Fingerprints of hot-phonon physics in time-resolved correlated quantum lattice dynamics

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Abstract

The time dynamics of the energy flow from electronic to lattice degrees of freedom in pump-probe setups could be strongly affected by the presence of a hot-phonon bottleneck, which can sustain longer coherence of the optically excited electronic states. Recently, hot-phonon physics has been experimentally observed and theoretically described in MgB\textsubscript{2}, the electron-phonon based superconductor with \( T_c \approx 39 \) K. By employing a combined ab-initio and a semiclassical approach and by taking MgB\textsubscript{2} as an example, here we propose a novel path for revealing the presence and characterizing the properties of hot phonons through a direct analysis of the information encoded in the lattice inter-atomic correlations. Such method exploits the underlying symmetry of the \( E_{2g} \) hot modes characterized by an out-of-phase in-plane motion of the two boron atoms. Since hot phonons occur typically at high-symmetry points of the Brillouin zone, with specific symmetries of the lattice displacements, the present analysis is quite general and it could aid in revealing the hot-phonon physics in other promising materials, such as graphene, boron nitride, black phosphorus, or even underdoped cuprates.

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1 Introduction

Ultrafast time-resolved measurements have proven in the past few decades to be a powerful tool for investigating fundamental mechanisms of a variety of physical phenomena and for revealing processes governing different states of the matter, where several degrees of freedom (e.g., electrons, lattice and magnetic modes) play a mutual role [1–13]. In a typical pump-probe setup, energy is initially injected into the electronic degrees of freedom by means of particle-hole excitations, giving rise to a non-thermal electronic distribution. The time evolution of such non-thermal excitations is governed by different scattering mechanisms that lead to an energy transfer towards other degrees of freedom, in particular in the lattice mode sector, until, on a long time scale, a new final steady state is reached where all the different degrees of freedom are thermalized and at equilibrium.

The possibility of sustaining non-thermal states for sufficiently long time opens striking opportunities in the field of quantum information as long as the scattering sources affecting such states can be kept under control. The electron-phonon (el-ph) coupling is of major importance in this context since it represents one of the primary channels responsible for the internal thermalization of the electronic degrees of freedom, and because it leads eventually, when it is not constrained, to a system heating detrimental for any coherent process [14].

However, the thermalization process of some materials can be hindered by the so-called phonon bottleneck [2,3,15–35] that quenches the energy transfer between electron and lattice degrees of freedom. Such a physical phenomenon is usually encountered in semiconductors and semimetals where the pump-driven particle-hole excitations are restricted to few single points (valleys) in the Brillouin zone. In such conditions only a few phonons with the right symmetry and with selected momentum \( \mathbf{q} \) connecting two valleys can be excited efficiently. Energy from the electron sub-system is thus prevalently transferred to these modes that get “hot”, meaning they acquire a phonon population \( b_\mathbf{q} \) much larger than other modes, giving rise to a non-thermal phonon distribution.

Within this context, the possibility of a phonon bottleneck, and hence of hot phonons, has been so far associated only to semiconductors and semimetals, whereas conventional metals, with a large Fermi surface allowing scattering with many \( \mathbf{q} \)-phonons, were thought to be incompatible with such a scenario. At odds with this belief, a novel path for inducing hot phonons has been recently proposed for unconventional metals characterized by a strong anisotropy of the el-ph coupling [36,37]. In the paradigmatic case of MgB\(_2\), the el-ph coupling is concentrated in a few in-plane modes at the Brillouin zone center possessing the \( E_{2g} \) symmetry [38–45], with a strong resemblance to the relevant modes in single- and multi-layer graphene. As a consequence of such remarkable anisotropy, the energy initially pumped into the electron sector is efficiently and rapidly (\( \sim 50 \) fs) transferred only to such few lattice degrees of freedom that get a much larger population compared to the remaining lattice modes, whereas a final thermalization among the whole phonon modes and among electron and lattice degrees of freedom occurs on a much larger time scale (\( \sim 0.4 \) ps) [37]. On the experimental ground, an indirect signature of such hot-phonon scenario has been observed in the onset of unconventional features in the time-resolved optical spectra [36]. More direct and precise fingerprints have been proposed at the theoretical level in the analysis of time-resolved Raman spectroscopy, both in spectral features as well as in integrated spectral weights [37]. An accurate measurement of time-resolved Raman spectra in MgB\(_2\) needs to face with the limitations of the uncertainty principle constraining time and energy resolution [46]. In addition,
it should be remarked that in both cases the presence of a non-thermal population of the in-plane \( E_{2g} \) modes is not directly probed via the properties of the lattice degrees of freedom, but indirectly through the el-ph driven many-body renormalization of the electronic response, i.e. in the optical response \([36]\) or in the phonon self-energy \([37, 47]\), which is strictly related to the electronic screening.

In the present work we suggest that a suitable evidence of the presence of hot phonons in MgB\(_2\) can be attained in a more straightforward way by the analysis of the time-resolved lattice dynamics, as obtained for instance by means of ultrafast electron diffuse scattering \([11–13, 35, 48–58]\). In particular, we show that the inter-atomic pair-distribution function, which encodes information about the correlated atomic motion, is highly sensitive to the presence of a hot phonon and it provides a useful tool for detecting them. As related to the analysis of time-independent quantities, our proposal is not affected by the limitations of uncertainty principle. Note that the present analysis, here applied to the paradigmatic case of MgB\(_2\), does not rely on specific properties of this material but it can be employed as well in other compounds, such as single-layer and multi-layer graphene \([59, 60]\), transition metal dichalcogenides \([61]\), black phosphorous \([35, 55]\), hole-doped diamond \([62, 63]\) and underdoped cuprates \([64, 65]\), where el-ph coupling plays a major role.

The paper is structured as follows: Sec. 2 introduces the current modelling for hot phonons in MgB\(_2\) as previously discussed in Ref. \([37]\). Such basic notions will be employed in Sec. 3 to investigate the effects of hot phonons on the correlated lattice dynamics in MgB\(_2\). A wider perspective of the present analysis in regards to other materials and possible experimental approaches is finally provided in Sec. 4.

## 2 Theoretical modelling

The crystal structure of MgB\(_2\) is rather simple, with hexagonal graphene-like planes of B atoms spaced vertically by Mg atoms located in the center of the hexagons (see Fig. 1a) \([66]\). In order to reproduce an \textit{ab-initio} ground state properties of this material, we employ here the \textsc{quantum espresso} package \([67]\). Norm-conserving pseudopotentials were employed with the Perdew-Burke-Ernzerhof exchange-correlation functional \([68]\). The in-plane lattice parameter and the distance between two boron planes were set to 3.083 Å and 3.521 Å, respectively. A 24 × 24 × 24 Monkhorst-Pack grid in momentum space and a plane-wave cutoff energy of 60 Ry were used for ground-state calculations. The phonon dispersion \( \omega_{q,\nu} \) was calculated on a 12 × 12 × 12 grid using density functional perturbation theory \([69]\). The el-ph coupling strength for each momentum \( q \) and each phonon branch \( \nu \) was computed by using the \textsc{epw} code \([70]\) according the standard expression:

\[
\lambda_{q,\nu} = \frac{2}{N(0)N} \sum_{k,n,m} \frac{|g_{kn,k+q,m}|^2}{\omega_{q,\nu}} \delta(\epsilon_{kn} - \mu) \delta(\epsilon_{k+q,m} - \mu),
\]

