

Multigap superconductivity in HgS under pressure

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Mercury chalcogenides are a class of materials that exhibit many structural phases under pressure, hosting exotic physical properties, including topological phases and chiral phonons. In particular, recent experimental results [Zhang *et al.*, *Phys. Rev. B* **110**, L060502 (2024)] on HgS report a new superconducting phase at ~ 21 GPa, whose origin is unknown. In this work, we theoretically investigate the pressure-induced structural phase transition in HgS and the resulting emergence of superconductivity. Remarkably, we find that this phase supports a two-gap superconducting state arising from distinct Fermi surface sheets. The unusually high critical temperature of ~ 11 K emerges naturally within this multiband scenario, highlighting the role of interband coupling beyond isotropic approximation. These results place HgS among the few systems where multiband superconductivity is observed.

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I. INTRODUCTION

The discovery of topological surface states in mercury monochalcogenide HgTe [1,2] represented one of the major recent achievements in science drawing new scenarios for research in condensed-matter physics. With this boost, the interest in related systems with similar topological properties have grown significantly. In particular, the topological properties of mercury monochalcogenides (HgS, HgSe, HgTe) are being increasingly investigated, with a particular focus on modifying their electronic properties and topology by applying pressure or strain [2–7], thereby exploring their phase diagrams in greater depth.

In this class of materials, mercury sulfide (HgS) is the less favorable candidate to exhibit topological features due to its structural and electronic differences with respect to the other mercury chalcogenides (HgTe and HgSe) [5,7].

In fact, at ambient pressure, both HgTe and HgSe crystallize in a zincblende structure and are semimetals with a single Dirac point at the center of the Brillouin zone [4,8]. In contrast, HgS zincblende phase is found to be metastable at ambient pressure [9] in favor of the cinnabar crystal structure that is the ground state of the system. The cinnabar structure is characterized by a threefold helical chains arranged in a hexagonal crystal structure, which gives rise to its chiral properties [10–12] (for more structural details see Appendix A). In this phase, HgS is a semiconductor [3,13]. As a function of pressure, HgS exhibits a transition to a rock salt (RS)

phase in which the helical chains are broken, the Hg-S bonds are symmetrized, and the ratio between the out-of-plane and the in-plane lattice constants of the hexagonal crystal lattice becomes $\sqrt{6}$. In this new phase the system becomes metallic (see Appendix B for more details). This phase transition was deeply studied both experimentally and theoretically [3,9,13–23], with a wide range of possible critical pressures reported, from ~ 13 – 15 GPa [17,21] up to ~ 24 – 29 GPa [13,16,22,23], depending from the experimental techniques and/or the theoretical details used for simulations.

Recently, the discovery of superconductivity in the RS phase of HgS [3], just after the phase transition from the cinnabar phase, opens new scientific scenarios in the high-pressure physics of this compound. The measured critical temperature of ~ 11 K at 25.4 GPa [3] results in the highest critical temperatures in RS-type metal sulfide superconductors [24–26].

The discovery of such high critical temperatures in Hg-based compounds is puzzling and partially unexpected [27–29], where complete understanding of its origin is still unknown. With this aim, we studied the pressure-driven superconducting phase in HgS by first-principles density functional theory (DFT) [30–32] and the superconducting density functional theory (SCDFT) [33,34] approach (all the computational details can be found in Appendix C), revealing that the superconducting phase of HgS is very peculiar with the critical temperature boosted by two distinct *s*-wave superconducting gaps.

Two-gap superconductors (of which MgB₂ is the most notable example) are rather rare, presenting two superconducting energy gaps in the excitation spectra, related to different pairing mechanisms on different bands [35]. When this scenario occurs it often leads to an increase in the superconducting critical temperature [36,37] resulting in interesting physical properties [38].

