Real-Time Observation of Phonon-Mediated σ-π Interband Scattering in MgB_2

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In systems having an anisotropic electronic structure, such as the layered materials graphite, graphene, and cuprates, impulsive light excitation can coherently stimulate specific bosonic modes, with exotic consequences for the emergent electronic properties. Here we show that the population of E_{2g} phonons in the multiband superconductor MgB_2 can be selectively enhanced by femtosecond laser pulses, leading to a transient control of the number of carriers in the σ-electronic subsystem. The nonequilibrium evolution of the material optical constants is followed in the spectral region sensitive to both the a- and c-axis plasma frequencies and modeled theoretically, revealing the details of the σ-π interband scattering mechanism in MgB_2.

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Exotic phenomena and novel functionalities emerge in solids due to the coupling between the charge carriers and collective modes of structural, electronic, and magnetic origin. Key to exploiting this phenomenology is the ability to tune the density of carriers and the strength of their coupling to such modes. To gain control over the electronic density of states, advanced materials have been designed, e.g., intercalated graphite [1], doped fullerenes [2], and doped charge-transfer insulators [3]. However, chemical doping often increases the disorder in the system, thus limiting the beneficial effect of modulating the charge density at will. Alternatively, photodoping [4] or phonon pumping [5] has been attempted to control the electronic density of states or the coupling between carriers and collective modes. The advantage of such an approach is that light does not induce structural disorder and can access new states of matter that only exist out of equilibrium.

Ultrafast techniques using visible light pulses have unveiled some of these phenomena by delivering excess energy to the electrons via an intense pump pulse and subsequently monitoring the transfer of such energy to the different underlying bosons via a delayed optical probe. Whenever a preferential electron-boson interaction channel exists, it dominates the carrier thermalization via simultaneous heating of the bosonic mode. In this regard, a body of work demonstrated the emergence of hot optical phonon effects in semimetals such as graphite [6–8] and graphene [9,10], where a strong electron-phonon coupling arises due to the ineffective screening of the Coulomb interaction. In this strong coupling regime, the photoexcited nonthermal electron distribution has an increased probability to generate hot optical phonon modes before decaying into a lower-energy quasiequilibrium distribution. A similar mechanism was shown to rule the normal-state ultrafast dynamics of cuprate superconductors and proposed to originate from the coupling with high-energy spin fluctuations [11].

A step further in hot phonon research involves the observation of an anisotropic coupling between different subsets of carriers and a specific phonon. In this respect, a prototypical system is represented by MgB_2, which below 41 K is a rare example of two-band phonon-mediated superconductivity in the strong coupling regime [12]. In its normal state, MgB_2 possesses two distinct types of electronic bands crossing the Fermi energy E_F: the quasi-two-dimensional holelike σ bands and the three-dimensional π bands. The holes of the σ bands, located along the Γ-A direction of the Brillouin zone, interact very strongly with the branch of the E_{2g} bond-stretching mode (characterized by an energy of $\sim$80 meV at Γ), displaying a coupling 3 times larger than the π-band carriers [13–16]. So far, the existence of a highly anisotropic electron-phonon coupling in the σ and π bands has been accessed experimentally only

in an indirect way, via quantum oscillations [14] or as a signature of the two superconducting gaps [17,18]. To overcome this limitation, one needs to disentangle the real-time dynamics of both types of carriers, by selectively monitoring suitable observables under nonequilibrium conditions. This aspect is of pivotal interest as it sheds light on a fascinating topic that has remained elusive over the years, namely, the mechanism responsible for connecting the two bands, which also lies at the origin of the sizes and temperature dependence of the superconducting gaps.

Here, we use an ultrashort near-infrared laser pulse to set the σ-and π-electronic subsystems of MgB_2 out of equilibrium and follow the change of the sample reflectivity ($\Delta R/R$) with a broadband probe covering the in-plane (a axis) and out-of-plane (c axis) plasma edges [19,20]. The main experimental result is the observation of an anomalous blueshift of the a-axis bare plasma frequency ($\omega_{p,a}$) during the first 170 fs after photoexcitation, followed by a delayed blueshift of the c-axis bare plasma frequency ($\omega_{p,c}$) on a longer time scale. By combining our data with theoretical calculations, we find that in this multiband system the behavior of $\omega_{p,a}$ can be explained by the change of the Fermi surface area due to the interaction of the σ carriers with strongly coupled hot phonons. The same microscopic model also accounts for the delayed blueshift of $\omega_{p,c}$, attributed to weak σ-π interband scattering, which allows for cross talk between the two bands. Our work shows that the photoinduced creation of a hot phonon bath in a multiband system can be used to selectively trigger a transient increase of the number of carriers in a given band, opening new perspectives for the selective carrier-density manipulation via near-infrared light.

