Ab initio calculation of low-energy collective charge-density excitations in MgB$_2$

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(Dated: September 6, 2009)

We present ab-initio time-dependent density-functional theory calculation results for low-energy collective electron excitations in MgB$_2$. The existence of a long-lived collective excitation corresponding to coherent charge density fluctuations between the boron $\sigma$- and $\pi$-bands ($\pi\pi$ mode) is demonstrated. This mode has a sine-like oscillating dispersion for energies below 0.5 eV. At even lower energy we find another collective mode ($\sigma\sigma$ mode). We show the strong impact of local-field effects on dielectric functions in MgB$_2$. These effects account for the long $q$-range behavior of the modes. We discuss the physics that these collective excitations bring to the energy region typical for lattice vibrations.

PACS numbers: 74.25.Kc, 71.45.Gm, 73.43.Lp, 74.70.Ad

After several years of intense experimental and theoretical study of the origin of unusually high-temperature superconductivity in MgB$_2$, nowadays there is a general belief that the superconductivity in MgB$_2$ is phonon-mediated with multiple gaps and an exceptional role played by $E_{2g}$ phonon mode in strong coupling to electrons in the tubular-shaped $\sigma$ bands at the Fermi level, $E_F$. However, despite the tremendous progress achieved in understanding of superconductivity in MgB$_2$, many of its fundamental properties related to phonons and electron-phonon ($e-ph$) coupling are still puzzling and remain under intense debate. Thus such important issues as, e.g., the reduced isotope effect, unusually broad linewidth of the $E_{2g}$ mode in Raman spectra, the unusually broad linewidth of the $E_{2g}$ phonon mode seen in Raman spectra, and the inconsistency between the results of Raman scattering and x-ray measurements and the role of non-adiabatic effects, have not yet found satisfactory explanations.

As for the electronic part of the $e-ph$ picture of superconductivity in MgB$_2$, it has received substantially less attention than the phonon part. In particular, in all evaluations of the $e-ph$ interaction the adiabatic approximation has been used, and even in ab initio calculations of $T_c$, the dynamical Coulomb interaction has been considered in its static form. Here we present a detailed ab initio study of the low-energy dynamical electronic properties of MgB$_2$. We demonstrate that the strongly anisotropic electronic structure of MgB$_2$ characterized by boron quasi two-dimensional $\sigma$ and three-dimensional $\pi$ bands leads to remarkable low-energy dielectric response in this compound: collective modes with a peculiar sine-like oscillating dispersion appear in the 0-0.5 eV energy range. This brings interesting physics to the energy region which was thought to be entirely dominated by lattice vibrations.

Our approach is based on time-dependent density functional theory calculations by lattice vibrations.
FIG. 1: (color). Calculated $-\text{Im}[\varepsilon^{-1}(q_c, \omega)]$ versus $\omega$ and $q_c$ in two energy regions. Calculations include local-field effects and the RPA kernel. In (a) the circles and squares mark the energy-loss peak positions measured in x-ray scattering experiments of Refs. 21 and 22, respectively. In (b) the dispersion of the upper sharp $\sigma\pi$ plasmon peak is described by $\omega_{\sigma\pi} = V_{\sigma\pi} \cdot \sin(E_{\text{f}} q_c)$ (green dashed line) with $V_{\sigma\pi} = 0.48$ eV. The lower broad feature with similar sine-like dispersion corresponds to the $\sigma\pi$ plasmon. Yellow solid lines present acoustic plasmon dispersion according to Ref. 32.

exchange-correlation potential of Ref. 21. In order to elucidate the role of exchange-correlation effects in the density-response function, we performed calculations of $\chi$ using two forms of the many-body kernel $K_{xc}$, namely the random-phase approximation (RPA) ($K_{xc}=0$), and an adiabatic extension of the local-density approximation (TDLDA).22

The calculated loss function, $-\text{Im}[\varepsilon^{-1}(q_c, \omega)]$ directly probed in inelastic scattering experiments is presented in Fig. 1 as a function of the momentum transfer $q$ along the $c^*$ axis. In the upper energy range (Fig. 1b) it is dominated by a well-defined collective mode dispersing in the 2.5-4.5 eV energy range in excellent agreement with x-ray experiments.21,22 The existence of this mode for momenta in the first BZ was demonstrated in Refs. 21 and 22, whereas its cosine-like oscillating dispersion in higher BZ’s was recently discovered in a joint experimental-theoretical study.23 This mode produces a strong impact on electrodynamical and optical properties of MgB$_2$, however, it has no relevance to superconductivity as it affects neither the dynamically screened Coulomb interaction at low energies nor phonon dispersion.22