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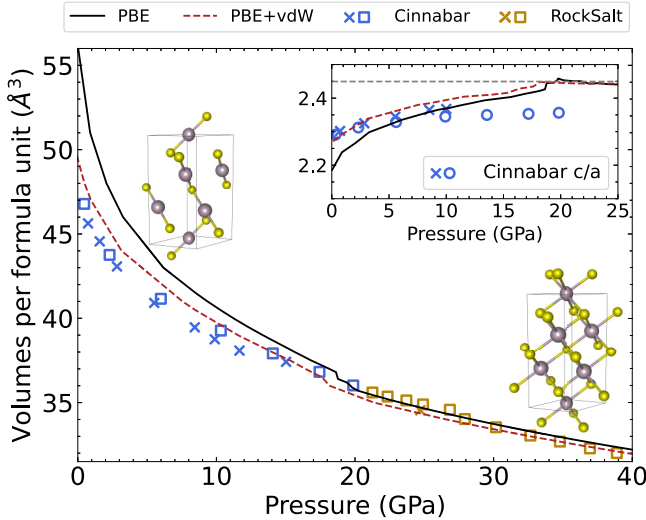


FIG. 1. Volume as a function of pressure. The solid black line represents the calculations performed using PBE exchange-correlation functional and the dashed red line the calculations performed using PBE exchange-correlation functional with vdW corrections. Symbols indicate the experimental values: $\square$ from Ref. [3] and $\times$ from Ref. [14]. Blue and gold symbols refer to the cinnabar and RS phases, respectively, as assigned by the authors (please note that the $\times$ point at highest pressure has not been unequivocally attributed to the RS phase by the authors). Inset: The c/a ratio as a function of pressure, computed with DFT (solid lines) and from the experimental values (blue $\circ$ and $\times$). The dashed gray line indicates $c/a = \sqrt{6}$.

II. STRUCTURAL PHASE TRANSITION UNDER PRESSURE

As anticipated, the pressure phase diagram of HgS hinders subtle aspects that have contributed to discrepancies in both experimental and theoretical studies in the determination of the cinnabar-to-rock salt transition pressure. In particular, the calculated equation of state under pressure using the PBE exchange-correlation functional reported a transition pressure of 15.8 GPa [21], while, using the meta-GGA SCAN functional, the transition pressure increases up to 21.9 GPa [21], much closer to the recent experimental observations by Zhang *et al.* [3] (~ 21 GPa).

Although this evidence points to the need of meta-GGA functional to describe the high-pressure physics of HgS, we decided to reconsider the problem using different functionals and tight computational parameters (see Appendix B for details). Considering the helical structure of the cinnabar phase, we corrected the PBE functional including van der Waals (vdW) contribution to account for interactions between the chains.

In Fig. 1 we report the calculated HgS volume as a function of pressure using PBE and PBE + vdW corrections compared with the experimental results [3,14] (blue and gold symbols for the cinnabar and RS phases, respectively). The theoretical transition pressure has been estimated as the pressure at which the c/a ratio reaches $\sqrt{6}$ (see the inset of Fig. 1). This marks the point where the helical structure of the cinnabar phase is fully suppressed and the system evolves continuously into the

more symmetric RS phase. In fact, the cinnabar phase can be viewed as a RS structure with the c axis compressed along the [111] direction of the primitive RS crystal lattice (more details on the crystal lattice and the transition from the cinnabar to the RS phase can be found in Appendix A).

As expected, the PBE functional fails in predicting the equilibrium volume and the equation of state for the semiconducting cinnabar phase, while the metallic RS phase is properly described. Van der Waals corrections strongly improves the theoretical results which are now in excellent agreement with the experimentally measured values (Fig. 1, dashed-red line).

At variance with the calculations reported by Shahi *et al.* [21], we find that the transition pressure obtained with PBE functional is in good agreement with that predicted using the SCAN functional and with the experimental data from Zhang *et al.* [3] (21 GPa).

We want to underline the importance of computational details in the determination of the right transition pressure: Due to the low energy gap of the cinnabar phase and its closure increasing the pressure, high electronic temperature results in a lower transition pressure. Properly converging this value, both functionals agree in predicting the critical transition pressure (see Appendices A and B).