In our experiments, we use a high-quality (0001)-oriented MgB_2 thin film, grown by hybrid physical-chemical vapor deposition. The pump beam at 1.55 eV is polarized in plane and hits the sample at normal incidence. The probe beam is a continuum covering the 1.77–2.90 eV spectral region and directed towards the sample at an angle of 15° [21]. Consequently, it primarily detects the in-plane plasma edge but also explores the c-axis response. Details on the methods are reported in the Supplemental Materials (SM) [22].

Figure 1(a) shows the color-coded map of $\Delta R/R$ at 10 K as a function of the probe photon energy and time delay between pump and probe, while Figs. 1(b) and 1(c) display the $\Delta R/R$ spectra during the rise and the decay of the response, respectively. Direct inspection of the spectra reveals three features evolving in time: (i) a broad positive contribution centered around 2.15 eV (labeled P_a), which has a straightforward correspondence with the in-plane plasma edge (see Fig. S1 in SM [22]), (ii) a broad negative background covering the 2.55–2.90 eV spectral region, which mirrors the σ-π interband transition (IB) centered around 2.78 eV, and (iii) a narrow feature around 2.67 eV (P_c), which overlaps with the broad IB and becomes

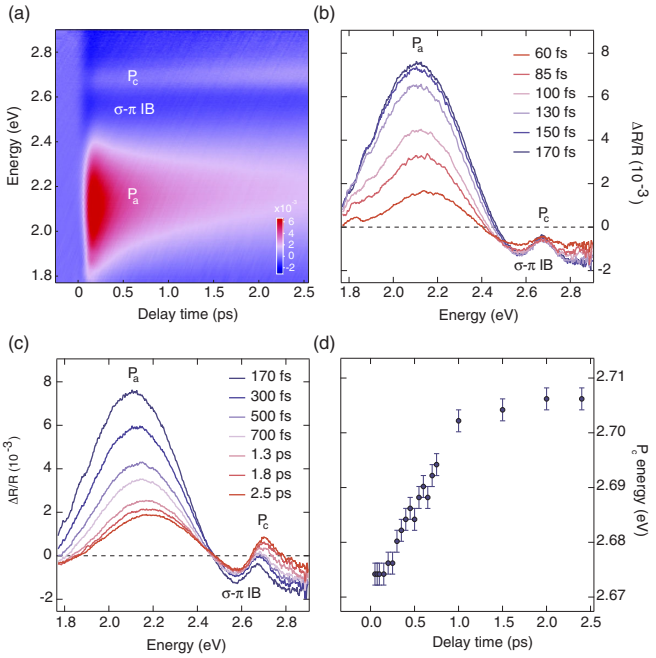

FIG. 1. (a) Color-coded map of $\Delta R/R$ at 10 K as a function of probe photon energy and time delay between pump and probe. The pump photon energy is 1.55 eV and the absorbed fluence is 1.2 mJ/cm^2. (b), (c) Transient spectra of $\Delta R/R$ for different time delays during (b) the rise and (c) the decay of the response. (d) Time evolution of the P_c peak energy.

stronger with increasing time delay. This structure corresponds to the c-axis plasmon and has been extensively investigated in a number of theoretical [60–62] and experimental [19,20,63–65] studies. During the rise [Fig. 1(b)], the feature P_a undergoes a pronounced increase of its amplitude, while the feature P_c is barely visible and does not evolve in energy. In the decay [Fig. 1(c)], both the low-energy zero-crossing point around 1.80 eV and the peak of P_a shift to higher energies as a function of time; moreover, P_c gradually increases its spectral weight while undergoing a sizable blueshift [Fig. 1(d)].