Figure 1 shows the calculated loss function in the low-energy domain that is our main finding. At all $q_c$ it is dominated by a sharp “$\sigma\pi$” peak with a sine-like dispersion. Figure 2 shows the dielectric and loss functions at $q_c = 0.205$ a.u. and $q_c = 0.322$ a.u. One can see how the presence of two types of carriers (in the $\sigma$ and $\pi$ bands) around $E_F$ (see Fig. 3b) with a large difference in the perpendicular component of the group velocity, $v^\perp$, (compare maximal $v^\perp$ in the $\pi$ bands (Fig. 3b) with that in the $\sigma$ bands (Figs. 3a and 3c)) produces in Im$\varepsilon$ a structure consisting of two main peaks (Fig. 3a). Thus, while the faster $\pi$ carriers give rise to a broad structure from 0 to 0.68 eV in Fig. 2a with the main peak at the upper-energy side, the $\sigma$ carriers which are moving more slowly in the $c^*$ direction produce a sharp peak in the low-energy part of Im$\varepsilon$. The reason of this sharpness resides in the fact that within both $\sigma$ bands, the number of states with maximal $v^\perp$ is greatly enhanced as seen in Figs. 3a and 3b. Therefore, the number of intra-band transitions involving these fast states is large which strongly enhances the $\sigma$ peak in Im$\varepsilon$ at the higher energies. In turn, this causes a dramatic drop in Re$\varepsilon$ at nearly the same energy which, combined with the presence of a local minimum around $\omega = 0.1$ eV in Im$\varepsilon$, produces a well-defined sharp peak in $-\text{Im}[\varepsilon^{-1}]$ corresponding to charge density fluctuations between the $\sigma$ and $\pi$ bands, a $\sigma\pi$ mode. Despite the presence of a non-vanishing value of Im$\varepsilon$ at the $\omega$ where the $\sigma\pi$ peak appears, its intrinsic width is extremely small, being in the meV range (which corresponds to a lifetime of few hundreds of femtoseconds), and is almost entirely determined by an extrinsic broadening parameter $\gamma$.

Since at small $q_c$ the two main peaks in Im$\varepsilon$ disperse linearly with momentum according to their maximal perpendicular Fermi velocity components, $\text{Im} \propto v_{F,\max}^\perp \cdot q_c$, the dispersion of the $\sigma\pi$ mode (linked to the upper side of the continuum for electron-hole excitations within the $\sigma$ bands) is also linear in $q_c$ and its group velocity $v_{\sigma\pi}$ is close to $v_{F,\max}^\sigma$. This corresponds to the acoustic plasmon proposed to exist in MgB$_2$ on the basis of a model tight-binding calculation.22 The concept of an acoustic plasmon goes back to Pines23 who showed that it can occur in a two-component electron plasma consisting of slow and fast carriers. The fast carriers (within the $\pi$ bands in MgB$_2$) can act to screen the repulsion between slow carriers (within the $\sigma$ bands in MgB$_2$) resulting in the appearance of a plasmon mode with a peculiar
sound-like dispersion. After the recognition of the role in the acoustic plasmon as a possible mechanism for superconductivity in transition metals, it has been regularly evoked for explaining superconductivity in materials with unusually high \( T_c \). Nevertheless, up to now the issue remains controversial since the very existence of such a collective mode in metals has been confirmed neither experimentally nor by \textit{ab initio} calculations. Only recently an acoustic-like plasmon was observed in the electron energy-loss measurements at a metal surface in excellent agreement with the \textit{ab initio} prediction, thus greatly increasing our confidence in the present results.

With increasing \( q_c \), the \( \sigma \) peak in \( \Im e^{-1} \), and consequently the \( \sigma \pi \) peak in \( -\Im e^{-1} \), starts to split into two peaks (Figs. 1a and 2b) since for holes, \( v_{\text{max}}^{\sigma \alpha} \) exceeds \( v_{\text{max}}^{\sigma \beta} \) by more than 20% (Figs. 3c and 3d). In this case the higher(lower)-energy plasmon peak in \( -\Im e^{-1} \) corresponds to the charge fluctuations between \( \sigma_1 \) and \( \pi \) \( (\sigma_1 \) and \( \sigma_2 \) bands. Whereas the \( \sigma \pi \) plasmon continues to be long-lived, the lower-energy \( \sigma \sigma \) plasmon has a significantly shorter lifetime due to more efficient scattering within the \( \sigma_1 \) band. We expect the two separate modes to exist at any \( q_c \), however, when the calculated broadening \( \gamma \) exceeds the energy difference between these modes only a single \( \sigma \pi \) peak arises in \( -\Im e^{-1} \) (Fig. 4).