The structural phase transition from cinnabar to rock salt is accompanied by a semiconducting to metal transition [3], this experimental evidence is confirmed by our band-structure calculations (see Appendix B). Experiments report a direct to indirect-gap transition as a function of pressure [3]. Our calculations indeed predict a change in slope of the (minimum) band gap as a function of the pressure, although the gap remains always indirect throughout the investigated pressure range. The discontinuity, observed in the calculation, is instead associated with the shift of the conduction band minimum within the Brillouin zone, suggesting an alternative interpretation of the experimental observation (see Appendix B).

III. ELECTRONIC STRUCTURE OF RS-HGS

When the system enters the RS phase, the electronic band structure, reported in Fig. 2, shows a metallic behavior with s -Hg electron-like band and s/p -S holelike derived bands cutting the Fermi level (ε_F) near the X and L points of the Brillouin zone (BZ), respectively (see Appendix D for further details of the band structure). Interestingly, the holelike and electron-like bands give rise to distinct sheets of the Fermi surface, characterized by nearly spherical pockets at the X point and S-derived tubular-like sheets connecting the equivalent L points of BZ (see inset in Fig. 2). These sheets do not cross and remain separate throughout the entire BZ. Furthermore, we point the presence of an incipient band very close to the Fermi level at Γ which, however, has a negligible density of states (as shown in details in Appendix G).

IV. LATTICE DYNAMICS AND ELECTRON-PHONON COUPLING

We explore the possible electron-phonon origin of the observed superconducting phase studying the dynamical

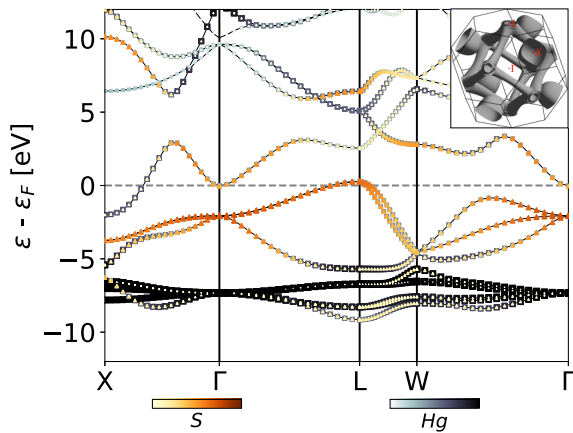


FIG. 2. Electronic band structure of HgS in the RS phase at 26 GPa calculated at PBE level. The red triangles represent the weight of the S-derived states, while the black squares of the Hg-derived states. Energies are referred to the Fermi level. The inset displays the Fermi surface of the system.

properties of HgS at 26 GPa. The phonon dispersion and density of states are presented in Fig. 3. The phonon modes show a separation between the low frequency branches, below 150 cm^{-1} , involving essentially Hg atoms and the optical S-derived modes, which slightly overlap around $120\text{--}150 \text{ cm}^{-1}$ energy range, as highlighted by the pseudogap in the phonon density of states. Interestingly, Hg-derived modes resembles that observed in pure Hg metal at ambient conditions, extending up to $\sim 130 \text{ cm}^{-1}$ [39]. Nevertheless, the characteristic strongly coupled low-energy branch which drives the superconducting phase in pure Hg [39] is now absent.