where \( \mu \) is the electron chemical potential, \( \epsilon_{kn} \) are the electron energies, \( \omega_{q,\nu} \) are the phonon frequencies, \( g_{kn,k+q,m}^\nu \) are the el-ph matrix elements, \( N(\mu) = \sum_{k,n} \delta(\epsilon_{kn} - \mu) \) is the electronic density of states per spin at the Fermi level, and \( N \) is the total number of sampling points in the Brillouin zone. The delta functions \( \delta(x) \) are modeled by Gaussian functions with finite broadenings. Electron energies, phonon frequencies, and electron-phonon coupling matrix elements were interpolated using maximally-localized Wannier functions \([71]\). The Eliashberg
Figure 1:  (a) Crystal structure of MgB$_2$. Also displayed are the lattice displacements of the in-plane $E_{2g}$ mode at $q = 0$.  (b) Electronic band dispersion of MgB$_2$. Bands are labelled as $\sigma$- and $\pi$-bands according to their symmetry.  (c) Phonon dispersions of MgB$_2$. The color code (color bar atop) represents the strength of the el-ph coupling $\lambda_{q\nu}$.  (d) Corresponding phonon density of states $F(\omega)$ (dashed line) and the total Eliashberg function $\alpha^2 F(\omega)$ (blue solid line). The solid red line shows the contribution to the Eliashberg function associated with the hot $E_{2g}$ modes. Readaptation from Ref. [37].

function, which shows a strength of the el-ph coupling for a particular phonon energy, was obtained on a 40 $\times$ 40 $\times$ 40 grid of electron and phonon momenta.

The well-known band structure is shown in Fig. 1b. Due to the symmetry of the systems, the in-plane $\sigma$-bands retain a strong two-dimensional character with a very weak amount of Mg, very similar to the $\sigma$ bands of graphene, whereas the $p_z$ B-orbitals strongly hybridize with Mg giving rise to $\pi$-bands with a strong three-dimensional character. As a consequence of such strong anisotropy in the electronic degrees of freedom, the el-ph coupling results to be highly anisotropic, as depicted in Fig. 1. The el-ph coupling among states in the $\pi$ bands and among $\sigma$ and $\pi$ states, involving $\pi$ bands with a good metallic character, is quite weak. On the other hand, the $\sigma$ bands appear to be only slightly doped, resulting in a poor screening of the in-plane B-B lattice modes, and in a corresponding large el-ph coupling between states in the $\sigma$ bands. A further consequence of the small hole-doping of the two-dimensional $\sigma$ bands is the intrinsic restriction, obeying to the Lindhard model, of a sizable el-ph coupling in a small momentum region $|q|| \leq 2k_F$, with $q|| = (q_x, q_y)$ and $k_F$ is the in-plane Fermi momentum of the $\sigma$ bands which is only weakly dependent on $k_z$.

Within the above framework, a predominant role is played by the in-plane $E_{2g}$ phonon modes at small $q||$, characterized by a strong el-ph coupling and which corresponds to out-
of-phase displacements of the two boron atoms within the unit cell, as depicted in Fig. 1. The overall strongly-coupled modes are thus limited, in a schematic way, to only two phonon branches within the energy window $\omega_{q,\nu} \in [60:75] \text{ meV}$, with roughly $|q| \leq 2k_F$ and weak dispersion along $q_z$, amounting roughly to 5% of the total phonon modes, and corresponding thus to a very small specific heat capacity. The crucial role of the few $E_{2g}$ modes in the total coupling can be clearly pointed out in the Eliashberg function (Fig. 1d) which shows a remarkable peak in the range $\omega_{q,\nu} \in [60:75] \text{ meV}$, in spite of the absence of any particular feature in the corresponding phonon density of states.

Sophisticated and powerful tools for evaluating the non-thermal time-evolution of the coupled electron-lattice system have been developed in the recent years \cite{34, 35, 57, 58, 61}. Such techniques appear particularly useful when in investigating the time range when effective electron and/or lattice temperatures cannot be properly defined. The hot-phonon physics we discuss here involves however macroscopical quantities integrated over momenta, where such level of accuracy is not needed and effective-temperature models can provide as well a reliable description. Within this context, following Ref. \cite{37}, the predominance of the hot-phonon modes in the total coupling can thus be captured by splitting the total Eliashberg function in a hot and cold component, $\alpha^2 F(\omega) = \alpha^2 F_{\text{hot}}(\omega) + \alpha^2 F_{\text{cold}}(\omega)$, where $\alpha^2 F_{\text{hot}}(\omega)$ contains the contribution of the hot $E_{2g}$ modes close to the $\Gamma - A$ path in the relevant energy range $\omega \in [60:75] \text{ meV}$ (the phonon modes colored in red in Fig. 1c), while $\alpha^2 F_{\text{cold}}(\omega)$ takes into account the other weakly coupled cold modes. A similar splitting can be performed for the phonon density of states $F(\omega) = F_{\text{hot}}(\omega) + F_{\text{cold}}(\omega)$.

Equipped with such first-principles input, we can describe the time-dynamics of the energy transfer between the different degrees of freedom in terms of three temperatures \cite{1,9,37,59,60,76–79}, i.e., an electron one $T_e$, a hot-phonon temperature $T_{\text{hot}}$, which governs the population of the $E_{2g}$-like strongly-coupled hot-phonon modes, and the cold-lattice temperature $T_{\text{cold}}$ that describes the temperature of the weakly coupled cold modes. The time evolution of the these characteristic temperatures upon a pump pulse can be described by the set of coupled equations

\begin{align}
C_e \frac{\partial T_e}{\partial t} &= S(z, t) + \nabla_z (\kappa \nabla_z T_e) - G_{\text{hot}}(T_e - T_{\text{hot}}) - G_{\text{cold}}(T_e - T_{\text{cold}}), \\
C_{\text{hot}} \frac{\partial T_{\text{hot}}}{\partial t} &= G_{\text{hot}}(T_e - T_{\text{hot}}) - C_{\text{hot}} \frac{T_{\text{hot}} - T_{\text{cold}}}{\tau_0}, \\
C_{\text{cold}} \frac{\partial T_{\text{cold}}}{\partial t} &= G_{\text{cold}}(T_e - T_{\text{cold}}) + C_{\text{hot}} \frac{T_{\text{hot}} - T_{\text{cold}}}{\tau_0}.
\end{align}

Here $C_e$, $C_{\text{hot}}$, and $C_{\text{cold}}$ are the specific heat capacities for the electron, hot-phonon, and cold-phonon states, respectively, and $G_{\text{hot}}/G_{\text{cold}}$ are the electron-phonon relaxation rates between
electronic states and hot/cold phonons modes. They can be computed as

\[ C_e = \int_{-\infty}^{\infty} d\varepsilon N(\varepsilon) \varepsilon \frac{\partial f(\varepsilon - \mu; T_e)}{\partial T_e}, \]  

(5)

\[ C_{\text{hot}} = \int_0^{\infty} d\omega F_{E_{\text{hot}}} (\omega) \frac{\partial b(\omega; T_{E_{\text{hot}}})}{\partial T_{E_{\text{hot}}}}, \]  

(6)

\[ C_{\text{cold}} = \int_0^{\infty} d\omega F_{E_{\text{cold}}} (\omega) \frac{\partial b(\omega; T_{\text{cold}})}{\partial T_{\text{cold}}}, \]  

(7)

\[ G_{\text{hot}} = \frac{2\pi k_B}{\hbar} N(\mu) \int d\Omega \Omega^2 F_{E_{\text{hot}}} (\Omega), \]  

(8)

\[ G_{\text{cold}} = \frac{2\pi k_B}{\hbar} N(\mu) \int d\Omega \Omega^2 F_{E_{\text{cold}}} (\Omega). \]  

(9)