Complementary information is provided by the $\Delta R/R$ temporal dynamics. Several time traces are displayed in Figs. 2(a) and 2(b) at representative probe photon energies. We observe that the signal displays a much longer rise time than the response function of our setup (50 fs), reaching its largest absolute amplitude at 170 fs. Remarkably, the $\Delta R/R$ decay depends on the probe photon energy, as the relaxation dynamics in correspondence to the feature P_c (2.67 eV) differs from the one governing the rest of the spectrum. The distinct dynamics shown by P_c reinforces the idea that this structure retains a different spectroscopic origin compared to the other features of the spectrum. Finally, as expected from Fig. 1(c), on the low-energy side [red trace at 1.80 eV in Fig. 2(a)] the signal undergoes a sign change over time, consistent with previous single-wavelength pump-probe experiments in the near-infrared and in the normal state [66,67].

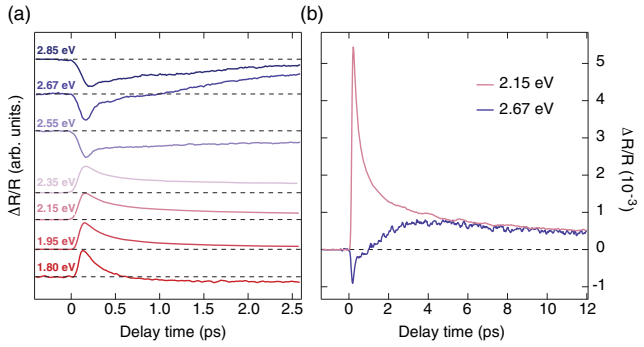

FIG. 2. (a) Normalized $\Delta R/R$ temporal traces up to 2.5 ps at 10 K for different probe photon energies, indicated in the labels. (b) $\Delta R/R$ temporal traces up to 12 ps in correspondence of the P_a and P_c spectral features.

To disentangle the carrier dynamics along the a and c axis and extract the significant parameters of the response, we fit an anisotropic Drude-Lorentz model to the static and time-resolved data at 300 K (Sec. IV in SM [22]). By iterating this procedure over the probed time window, we map the temporal evolution of the bare plasma frequencies [$\omega_{p,a/c}$ in Fig. 3(a)] and optical scattering rates [$\Gamma_{p,a/c}$ in Fig. 3(b)], which reflect, respectively, the position and damping of the plasma edge. We obtain an ultrafast blueshift of $\omega_{p,a}$ [purple dots, Fig. 3(a)], accompanied by a simultaneous increase of the a-axis scattering rate Γ_a [purple dots, Fig. 3(b)]. After 170 fs, $\omega_{p,a}$ redshifts on a time scale of several ps, whereas Γ_a relaxes to its equilibrium value within ~1 ps. The dynamics of Γ_a agree with the results of Ref. [11], and while signatures of the temporal evolution of $\omega_{p,a}$ were evident in Ref. [67], they were never discussed. With broadband measurements that cover the spectral range of the reflectance edges, we can provide a more complete and convincing description of the underlying physics. More remarkable is the temporal evolution of the c-axis Drude contribution [blue dots, Figs. 3(a) and 3(b)]: $\omega_{p,c}$ undergoes a slow blueshift within 1 ps, followed by its stabilization around a constant value, whereas, instead, Γ_c slowly rises on a time scale of ~300 fs, before decreasing again after 1 ps.

The most striking aspect of our experimental data is the observation of the blueshift of $\omega_{p,a}$ and $\omega_{p,c}$. Upon photoexcitation at 1.55 eV, the electronic system is expected to rapidly reach a thermal distribution with a higher effective temperature and, therefore, to produce a *redshift* of the bare plasma frequency [68], as it is observed both in conventional and correlated metals under equilibrium conditions [69] (Sec. VI.A in SM [22]). The sharpness of the P_c feature and its delayed appearance also rule out an active role of the particle-hole σ-π IB transitions (Sec. VI.B in SM [22]). Hence, the blueshift of $\omega_{p,a}$ and $\omega_{p,c}$ in MgB_2 is highly anomalous. In the following, we present a many-body theory that provides a possible explanation of this anomaly as well as of the very different time scales shown by $\omega_{p,a}$ and $\omega_{p,c}$.

