observe a contribution from the clean state, through the presence of $\Delta_\pi(T)$, closing at $T_{c,\text{on}}$.

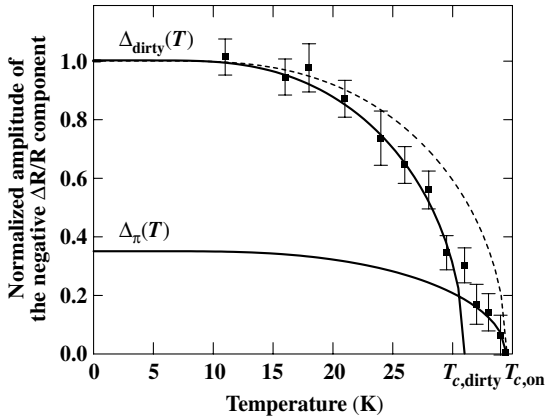

FIG. 3. Temperature dependence of the amplitude of the negative $\Delta R/R$ component (closed squares). The dashed line is the BCS $\Delta(T)$ dependence; the solid lines are the two-gap model fits, each based on BCS theory. $T_{c,\text{on}} = 34.7$ K and $T_{c,\text{dirty}} = 30.5$ K. The error bars are error margins obtained from the least squares fitting procedure.

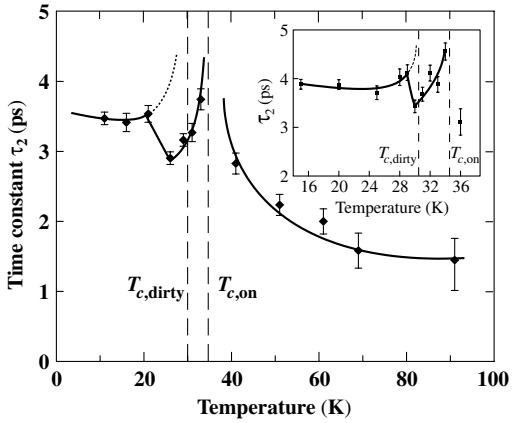

FIG. 4. Temperature dependence of the $\Delta R/R$ picosecond e-ph time constant τ_2. The lines (solid and dotted) are only guides to the eye. The vertical dashed lines correspond to the $T_{c,\text{dirty}}$ and $T_{c,\text{on}}$ values obtained from Fig. 3. The inset shows the same double-divergence behavior observed in a different experimental run.

The picosecond (τ_2) e-ph relaxation process exists both below and above T_c, and its time constant τ_2 is strongly dependent on T below 70 K, as shown in Fig. 4. First, we notice a divergence of τ_2. The divergence of the relaxation time constant at T_c was reported previously in different HTS materials [23,24]. It indicates an opening of the superconducting gap and is associated with the quasiparticle inelastic scattering and Cooper-pair formation, as the excited carriers pile up at the edge of Δ. In our case, τ_2 clearly diverges at $T_{c,\mathrm{on}}$, but there is an anomaly in the $\tau_2(T)$ behavior that indicates a second, lower temperature divergence at T corresponding to $T_{c,\mathrm{dirty}}$. To confirm our findings, the inset of Fig. 4 shows the same $\tau_2(T)$ dependence measured in a different experimental run with more accurate temperature resolution — the double-divergence is clearly visible. At the same time, no hysteresis in $\tau_2(T)$ with respect to ramping the temperature up or down was observed. Since the two temperatures at which τ_2 diverges in Fig. 4 are the same as the T_c values for the Δ_{dirty} and Δ_π gaps in Fig. 3, the double divergence in $\tau_2(T)$ directly supports our earlier conclusion that in our postannealed MgB_2 films, the superconducting state is characterized by two superconducting gaps closing at two different T_c's, with Δ_π being the main gap corresponding to $T_{c,\mathrm{on}}$.

Above T_c, τ_2 decreases gradually over a wide T range from T_c to 70 K. Our fitting procedure returns nonzero τ_2 values even at temperatures above 90 K. But as we discussed in Fig. 1, the amplitude of this τ_2 relaxation process above 70 K becomes very small and the dynamics of the $\Delta R/R$ signal in the > 70 K range is dominated by the subps e-ph relaxation. However, the fact that this few-ps relaxation component with the T-dependent τ_2 extends to so far above $T_{c,\mathrm{on}}$ is in direct contradiction with previous reports on HTS materials, in which τ_2 would vanish within a few kelvins above T_c [23,24]. We have no solid explanation of this effect and tentatively interpret this few-ps relaxation process as an additional e-ph interaction. The e-ph coupling in MgB_2 is complicated, and the phonon modes are highly inharmonic [9]. Thus, the τ_1 and τ_2 relaxation processes could be associated as electron interactions with different phonon modes.

In conclusion, we have found that at room temperature and down to approximately 70 K, MgB_2 thin films respond to femtosecond optical photoexcitation as ordinary metallic thin films with a dominant sub-ps e-ph relaxation process. Below 70 K, a few-ps long relaxation component becomes significant, indicating additional e-ph interaction. Finally, below T_c, there is a third photoresponse component, which we associate with the dynamics of the superconducting state and the recombination of quasiparticles into Cooper pairs. The time evolution of this latter component is sub-ns and corresponds to the phonon escape from the MgB_2 films. The temperature dependence of the amplitude of this superconducting component follows the $\Delta(T)$ anomalous temperature dependence, which can be interpreted for our MgB_2 films in the mixed clean/dirty limit as the two energy gaps, Δ_{dirty} and Δ_π closing at two different values of T_c ($T_{c,\mathrm{dirty}}$ and $T_{c,\mathrm{on}}$, respectively). The same two T_c's are also visible in the double divergence of the relaxation time constant of the few-ps e-ph photoresponse component. Our work confirms that the three-dimensional, small π band gap is the intrinsic, bulk property of MgB_2 and can be observed even in the dirty case.

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