Here \( N(\varepsilon) \) is the electronic density of states, \( \mu \) the electronic chemical potential, and \( f(x; T) = 1/[\exp(x/T) + 1], b(x; T) = 1/[\exp(x/T) - 1] \) are the Fermi-Dirac and the Bose-Einstein distribution functions, respectively. The values obtained from the first-principles calculations are \( C_e = 90 \text{ J/m}^3\text{K}^2 \times T_e, \) \( C_{\text{hot}} = 0.13 \text{ J/m}^3\text{K}, \) and \( C_{\text{cold}} = 4.1 \text{ J/m}^3\text{K}, \) \( G_{\text{hot}} = 2.8 \times 10^{18} \text{ W/m}^3\text{K}, \) and \( G_{\text{cold}} = 3.6 \times 10^{18} \text{ W/m}^3\text{K}. \) Furthermore, modelling a pump-probe setup, the term \( S(z, t) = I(t)e^{-z/\delta} \) takes into account the energy absorption from the laser pulse into the electronic degrees of freedom, where \( I(t) \) is the intensity of the absorbed fraction of the laser pulse (with a Gaussian profile) and \( \delta \) is the penetration depth. Finally, the relaxation time \( \tau_0 \) takes into account the scattering between hot and cold modes driven by the anharmonic phonon-phonon coupling, for which we take an estimate of 400 fs \cite{80}.

The time evolution of the three characteristic temperatures \( T_e, T_{\text{hot}}, T_{\text{cold}} \) (Fig. 2a) shows a remarkable increase of the effective temperature of the hot modes \( T_{\text{hot}} \), which reaches a peak \( T_{\text{hot}}^{\text{max}} \approx 1250 \text{ K} \) at \( t^* \approx 50 \text{ fs} \) with a small delay compared to the time behavior of the electronic temperature \( T_e \). The remnant cold phonon modes follow, on the other hand, a completely different behavior with a slow monotonic increase towards the final equilibrium state at \( t \geq 0.3 - 0.4 \text{ ps} \) where all the degrees of freedom are thermalized with each other.

Such a behavior, showing a clear hot-phonon scenario, can be compared with the isotropic case where the energy from the electronic degrees of freedom is transferred in an equal way to all the lattice modes, without a preferential channel, and one can thus define a unique phonon temperature \( T_{\text{ph}} \) for all the modes \cite{76}. The coupled equations of the two temperature model can be obtained by setting \( T_{\text{hot}} = T_{\text{cold}} = T_{\text{ph}} \) in Eqs. (2)-(4):

\[ C_e \frac{dT_e}{dt} = S(z, t) + \nabla_z (\kappa \nabla_z T_e) - G_{\text{ph}}(T_e - T_{\text{ph}}), \]  

(10)

\[ C_{\text{ph}} \frac{dT_{\text{ph}}}{dt} = G_{\text{ph}}(T_e - T_{\text{ph}}), \]  

(11)

where \( C_{\text{ph}} = C_{\text{hot}} + C_{\text{cold}} \) and \( G_{\text{ph}} = G_{\text{hot}} + G_{\text{cold}}. \) The time evolution of \( T_e, T_{\text{ph}} \) is displayed in Fig. 2a. In the absence of the hot-phonon bottleneck, a much faster thermalization between the electrons and the lattice degrees of freedom is obtained, within a time-scale of \( t \sim 0.08 \text{ ps} \), while the average phonon temperature \( T_{\text{ph}} \) reaches the maximum of about 420 K.
Figure 2: (a) Time evolution of the characteristic effective temperatures $T_e$, $T_{\text{hot}}$, $T_{\text{cold}}$ for the three-temperature model suitable for hot phonons. The grey dashed line shows the pulse profile, with the pulse duration of 45 fs and an absorbed fluence of 12 J/m$^2$. (b) Similar as in panel (a) within the assumption of thermal distribution (two-temperature model) of the lattice modes as described with Eqs. (10) and (11). Partial readaptation from Ref. [37].

3 Time-resolved lattice dynamics

As discussed above, the hot-phonon scenario is characterized by the regime $T_{\text{hot}} \gg T_{\text{cold}}$, where the population of the hot-lattice modes is singled out and is significantly larger than the population of the other cold modes. Equipped with the detailed input from the ab initio calculations, we discuss now how this scenario in MgB$_2$ can be revealed directly in the dynamical lattice properties, i.e., in the amplitude of the mean square lattice displacements, resolved for atomic species and for different directions; and more strikingly in the degree of correlation of the atomic motion. The peculiar properties of hot phonons in MgB$_2$ rely on the $E_{2g}$ symmetry of the strongly coupled hot modes, in particular: (i) the pure in-plane B character of the $E_{2g}$ modes; (ii) the counter-phase motion of the two B atoms per cell that move in opposite direction, as depicted in Fig. 1a.

The evaluation of the mean square lattice displacements based on the force-constant-model calculations has been detailed in Refs. [81, 82]. Here, we extend such computation by using fully ab initio methodology and, more importantly, by introducing the hot-phonon scenario and specifying a different temperatures for each relevant modes. More explicitly, we can define the projected mean-square lattice displacement $\sigma^2(i_\alpha)$ as

$$\sigma^2(i_\alpha) = \langle [u_i \cdot \hat{r}_\alpha]^2 \rangle, \quad (12)$$

where $u_i$ is the lattice displacement of atom $i$ from its average position and $\hat{r}_\alpha$ is the unit
Figure 3: Time evolution of the mean square lattice displacements $\sigma^2$ for each atom and for different axis directions in the case of the hot-phonon scenario, described by Eqs. (2)-(4) (full lines). The corresponding results for the thermal phonon distribution [described by Eqs. (10)-(11)] are shown with the dashed lines.

vector pointing along the direction $\alpha = x, y, z$. On the microscopic ground we can write

$$\sigma^2(i_\alpha) = \frac{\hbar}{N} \sum_{q,\mu} \left| \epsilon_{q,\mu}^{i_\alpha} \right|^2 \frac{1}{2} \left[ 1 + 6 \left( \frac{\omega_{q,\mu}}{T_{q,\mu}} \right) \right],$$

where $N$ is the total number of $q$-points considered in the phonon Brillouin zone, $M_i$ is the atomic mass of atom $i$, $\omega_{q,\mu}$ is the frequency of a phonon mode of branch $\mu$ with momentum $q$, $T_{q,\mu} = T_{\text{hot}}, T_{\text{cold}}$ is the appropriate temperature for such mode, and $\epsilon_{q,\mu}^{i_\alpha}$ is the component of the corresponding eigenvector $\hat{\epsilon}_{q,\mu}$ describing the displacement of the $i$ atom along the $\alpha$ direction.

The behavior of the mean square lattice displacements resolved for each atom and for different axis directions in the case of hot non-thermal phonon distribution is shown in Fig. 3 (solid lines). As expected, compared with the case of a thermal phonon distribution described by Eqs. (10)-(11) (dashed lines), we do not see any remarkable difference for the phonon modes with Mg character and with out-of-plane lattice displacements, apart from a slower thermalization in the case of hot phonons, due to the longer storage of energy in the hot-phonon modes. A slight effect of the presence of hot phonons can be detected in the behavior of the mean square in-plane B lattice displacements which shows a non-monotonic behavior with a peak value larger than the final equilibrium state, at $t^* = 50$ fs, in fair accordance with the peak of $T_{\text{hot}}$.