In multiband systems the Fermi-surface volume in each band is controlled by the electron-boson interaction (where the boson can be a phonon, a spin fluctuation, a plasmon, etc.). As a consequence, the corresponding effective charge density acquires a sizable temperature dependence that is strictly related to the thermal activation of the interaction processes. This framework was established to explain de Haas–van Alphen [70] and angle-resolved photoemission experiments [71] at equilibrium in the case of pnictides, where the strongly coupled bosonic modes are spin fluctuations [72]. Here, we investigate the consequences of a similar many-body scenario in the case of a pump-probe experiment in multiband MgB_2.

At equilibrium, dynamical many-body effects manifest themselves in the strong coupling between the electrons

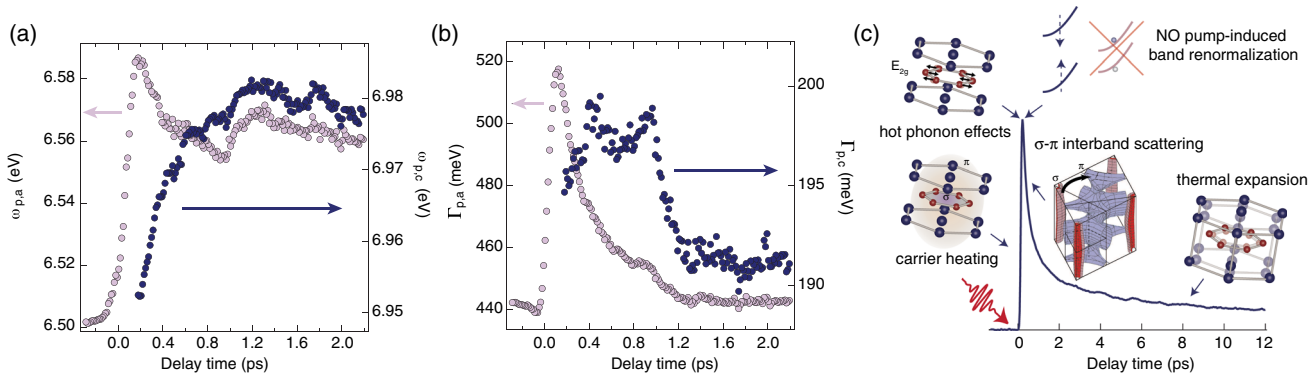

FIG. 3. Temporal evolution of (a) the bare plasma frequency $\omega_{p,a/c}$ and (b) the optical scattering rate $\Gamma_{a/c}$ along the a axis (purple dots) and the c axis (blue dots). (c) Illustration of the ultrafast dynamics. After the interaction with the solid, the ultrashort laser pulse leads to the excitation of both σ and π carriers. The nonthermal σ carriers are strongly coupled to the branch of the E_{2g} phonon mode and efficiently generate hot phonons during the first 170 fs. Subsequently, the energy stored in the hot phonon subsystem is released to the π carriers via interband scattering and to low-energy phonons via anharmonic decay.

and the vibrational degrees of freedom. In particular, the σ bands interact strongly (coupling constant $\lambda \approx 1$) with the phonon branch of the E_{2g} mode, mainly at small momenta; a residual electron-phonon interaction ($\lambda \approx 0.3$ in average) connects the σ and π bands [13]. Within this multiband scenario at $T = 0$, a band β induces a shift of E_F on a band α due to the strong coupling with a phonon of energy $\hbar\omega_{\mathrm{ph}}$. This shift can be quantified as $\chi_\alpha \propto \hbar\omega_{\mathrm{ph}}\lambda_{\alpha\beta}\ln(E_\beta^{\mathrm{top}}/E_\beta^{\mathrm{bottom}})$, where E_β^{top}, $E_\beta^{\mathrm{bottom}}$ are the bandwidths of the band β above and below E_F, respectively. For low-density quasi-two-dimensional bands (as in MgB_2 or in pnictides) with effective mass m, such a shift of E_F induces a change of the charge density $\Delta\tilde{n}_\alpha \approx m\chi_\alpha/\pi$. During the photoexcitation of MgB_2, the pump provides energy to the carriers in both bands, bringing the σ and π carriers to high temperatures $T_{e,\sigma}$ and $T_{e,\pi}$. While in conventional metals the phonon bath remains at a temperature $T_{\mathrm{ph}} \ll T_e$, in MgB_2 the scenario is expected to differ dramatically. Indeed, since the σ holes are strongly coupled to the single E_{2g} phonon mode, this mode can become hot after the photoexcitation, analogously to what has been proven in graphite [6–8] and graphene [9,10]. As a consequence, we expect both $T_{e,\sigma}$ and the E_{2g} phonon temperature $T_{\mathrm{ph}}^{E_{2g}}$ to increase right after the interaction with the pump pulse. Thus, it is essential to elucidate the separate effects produced on $\omega_{p,a/c}$ by an increase of the electronic or the E_{2g} phononic temperatures.