In Fig. 1b one can see how with increasing \( q_c \) both of these plasmon modes reach maximum energy at the A point and, as momentum increases further, their dispersions change from positive to negative and approach \( \omega = 0 \) at the \( \Gamma \) point in the second BZ, in striking contrast to results of Ref. 32. The origin of this periodic behavior resides in the fact that strong local-field effects in \( \text{MgB}_2 \) feed the strength from the small \( q_c \) modes into the charge density fluctuations at large \( (q_c + G_z) \) in a similar fashion as occurs in the case of the higher energy mode. These sine-like dispersing modes continue to have strength at momenta in subsequent BZ’s and this is a direct consequence of a layered \( \text{MgB}_2 \) structure. Additionally, as seen in Fig. 2 the local-field effects lead to a blue shift of the \( \sigma \sigma \) and \( \sigma \pi \) energy and make the \( \sigma \pi \) peak more narrow as it occurs for \( \omega \) corresponding to smaller \( \Im e^{-1} \). We also analyzed the role of exchange-correlation effects beyond the RPA and found that the RPA picture is essentially sufficient for the description of low-energy collective excitations in \( \text{MgB}_2 \). The inclusion of the TDLCDA kernel in the calculation of \( \chi(q_c, \omega) \) leads to only a small (few percent) downward shift of the plasmon mode dispersions with a slight reduction of their lifetimes, i.e., in part compensating the local-field effects.

The \( \sigma \pi \) plasmon can have deep impact on both low-energy-electron and phonon dynamics in \( \text{MgB}_2 \). Our calculation reveals dramatic modification of the dynamical Coulomb interaction in the energy range vital for superconductivity. In Fig. 2 one can see that in the neighborhood of the \( \sigma \pi \) plasmon energy the calculated \( \Re e\{\epsilon(q_c, \omega)\} \) differs dramatically from static \( \epsilon(q_c, \omega = 0) \) as well as from the free electron gas result. In particular, in a certain momentum-energy phase space region, \( \Re e \) is even negative leading to overall reduction of Coulomb repulsion between carriers. This could explain in part the observed reduced isotope effect in \( \text{MgB}_2 \). It would be of great interest to quantify this effect within the \textit{ab}
initio approach.\textsuperscript{15} Note, that the $\sigma\pi$ plasmon does not influence inter-band $\sigma\pi$ and intra-band $\sigma$ scattering due to the phase-space restrictions, although could have some effect in the intra-band $\pi$ one.

The $\sigma\pi$ plasmon can dramatically affect the dispersion of the optical phonon modes in the “pathological” region of small $\mathbf{q}$\textsuperscript{14} offering an unexpected explanation of widely-discussed discrepancies between the Raman and x-ray measurements of the phonon structure in MgB$\textsubscript{2}$. The $\sim 77$ meV peak observed in Raman-scattering experiments and commonly attributed to the boron $E_{2g}$ phonon mode is always strongly renormalized in comparison with a bare phonon dispersion, whereas the x-ray experiments performed for large $q_e$ do not see any appreciable renormalization. In Fig.\textsuperscript{4} we show the calculated dispersion of the bare $\sigma\pi$ mode along with the bare $E_{2g}$ phonon mode\textsuperscript{2} compared to the experimental data.$^8$\textsuperscript{15} One can see how the two bare curves cross each other close to the $\Gamma$ point. Due to its localization in the boron plane the $\sigma\pi$ plasmon strongly interacts with the boron $E_{2g}$ phonon mode resulting in strong hybridization of these boson modes. The result shown by green and blue dashed lines in Fig.\textsuperscript{4} demonstrates that the mode seen in the Raman experiments is indeed a strongly hybridized “$\sigma\pi\cdot E_{2g}$” $P^\circ$ mode. Note, that the finite electron lifetime effect\textsuperscript{11,14} can also contribute to the upward shift of this mode. Additionally, a steep $\sigma\pi$ plasmon dispersion at small momenta might explain the existence of the strong unstructured background (commonly mentioned as being of unknown electronic origin) observed in the Raman experiments. This is corroborated by the fact that, e.g., in AlB$\textsubscript{3}$, where we do not expect the existence of such a plasmon, this background does not appear.$^5$\textsuperscript{38}

In conclusion, our detailed \textit{ab initio} calculation demonstrates the existence in MgB$\textsubscript{2}$ in the 0-0.5 eV energy range of hitherto unknown long-lived collective mode that corresponds to coherent charge fluctuations between the boron $\sigma$ – and $\pi$ – bands ($\sigma\pi$ mode) with striking periodic sine-like dispersion. This mode shows an acoustic-like behavior at small momenta where it can strongly interact with optical phonons. Additionally we find at slightly lower energy a more strongly damped mode that corresponds to charge fluctuations between two different $\sigma$ bands ($\sigma\sigma$ mode). Both these modes have profound impact on the low-energy dynamical Coulomb interaction which should be explicitly taken into account in \textit{ab initio} theories of superconductivity to have the predictive power.

We acknowledge partial support from the University of the Basque Country (Grant No. GIC07IT36607), the Departamento de Educación del Gobierno Vasco, and the Spanish Ministerio de Ciencia y Tecnología (MCyT) (Grant No. FIS20076671C0101).

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