A more striking signature of the hot-phonon scenario can be detected from the analysis of the correlated lattice dynamics. More explicitly, we focus on the mean-square relative...
displacement of atomic pairs projected onto the vector joining the atom pairs $\mathbf{u}_i - \mathbf{u}_j$:

$$\sigma_{ij}^2 = \langle \left( \mathbf{u}_i - \mathbf{u}_j \right) \cdot \hat{r}_{ij} \rangle^2, \quad (14)$$

where $\mathbf{u}_i$ and $\mathbf{u}_j$ are the lattice displacements of atoms $i$ and $j$ from their average positions, $\hat{r}_{ij}$ is the unit vector connecting atoms $i$ and $j$.

This physical quantity can be evaluated microscopically as:

$$\sigma_{ij}^2 = \frac{\hbar}{N} \sum_{q,\mu} \left[ \frac{1}{2} + b \left( \frac{\omega_{q,\mu}}{T_{q,\mu}} \right) \right] \left\{ \frac{\left| \hat{c}_{q,\mu} \cdot \hat{r}_{ij} \right|^2}{M_i \omega_{q,\mu}} + \frac{\left| \hat{c}_{q,\mu} \cdot \hat{r}_{ij} \right|^2}{M_j \omega_{q,\mu}} 
- 2 \text{Re} \left[ \left( \hat{c}_{q,\mu} \cdot \hat{r}_{ij} \right) \left( \hat{c}_{q,\mu}^* \cdot \hat{r}_{ij} \right) e^{i u_j \cdot \hat{r}_{ij}} \right] \right\}, \quad (15)$$

It is useful to quantify the degree of correlation by introducing a convenient dimensionless correlation factor $\rho_{ij}$ defined as

$$\sigma_{ij}^2 = \sigma^2(i_j) + \sigma^2(j_i) - 2\sigma(i_j)\sigma(j_i)\rho_{ij}, \quad (16)$$

where

$$\sigma^2(i_j) = \langle \left( \mathbf{u}_i \cdot \hat{r}_{ij} \right)^2 \rangle = \frac{\hbar}{N} \sum_{q,\mu} \left[ \frac{1}{2} + b \left( \frac{\omega_{q,\mu}}{T_{q,\mu}} \right) \right] \frac{\left| \hat{c}_{q,\mu} \cdot \hat{r}_{ij} \right|^2}{M_i \omega_{q,\mu}}. \quad (17)$$

The inter-atomic correlation factor can be thus calculated as $\rho_{ij}$

$$\rho_{ij} = \frac{\sigma^2(i_j) + \sigma^2(j_i) - \sigma_{ij}^2}{2\sigma(i_j)\sigma(j_i)}. \quad (18)$$

Positive values of correlation factor $\rho_{ij} > 0$ describe a situation where the couple of atoms $i$, $j$ move in phase, so that the resulting value of $\sigma_{ij}^2$ is smaller than for the uncorrelated case. On the other hand, a predominance of counter-phase atomic vibrations is expected to result in a negative correlation factor $\rho_{ij} < 0$.

Equations (13) and (18) provide fundamental tools for investigating the effects of the hot-phonon scenario on the time evolution of the correlated lattice dynamics. At the initial thermal equilibrium at room temperature we find positive values $\rho_{B-B} \approx 0.24$ $\rho_{B-Mg} \approx 0.22$, reflecting a slight dominance of the acoustic (in-phase) modes in contributing to the lattice dynamics. The time dependence of the mean-square relative displacement for the in-plane boron-boron pair, $\sigma_{B-B}$, and for the interplane boron-magnesium one $\sigma_{B-Mg}$ is reported in Fig. 4a. The inter-atomic boron-magnesium lattice displacement (blue full line) does not show any significant feature, just a monotonic increase between the two equilibrium states, as in the absence of hot phonons (blue dashed line).

A definitive fingerprint of the crucial role of the hot-phonon is provided by the time evolution of the mean-square relative in-plane boron-boron displacements $\sigma_{B-B}$ as shown in Fig. 4a. For the assumption of a thermal phonon distribution (red dashed line), $\sigma_{B-B}$ increases monotonically obeying to a thermal heating of the lattice (similar as $\sigma_{B-Mg}^2$). Within the hot-phonon scenario, however, the in-plane nearest neighbor mean-square relative lattice
displacement $\sigma_{B-B}^2$ presents a remarkable peak at the highest $T_{\text{hot}}$ achievable at $t^* = 50$ fs, with a following decrease towards a new equilibrium conditions (red full line). Such a peak is a direct consequence of a dominance of a larger population of the in-plane boron modes with the $E_{2g}$ symmetry.

The relevance of hot-phonon physics is revealed in a even more striking way in the analysis of the lattice displacement correlation factor $\rho_{ij}$. As shown in Fig. 4b, the onset of $E_{2g}$ hot phonons in MgB$_2$ is reflected in a direct way in a remarkable anomaly in the time evolution of the relative boron-boron in-plane lattice correlation, with a sharp decrease of $\rho_{B-B}$ in the first 50 fs. The presence of hot-phonon modes with pure in-plane boron character is visible also in the interplane boron-magnesium correlation factor $\rho_{B-Mg}$, although in a weaker way. Such anomalies are peculiar of the hot-phonon scenario and are not predicted to show when the lattice modes are assumed to obey a thermal distribution (dashed lines).

Our analysis provides thus a simple and straightforward way to probe the presence of hot phonons in MgB$_2$ directly in the analysis of the lattice dynamics properties, as it can be revealed in time-resolved pump-probe experiments. More precisely, we predict a marked anomaly in the time behavior of lattice correlation factor $\rho_{B-B}$ occurring at the delay time $t^*$ when the hot-phonon lattice modes reach their largest population. The time scale over which such anomaly disappears prompts also a possible direct procedure for evaluating experimentally the time scale when all the lattice degrees of freedom reach their final thermalization.
4 Wider perspective on other materials and experimental observations

The approach described in the present work suggests a possible way to detect hot phonons not in an indirect way through the effects on the electronic properties but directly in the lattice dynamics, exploiting the consequences in the correlation of inter-atomic motion. In the specific case of MgB$_2$, the candidate modes for hot phonons are the $q = 0$ optical $E_{2g}$ ones that correspond to out-of-phase in-plane motion of the two B atoms. The large non-thermal population of these modes gives rise thus to a marked anomaly in the in-plane correlation factor $\rho_{B-B}$ with respect to the steady conditions, as depicted in Fig. 4.

As we stressed above, such approach is not specific of MgB$_2$ but it is quite general and it can be usefully applied to other materials. The overall scheme, for a given material candidate to hot-phonon physics, can be summarized as follows ($i$) identifying the lattice modes with particularly large el-ph coupling, likely thus to sustain hot-phonon physics; ($ii$) analyzing how the eigenvectors of such modes affect the inter-atomic correlated motion; ($iii$) thus investigating and predicting specific anomalies in the appropriate correlation factors, validating such prediction with the comparison with a overall thermal heating of the lattice with no hot phonons included. The most straightforward generalization is probably graphene, where hot phonons have been assessed in many ways, and which shares many similarities with MgB$_2$. The $E_{2g}$ modes of the hexagonal B plane MgB$_2$ are the same $E_{2g}$ modes of the hexagonal C plane that get hot in graphene. We can hence predict that a similar anomaly can be observable also for graphene.