By explicit calculations (Sec. VI.C of SM [22]), we find that the heating of the E_{2g} phonon to a high temperature ($T_{\mathrm{ph}}^{E_{2g}} \approx 450$ K) has a novel and dominant effect on the effective charge density of the in-plane σ bands, explaining quantitatively the initial increase of $\omega_{p,a}$. Importantly, this model also allows us to describe the delayed increase of $\omega_{p,c}$, controlled solely by the subset of π carriers [19,73]. This can be understood by considering that the initial rise of the σ-hole density (due to heating of the E_{2g} phonon) is later compensated in the relaxation process by the increase of the carrier density in the π bands, in order to preserve the overall charge density of the multiband system. The most plausible mechanism behind this compensation involves the transfer of holes from the σ to the π band of MgB_2 via interband scattering. Consistent with this hypothesis, previous theoretical and experimental studies showed that a blueshift of $\omega_{p,c}$ in MgB_2 is related to a hole doping of the π bands, while a redshift is a consequence of electron doping [20,73,74]. In our nonequilibrium situation, the transfer of holes has to be mediated by the interband electron-phonon exchange, controlled by a coupling constant much smaller than the coupling of σ carriers to the E_{2g} phonon. The small size of the electron-phonon coupling responsible for such charge redistribution is a natural explanation for the longer time scale involved in the blueshift of $\omega_{p,c}$. Therefore, the present calculations account for the behavior of $\omega_{p,a}$ and $\omega_{p,c}$ as observed in our pump-probe experiments.

We have also considered a purely electronic scenario in which a renormalization of the electronic structure occurs via the nonlinear interaction with the ultrashort laser pulse (Sec. VI.D of SM [22]). To quantify this effect, we performed an *ab initio* calculation of the coherent electron dynamics triggered by the laser. In this analysis, the lattice was kept frozen, thus disregarding effects related to the electron-phonon coupling. We find that this model explains neither the initial blueshift of $\omega_{p,a}$ nor the subsequent opposite trends of $\omega_{p,a}$ and $\omega_{p,c}$.

Therefore, on the base of this analysis, we conclude that the presence of strong multiband many-body effects mediated by the electron-phonon interaction is the most likely scenario to rationalize the anomalous blueshift of $\omega_{p,a}$ and $\omega_{p,c}$ in MgB_2. We also note that $\omega_{p,a}$ is still above its equilibrium value beyond 1.2 ps, and progressively begins to redshift together with $\omega_{p,c}$. This observation naturally leads us to discuss the relaxation mechanism of the hot phonons, which is expected to proceed on time scales in the 2–10 ps range [7,67] and is governed by anharmonic coupling to lower frequency modes. To this aim, we calculate how the c-axis plasmon energy is modified in the presence of the lattice expansion induced by anharmonic effects (see Sec. VII of SM [22]). In these calculations, we assume equilibrium among the electronic structure and all lattice degrees of freedom. This leads us to obtain a redshift of the c-axis plasmon peak as the distance between the atomic planes of MgB_2 increases. A hint of this behavior can be seen in Fig. 3(a) for long time scales while the lattice temperature decays.

An illustration summarizing the various steps of the ultrafast dynamics as retrieved by our combined experimental-theoretical study is shown in Fig. 3(c).

In conclusion, we combined ultrafast optical spectroscopy and state-of-the-art calculations to map the anisotropic dynamics in MgB_2. Our results show that ultrafast light excitation can be used to control the carrier density in multiband materials via hot phonon effects. More generally, by setting a multiband system out of equilibrium, the microscopic details of the scattering mechanism between distinct electronic subsets can be unraveled via selective observables in the time domain.

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