A similar approach is expected to work also for more complex materials with several atoms in unit cell. A suitable class of compounds, along this perspective, is the family of superconducting cuprates, as for instance the representative system La$_{2-x}$Sr$_x$CuO$_4$ where the occurence of hot-phonon physics has been already discussed in literature $[65]$. The lattice modes that get hot in this compound are predicted to belong mainly to the $A_{1g}$ symmetry, involving out-of-plane displacements either of the La atoms or of the apical oxygen atoms [often labelled as O(3)] $[64]$. A residual el-ph coupling also involves $E_g$ modes of the O(3) oxygens. A sketch of the relevant modes is provided in Fig. 5. A time-resolved assessment of the correlated inter-atomic motion can be a poweful tool also in this case since it could distinguish the role of the different modes in the La-La or in the O(i)-O(i) inter-atomic correlations ($i = 1, 2, 3$). Note that the different contribution of the in-plane or apical oxygens in the inter-atomic lattice correlations, as probed for instance by the inter-atomic probability distribution function, could be easily reveled due to the different bond lengths of the different oxygens $[84,85]$.

Other more complex materials with several atoms for cell, sustaining hot-phonon physics, could be in principle devised. In such a framework, on the theoretical side, one cannot exclude that in-phase motions can be favoured, resulting in a positive anomaly in a specific inter-atomic correlation function, when the out-of-phase motion of a subset of atoms is accompanied by an in-phase motion of another subset of atoms.

From the experimental point of view, it should be noticed that the most accurate probes of the inter-atomic correlated motion under equilibrium conditions are presently provided by neutron diffraction measurements that are probably not best suited for time-resolved femtosecond resolution. Our theoretical proposal does not however rely on a specific experimental setup. It should be noticed indeed that, even in the steady neutron diffraction measurements,
Figure 5: Main optical lattice modes of La$_{2-x}$Sr$_x$CuO$_4$ displaying sizable el-ph coupling and which are thought to support hot-phonon physics. Sr is a random substitutional atom for La and it is not shown here. La$_{2-x}$Sr$_x$CuO$_4$ has an layered perovskite structure with apical-oxygen distance larger than the in-plane oxygens.

raw data are collected in the momentum space, and later translated in the real-space by Fourier transform. In this perspective ultrafast electron diffuse scattering [11, 53, 86], as well as time-resolved resonant inelastic X-ray scattering [87, 88], represent two promising alternative techniques which are rapidly ramping up and constantly expanding their accuracy and limits.

5 Conclusions

In this paper, using first-principle calculations, we have analyzed the presence of the hot-phonon physics in MgB$_2$ and its effect on the time evolution of lattice dynamics in a typical pump-probe experiment. We have shown that hot phonons in MgB$_2$, with their characteristic $E_{2g}$ symmetry that implies an in-plane counter-phase motion of the boron atoms, can be directly traced down in the analysis of the atom-resolved mean-square lattice displacements, and more evidently in the analysis of the mean square relative lattice displacements $\sigma^2_{ij}$ and lattice correlation factors $\rho_{ij}$. Even though we apply our investigation to the specific case of MgB$_2$, the analysis here described is quite generic and it can be extended to a wide range of materials (semiconductors, metals or semimetals) sustaining hot phonons, since they are commonly established at high-symmetry points of the Brillouin zone, with well-defined and well-known symmetry and atomic contents. Promising compounds might be for instance single-layer and multi-layer graphene [59, 60], transition metal dichalcogenides [61], black phosphorous [35, 55], hole-doped diamond [62, 63] and underdoped cuprates [64, 65]. Our work provides thus a guideline for future direct experimental verification and characterization of hot-phonon mechanisms in several families of compounds.
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References

[1] L. Perfetti, P. A. Loukakos, M. Lisowski, U. Bovensiepen, H. Eisaki and M. Wolf, Ultrafast Electron Relaxation in Superconducting Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ by Time-Resolved Photoelectron Spectroscopy, Phys. Rev. Lett. 99, 197001 (2007), doi:10.1103/PhysRevLett.99.197001.

[2] K. Ishioka, M. Hase, M. Kitajima, L. Wirtz, A. Rubio and H. Petek, Ultrafast electron-phonon decoupling in graphite, Phys. Rev. B 77, 121402 (2008), doi:10.1103/PhysRevB.77.121402.

[3] H. Yan, D. Song, K. F. Mak, I. Chatzakis, J. Maultzsch and T. F. Heinz, Time-resolved Raman spectroscopy of optical phonons in graphite: Phonon anharmonic coupling and anomalous stiffening, Phys. Rev. B 80, 121403 (2009), doi:10.1103/PhysRevB.80.121403.

[4] C. Gadermaier, A. S. Alexandrov, V. V. Kabanov, P. Kusar, T. Mertelj, X. Yao, C. Manzoni, D. Brida, G. Cerullo and D. Mihailovic, Electron-Phonon Coupling in High-Temperature Cuprate Superconductors Determined from Electron Relaxation Rates, Phys. Rev. Lett. 105, 257001 (2010), doi:10.1103/PhysRevLett.105.257001.

[5] R. Ulbricht, E. Hendry, J. Shan, T. F. Heinz and M. Bonn, Carrier dynamics in semiconductors studied with time-resolved terahertz spectroscopy, Rev. Mod. Phys. 83, 543 (2011), doi:10.1103/RevModPhys.83.543.

[6] R. Cortés, L. Rettig, Y. Yoshida, H. Eisaki, M. Wolf and U. Bovensiepen, Momentum-Resolved Ultrafast Electron Dynamics in Superconducting Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, Phys. Rev. Lett. 107, 097002 (2011), doi:10.1103/PhysRevLett.107.097002.

[7] D. Rudolf, C. La-O-Vorakiat, M. Battiato, R. Adam, J. M. Shaw, E. Turgut, P. Maldonado, S. Mathias, P. Grychtol, H. T. Nembach, T. J. Silva, M. Aeschlimann et al., Ultrafast magnetization enhancement in metallic multilayers driven by superdiffusive spin current, Nature Communications 3(1) (2012), doi:10.1038/ncomms2029.

[8] B. Arnaud and Y. Giret, Electron Cooling and Debye-Waller Effect in Photoexcited Bismuth, Phys. Rev. Lett. 110, 016405 (2013), doi:10.1103/PhysRevLett.110.016405.

[9] J. C. Johannsen, S. Ulstrup, F. Cilento, A. Crepaldi, M. Zacchigna, C. Cacho, I. C. E. Turcu, E. Springate, F. Fromm, C. Raidel, T. Seyller, F. Parmigiani et al., Direct View of Hot Carrier Dynamics in Graphene, Phys. Rev. Lett. 111, 027403 (2013), doi:10.1103/PhysRevLett.111.027403.
[10] S. A. Jensen, Z. Mics, I. Ivanov, H. S. Varol, D. Turchinovich, F. H. L. Koppens, M. Bonn and K. J. Tielrooij, *Competing Ultrafast Energy Relaxation Pathways in Photoexcited Graphene*, Nano Letters 14(10), 5839 (2014), doi:10.1021/nl502740g.

[11] T. Chase, M. Trigo, A. H. Reid, R. Li, T. Vecchione, X. Shen, S. Weathersby, R. Coffee, N. Hartmann, D. A. Reis, X. J. Wang and H. A. Dürr, *Ultrafast electron diffraction from non-equilibrium phonons in femtosecond laser heated Au films*, Applied Physics Letters 108(4), 041909 (2016), doi:10.1063/1.4940981.

[12] L. Waldecker, R. Bertoni, R. Ernstorfer and J. Vorberger, *Electron-Phonon Coupling and Energy Flow in a Simple Metal beyond the Two-Temperature Approximation*, Phys. Rev. X 6, 021003 (2016), doi:10.1103/PhysRevX.6.021003.

[13] L. P. René de Cotret, J.-H. Pohls, M. J. Stern, M. R. Otto, M. Sutton and B. J. Siwick, *Time- and momentum-resolved phonon population dynamics with ultrafast electron diffuse scattering*, Phys. Rev. B 100, 214115 (2019), doi:10.1103/PhysRevB.100.214115.

[14] M. Sentef, A. F. Kemper, B. Moritz, J. K. Freericks, Z.-X. Shen and T. P. Devereaux, *Examining Electron-Boson Coupling Using Time-Resolved Spectroscopy*, Phys. Rev. X 3, 041033 (2013), doi:10.1103/PhysRevX.3.041033.

[15] P. J. Price, *Hot phonon effects in heterolayers*, Superlattices and Microstructures 1(3), 255 (1985), doi:10.1016/0749-6036(85)90013-8.

[16] P. Kocevar, *Hot phonon dynamics*, Physica B+C 134(1), 155 (1985), doi:10.1016/0378-4363(85)90336-5.

[17] W. Pötz, *Hot-phonon effects in bulk GaAs*, Phys. Rev. B 36, 5016 (1987), doi:10.1103/PhysRevB.36.5016.

[18] R. P. Joshi and D. K. Ferry, *Hot-phonon effects and interband relaxation processes in photoexcited GaAs quantum wells*, Phys. Rev. B 39, 1180 (1989), doi:10.1103/PhysRevB.39.1180.

[19] P. Langot, N. Del Fatti, D. Christofilos, R. Tommasi and F. Vallée, *Femtosecond investigation of the hot-phonon effect in GaAs at room temperature*, Phys. Rev. B 54, 14487 (1996), doi:10.1103/PhysRevB.54.14487.

[20] S. Butscher, F. Milde, M. Hirtschulz, E. Malić and A. Knorr, *Hot electron relaxation and phonon dynamics in graphene*, Applied Physics Letters 91(20), 203103 (2007), doi:10.1063/1.2809413.

[21] K. Kang, D. Abdula, D. G. Cahill and M. Shim, *Lifetimes of optical phonons in graphene and graphite by time-resolved incoherent anti-Stokes Raman scattering*, Phys. Rev. B 81, 165405 (2010), doi:10.1103/PhysRevB.81.165405.

[22] S. Berciaud, M. Y. Han, K. F. Mak, L. E. Brus, P. Kim and T. F. Heinz, *Electron and Optical Phonon Temperatures in Electrically Biased Graphene*, Phys. Rev. Lett. 104, 227401 (2010), doi:10.1103/PhysRevLett.104.227401.

[23] C. H. Lui, K. F. Mak, J. Shan and T. F. Heinz, *Ultrafast Photoluminescence from Graphene*, Phys. Rev. Lett. 105, 127404 (2010), doi:10.1103/PhysRevLett.105.127404.
[24] L. Huang, B. Gao, G. Hartland, M. Kelly and H. Xing, *Ultrafast relaxation of hot optical phonons in monolayer and multilayer graphene on different substrates*, Surface Science 605(17), 1657 (2011), doi:https://doi.org/10.1016/j.susc.2010.12.009.

[25] M. Scheuch, T. Kampfrath, M. Wolf, K. von Volkmann, C. Frischkorn and L. Perfetti, *Temperature dependence of ultrafast phonon dynamics in graphite*, Applied Physics Letters 99(21), 211908 (2011), doi:10.1063/1.3663867.

[26] S. Wu, W.-T. Liu, X. Liang, P. J. Schuck, F. Wang, Y. R. Shen and M. Salmeron, *Hot Phonon Dynamics in Graphene*, Nano Letters 12(11), 5495 (2012), doi:10.1021/nl301997r.

[27] D. C. Hannah, K. E. Brown, R. M. Young, M. R. Wasielewski, G. C. Schatz, D. T. Co and R. D. Schaller, *Direct Measurement of Lattice Dynamics and Optical Phonon Excitation in Semiconductor Nanocrystals Using Femtosecond Stimulated Raman Spectroscopy*, Phys. Rev. Lett. 111, 107401 (2013), doi:10.1103/PhysRevLett.111.107401.

[28] D. Golla, A. Brasington, B. J. LeRoy and A. Sandhu, *Ultrafast relaxation of hot phonons in graphene-hBN heterostructures*, APL Materials 5(5), 056101 (2017), doi:10.1063/1.4982738.

[29] Y. Yang, D. Ostrowski, R. France, K. Zhu, J. van de Lagemaat, J. Luther and M. Beard, *Observation of a hot-phonon bottleneck in lead-iodide perovskites*, Nat. Photon. 10, 53 (2016), doi:org/10.1038/nphoton.2015.213.

[30] J. Koivistoinen, P. Myllyperkiö and M. Pettersson, *Time-Resolved Coherent Anti-Stokes Raman Scattering of Graphene: Dephasing Dynamics of Optical Phonon*, The Journal of Physical Chemistry Letters 8(17), 4108 (2017), doi:10.1021/acs.jpclett.7b01711.

[31] E. M. Hamham, J. M. Iglesias, E. Pascual, M. J. Martín and R. Rengel, *Impact of the hot phonon effect on electronic transport in monolayer silicene*, Journal of Physics D: Applied Physics 51(41), 415102 (2018), doi:10.1088/1361-6463/aad94c.

[32] C. C. S. Chan, K. Fan, H. Wang, Z. Huang, D. Novko, K. Yan, J. Xu, W. C. H. Choy, I. Lončarić and K. S. Wong, *Uncovering the Electron-Phonon Interplay and Dynamical Energy-Dissipation Mechanisms of Hot Carriers in Hybrid Lead Halide Perovskites*, Advanced Energy Materials 11(9), 2003071 (2021), doi:https://doi.org/10.1002/aenm.202003071.

[33] F. Sekiguchi, H. Hirori, G. Yumoto, A. Shimazaki, T. Nakamura, A. Wakamiya and Y. Kanemitsu, *Enhancing the Hot-Phonon Bottleneck Effect in a Metal Halide Perovskite by Terahertz Phonon Excitation*, Phys. Rev. Lett. 126, 077401 (2021), doi:10.1103/PhysRevLett.126.077401.

[34] X. Tong and M. Bernardi, *Toward precise simulations of the coupled ultrafast dynamics of electrons and atomic vibrations in materials*, Phys. Rev. Res. 3, 023072 (2021), doi:10.1103/PhysRevResearch.3.023072.

[35] H. Seiler, D. Zahn, M. Zacharias, P.-N. Hildebrandt, T. Vasileiadis, Y. W. Windsor, Y. Qi, C. Carbogno, C. Draxl, R. Ernstorfer and F. Caruso, *Accessing the Anisotropic Nonthermal Phonon Populations in Black Phosphorus*, Nano Letters 0(0), null (0), doi:10.1021/acs.nanolett.1c01786.
[36] E. Baldini, A. Mann, L. Benfatto, E. Cappelluti, A. Acocella, V. M. Silkin, S. V. Eremeev, A. B. Kuzmenko, S. Borroni, T. Tan, X. X. Xi, F. Zerbetto et al., Real-Time Observation of Phonon-Mediated $\sigma-\pi$ Interband Scattering in MgB$_2$, Phys. Rev. Lett. 119, 097002 (2017), doi:10.1103/PhysRevLett.119.097002

[37] D. Novko, F. Caruso, C. Draxl and E. Cappelluti, Ultrafast Hot Phonon Dynamics in MgB$_2$ Driven by Anisotropic Electron-Phonon Coupling, Phys. Rev. Lett. 124, 077001 (2020), doi:10.1103/PhysRevLett.124.077001

[38] A. Y. Liu, I. I. Mazin and J. Kortus, Beyond Eliashberg Superconductivity in MgB$_2$: Anharmonicity, Two-Phonon Scattering, and Multiple Gaps, Phys. Rev. Lett. 87, 087005 (2001), doi:10.1103/PhysRevLett.87.087005

[39] J. M. An and W. E. Pickett, Superconductivity of MgB$_2$: Covalent Bonds Driven Metallic, Phys. Rev. Lett. 86, 4366 (2001), doi:10.1103/PhysRevLett.86.4366

[40] T. Yildirim, O. Gülsen, J. Lynn, C. Brown, T. Udovic, Q. Huang, N. Rogado, K. Regan, M. Hayward, J. Slusky, T. He, M. Haas et al., Giant Anharmonicity and Nonlinear Electron-Phonon Coupling in MgB$_2$: A Combined First-Principles Calculation and Neutron Scattering Study, Phys. Rev. Lett. 87, 037001 (2001), doi:10.1103/PhysRevLett.87.037001

[41] H. J. Choi, D. Roundy, H. Sun, M. L. Cohen and S. G. Louie, First-principles calculation of the superconducting transition in MgB$_2$ within the anisotropic Eliashberg formalism, Phys. Rev. B 66, 020513 (2002), doi:10.1103/PhysRevB.66.020513

[42] H. J. Choi, D. Roundy, H. Sun, M. L. Cohen and S. G. Louie, The origin of the anomalous superconducting properties of MgB$_2$, Nature 418, 758 (2002), doi:10.1038/nature00898

[43] Y. Kong, O. Dolgov, O. Jepsen and O. Andersen, Electron-phonon interaction in the normal and superconducting states of MgB$_2$, Phys. Rev. B 64, 020501 (2001), doi:10.1103/PhysRevB.64.020501

[44] A. Golubov, J. Kortus, O. Dolgov, O. Jepsen, Y. Kong, O. Andersen, B. Gibson, K. Ahn and R. Kremer, Specific heat of MgB$_2$ in a one- and a two-band model from first-principles calculations, J. Phys.: Condens. Matter 14, 1353 (2002), doi:10.1088/0953-8984/14/6/320

[45] R. Gonnelli, D. Daghero, G. Ummarino, V. Stepanov, J. Jun, S. Kazakov and J. Karpinski, Direct Evidence for Two-Band Superconductivity in MgB$_2$ Single Crystals from Directional Point-Contact Spectroscopy in Magnetic Fields, Phys. Rev. Lett. 89, 247004 (2002), doi:10.1103/PhysRevLett.89.247004

[46] R. B. Versteeg, J. Zhu, P. Padmanabhan, C. Boguschewski, R. German, M. Goeddeke, P. Becker and P. H. M. van Loosdrecht, A tunable time-resolved spontaneous Raman spectroscopy setup for probing ultrafast collective excitation and quasiparticle dynamics in quantum materials, Structural Dynamics 5(4), 044301 (2018), doi:10.1063/1.5037784

[47] D. Novko, Nonadiabatic coupling effects in MgB$_2$ reexamined, Phys. Rev. B 98, 041112 (2018), doi:10.1103/PhysRevB.98.041112
[48] F. Carbone, D.-S. Yang, E. Giannini and A. H. Zewail, *Direct role of structural dynamics in electron-lattice coupling of superconducting cuprates*, Proc. Nat. Ac. of Sci. **105**, 20161 (2008), doi:10.1073/pnas.0811335106.

[49] F. Carbone, N. Gedik, J. Lorenzana and A. H. Zewail, *Real-Time Observation of Cuprates Structural Dynamics by Ultrafast Electron Crystallography*, Adv. Condens. Matter Phys. **2010**, 958618 (2010), doi:10.1155/2010/958618.

[50] R. P. Chatelain, V. R. Morrison, B. L. M. Klarenaar and B. J. Siwick, *Coherent and Incoherent Electron-Phonon Coupling in Graphite Observed with Radio-Frequency Compressed Ultrafast Electron Diffraction*, Phys. Rev. Lett. **113**, 235502 (2014), doi:10.1103/PhysRevLett.113.235502.

[51] M. Harb, H. Enquist, A. Jurgilaitis, F. Tuyakova, A. N. Obraztsov and J. Larsson, *Phonon-phonon interactions in photoexcited graphite studied by ultrafast electron diffraction*, Phys. Rev. B **93**, 104104 (2016), doi:10.1103/PhysRevB.93.104104.

[52] L. Waldecker, R. Bertoni, H. Hübener, T. Brumme, T. Vasileiadis, D. Zahn, A. Rubio and R. Ernstorfer, *Momentum-Resolved View of Electron-Phonon Coupling in Multilayer WSe2*, Phys. Rev. Lett. **119**, 036803 (2017), doi:10.1103/PhysRevLett.119.036803.

[53] M. J. Stern, L. P. René de Cotret, M. R. Otto, R. P. Chatelain, J.-P. Boisvert, M. Sutton and B. J. Siwick, *Mapping momentum-dependent electron-phonon coupling and nonequilibrium phonon dynamics with ultrafast electron diffuse scattering*, Phys. Rev. B **97**, 165416 (2018), doi:10.1103/PhysRevB.97.165416.

[54] T. Konstantinova, J. D. Rameau, A. H. Reid, O. Abdurazakov, L. Wu, R. Li, X. Shen, G. Gu, Y. Huang, L. Rettig, I. Avigo, M. Ligges et al., *Nonequilibrium electron and lattice dynamics of strongly correlated Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ single crystals*, Sci. Adv. **4**, eaap7427 (2018), doi:10.1126/sciadv.aap7427.

[55] D. Zahn, P.-N. Hildebrandt, T. Vasileiadis, Y. W. Windsor, Y. Qi, H. Seiler and R. Ernstorfer, *Anisotropic Nonequilibrium Lattice Dynamics of Black Phosphorus*, Nano Letters **20**(5), 3728 (2020), doi:10.1021/acs.nanolett.0c00734.

[56] M. R. Otto, J.-H. Pöhls, L. P. R. de Cotret, M. J. Stern, M. Sutton and B. J. Siwick, *Mechanisms of electron-phonon coupling unraveled in momentum and time: The case of soft phonons in TiSe$_2$*, Sci. Adv. **7**(20), eabf2810 (2021), doi:10.1126/sciadv.abf2810.

[57] M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. C. Kelires and R. Ernstorfer, *Multiphonon diffuse scattering in solids from first principles: Application to layered crystals and two-dimensional materials*, Phys. Rev. B **104**, 205109 (2021), doi:10.1103/PhysRevB.104.205109.

[58] M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. C. Kelires and R. Ernstorfer, *Efficient First-Principles Methodology for the Calculation of the All-Phonon Inelastic Scattering in Solids*, Phys. Rev. Lett. **127**, 207401 (2021), doi:10.1103/PhysRevLett.127.207401.

[59] D. Novko and M. Kralj, *Phonon-assisted processes in the ultraviolet-transient optical response of graphene*, npj 2D Materials and Applications **3**(1) (2019), doi:10.1038/s41699-019-0131-5.
[60] F. Caruso, D. Novko and C. Draxl, Photoemission signatures of nonequilibrium carrier dynamics from first principles, Phys. Rev. B 101, 035128 (2020), doi:10.1103/PhysRevB.101.035128.

[61] F. Caruso, Nonequilibrium Lattice Dynamics in Monolayer MoS$_2$, The Journal of Physical Chemistry Letters 12(6), 1734 (2021), doi:10.1021/acs.jpclett.0c03616.

[62] L. Boeri, J. Kortus and O. K. Andersen, Three-Dimensional MgB$_2$-Type Superconductivity in Hole-Doped Diamond, Phys. Rev. Lett. 93, 237002 (2004), doi:10.1103/PhysRevLett.93.237002.

[63] F. Giustino, J. R. Yates, I. Souza, M. L. Cohen and S. G. Louie, Electron-Phonon Interaction via Electronic and Lattice Wannier Functions: Superconductivity in Boron-Doped Diamond Reexamined, Phys. Rev. Lett. 98, 047005 (2007), doi:10.1103/PhysRevLett.98.047005.

[64] B. Mansart, M. J. G. Cottet, G. F. Mancini, T. Jarlborg, S. B. Dugdale, S. L. Johnson, S. O. Mariager, C. J. Milne, P. Beaud, S. Grübel, J. A. Johnson, T. Kubacka et al., Temperature-dependent electron-phonon coupling in La$_{2-x}$Sr$_x$CuO$_4$ probed by femtosecond x-ray diffraction, Phys. Rev. B 88, 054507 (2013), doi:10.1103/PhysRevB.88.054507.

[65] S. L. Johnson, M. Savoini, P. Beaud, G. Ingold, U. Staub, F. Carbone, L. Castiglioni, M. Hengsberger and J. Osterwalder, Watching ultrafast responses of structure and magnetism in condensed matter with momentum-resolved probes, Struct. Dyn. 4, 061506 (2017), doi:10.1063/1.4996176.

[66] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov and L. L. Boyer, Superconductivity of Metallic Boron in MgB$_2$, Phys. Rev. Lett. 86, 4656 (2001), doi:10.1103/PhysRevLett.86.4656.

[67] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo and et al., QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, Journal of Physics: Condensed Matter 21(39), 395502 (2009), doi:10.1088/0953-8984/21/39/395502.

[68] J. P. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865 (1996), doi:10.1103/PhysRevLett.77.3865.

[69] S. Baroni, S. de Gironcoli, A. Dal Corso and P. Giannozzi, Phonons and related crystal properties from density-functional perturbation theory, Rev. Mod. Phys. 73, 515 (2001), doi:10.1103/RevModPhys.73.515.

[70] S. Poncé, E. Margine, C. Verdi and F. Giustino, EPW: Electron–phonon coupling, transport and superconducting properties using maximally localized Wannier functions, Computer Physics Communications 209, 116 (2016), doi:https://doi.org/10.1016/j.cpc.2016.07.028.

[71] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza and D. Vanderbilt, Maximally localized Wannier functions: Theory and applications, Rev. Mod. Phys. 84, 1419 (2012), doi:10.1103/RevModPhys.84.1419.
[72] K.-P. Bohnen, R. Heid and B. Renker, *Phonon Dispersion and Electron-Phonon Coupling in MgB$_2$ and AlB$_2$*, Phys. Rev. Lett. **86**, 5771 (2001), doi:10.1103/PhysRevLett.86.5771.

[73] B. Renker, K. Bohnen, R. Heid, D. Ernst, H. Schober, M. Koza, P. Adelmann, P. Schweiss and T. Wolf, *Strong Renormalization of Phonon Frequencies in Mg$_{1-x}$Al$_x$B$_2$*, Phys. Rev. Lett. **88**, 067001 (2002), doi:10.1103/PhysRevLett.88.067001.

[74] A. Shukla, M. Calandra, M. d’Astuto, M. Lazzeri, F. Mauri, C. Bellin, M. Krisch, J. Karpinski, S. M. Kazakov, J. Jun, D. Daghero and K. Parlinski, *Phonon Dispersion and Lifetimes in MgB$_2$*, Phys. Rev. Lett. **90**, 095506 (2003), doi:10.1103/PhysRevLett.90.095506.

[75] M. d’Astuto, M. Calandra, S. Reich, A. Shukla, M. Lazzeri, F. Mauri, J. Karpinski, N. D. Zhigadlo, A. Bossak and M. Krisch, *Weak anharmonic effects in MgB$_2$: A comparative inelastic x-ray scattering and Raman study*, Phys. Rev. B **75**, 174508 (2007), doi:10.1103/PhysRevB.75.174508.

[76] P. B. Allen, *Theory of thermal relaxation of electrons in metals*, Phys. Rev. Lett. **59**, 1460 (1987), doi:10.1103/PhysRevLett.59.1460.

[77] C. Lui, K. Mak, J. Shan and T. Heinz, *Ultrafast Photoluminescence from Graphene*, Phys. Rev. Lett. **105**, 127404 (2010), doi:10.1103/PhysRevLett.105.127404.

[78] S. Dal Conte, C. Giammelli, G. Coslovich, F. Clineto, D. Bossini, T. Abebaw, F. Banfi, G. Ferrini, H. Eisaki, M. Greven, A. Damascelli, D. van der Marel et al., *Disentangling the Electronic and Phononic Glue in a High-Tc Superconductor*, Science **335**(6076), 1600 (2012), doi:10.1126/science.1216765.

[81] I.-K. Jeong, R. H. Heffner, M. J. Graf and S. J. L. Billinge, *Lattice dynamics and correlated atomic motion from the atomic pair distribution function*, Phys. Rev. B **67**, 104301 (2003), doi:10.1103/PhysRevB.67.104301.

[82] G. Campi, E. Cappelluti, T. Proffen, X. Qiu, E. Bozin, S. Billinge, S. Agrestini, N. Saini and A. Bianconi, *Study of temperature dependent atomic correlations in MgB$_2$*, Eur. Phys. J. B **52**, 15 (2006), doi:10.1140/epjb/e2006-00269-7.

[83] The values of $\rho_{B-B}$ at steady conditions computed here appears larger than the values experimentally estimated in Ref. [82]. One should consider however that we evaluate here only the contribution of the lattice dynamics to the lattice correlations $\sigma_{B-B}$. The effects of static disorder was modelled in Ref. [82] by means of a constant correction term $\sigma_0^2(i\alpha)$ in the lattice mean-square displacements $\sigma^2(i\alpha)$, but, in the absence of a well-accepted modelling of the effects of disorder of the interatomic correlation, no effect of disorder was included in the analysis of $\sigma_{B-B}$. We note that a constant upwards offshift of
the theoretical $\sigma_{B-B}$ would improve significantly the agreement between theoretical and experimental estimates of $\sigma_{B-B}$, and bring thus the experimental estimation of $\rho_{B-B}$ closer to the theoretical predictions $\rho_{B-B} \approx 0.24$. Also, the presence of nonadiabatic effects and the possible breaking of the harmonic approximation might account for such discrepancy.

[84] R. E. Cohen, W. E. Pickett and H. Krakauer, *First-Principles Phonon Calculations for La$_2$CuO$_4*, Phys. Rev. Lett. 62, 831 (1989), doi:10.1103/PhysRevLett.62.831.

[85] W. E. Pickett, *Electronic structure of the high-temperature oxide superconductors*, Rev. Mod. Phys. 61, 433 (1989), doi:10.1103/RevModPhys.61.433.

[86] M. Trigo, J. Chen, V. H. Vishwanath, Y. M. Sheu, T. Graber, R. Henning and D. A. Reis, *Imaging nonequilibrium atomic vibrations with x-ray diffuse scattering*, Phys. Rev. B 82, 235205 (2010), doi:10.1103/PhysRevB.82.235205.

[87] L. J. P. Ament, M. van Veenendaal, T. P. Devereaux, J. P. Hill and J. van den Brink, *Resonant inelastic x-ray scattering studies of elementary excitations*, Rev. Mod. Phys. 83, 705 (2011), doi:10.1103/RevModPhys.83.705.

[88] M. Mitrano and Y. Wang, *Probing light-driven quantum materials with ultrafast resonant inelastic X-ray scattering*, Comm. Phys. 3 (2020), doi:10.1038/s42005-020-00447-6.