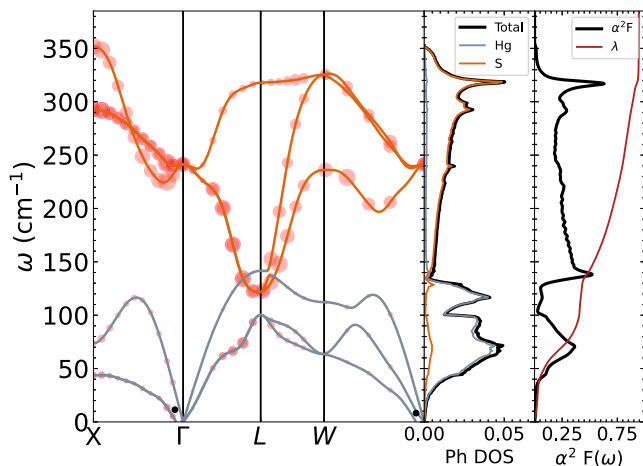


FIG. 3. The harmonic phonon dispersion of the RS phase at 26 GPa, calculated using the PBE exchange-correlation functional is reported in the left panel. Gray lines indicate Hg modes and orange ones the S modes. The relative strength of the electron-phonon interaction is visualized by circles whose area scales with the phonon linewidth γ_{qv} . The two black dots represent the calculated phonon frequencies at near- Γ q -point without interpolation (see text). In the central panel the projected phonon density of states is shown. In the right panel the Eliashberg function ($\alpha^2 F$) is reported in black. The solid red line is the electron-phonon coupling parameter as a function of frequency.

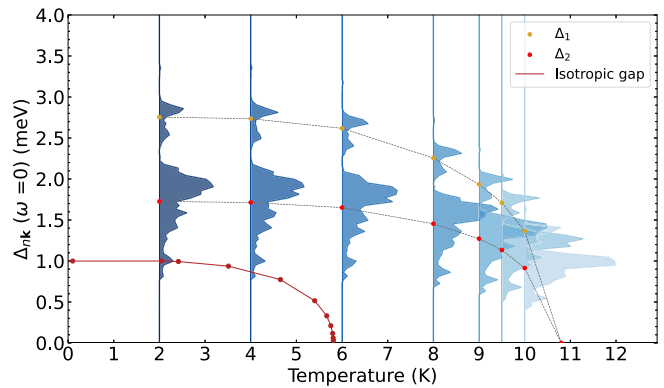


FIG. 4. Solution of the SCDFT anisotropic equation for the $\mathbf{k}$ -resolved superconducting gap as a function of temperature. A histogram shows the distribution of the superconducting gap as a function of the energy for each temperature. Red (Δ_2) and gold (Δ_1) points represent the “averaged” gaps at each temperature, obtained through a weighted average of the histograms in the two branches, and the dashed black-line connecting them is a guide for the eyes. In dark red, the isotropic solution.

The system presents many softenings: one in the Hg-acoustic phonon branches around the X and W points of the BZ, as well as along the Γ -L path, and a more evident anomaly in the S-optical mode at the L point, which causes the overlap between S and Hg modes. This overlap has a nontrivial aspect related to the character inversion between branches, as discussed in Appendix E. The slight instability observed close to Γ (along the Γ -X and W- Γ directions) originates from numerical aspects related to the fast Fourier transform interpolation to calculate the dispersion. In fact, first-principles calculations of the phonon frequency at the corresponding $\mathbf{q}$ -point (black points in Fig. 3) results in $\omega = 11 \text{ cm}^{-1}$, indicating that the system is indeed dynamically stable (this mode, however, has a negligible electron-phonon contribution). Notably, the RS phase remains dynamically stable even at lower pressure, below the thermodynamic transition pressure (19.6 GPa) up to 15.4 GPa, where the system becomes dynamically unstable (see Appendix E). This evidence suggests that the RS phase could persist as a metastable configuration in the $\sim 15\text{--}20 \text{ GPa}$ range opening to the possibility of enhancing electron-phonon coupling in this intermediate pressure regime.

The Eliashberg spectral function, shown in Fig. 3, yields an electron-phonon coupling constant of $\lambda = 0.95$. A significant contribution to this value arises from the softening of the lowest acoustic mode along the high-symmetry Γ -L direction, around 70 cm^{-1} . Both Hg- and S-derived phonon modes contribute roughly equally to the total coupling strength.

In order to explore the superconducting properties, we used the first-principles SCDFT [33,34] method, treating both the attractive electron-phonon and the repulsive screened electron-electron interactions equally (see Appendix F for further theoretical and computational details).

In Fig. 4, we report the isotropic solution of the SCDFT gap equation (red line) predicting $T_c = 5.8 \text{ K}$, a value that strongly disagrees with experimental observations.

Considering the peculiar Fermi surface of the system formed by distinct sheets with different orbital character, we explored the possibility of a multigap superconducting phase

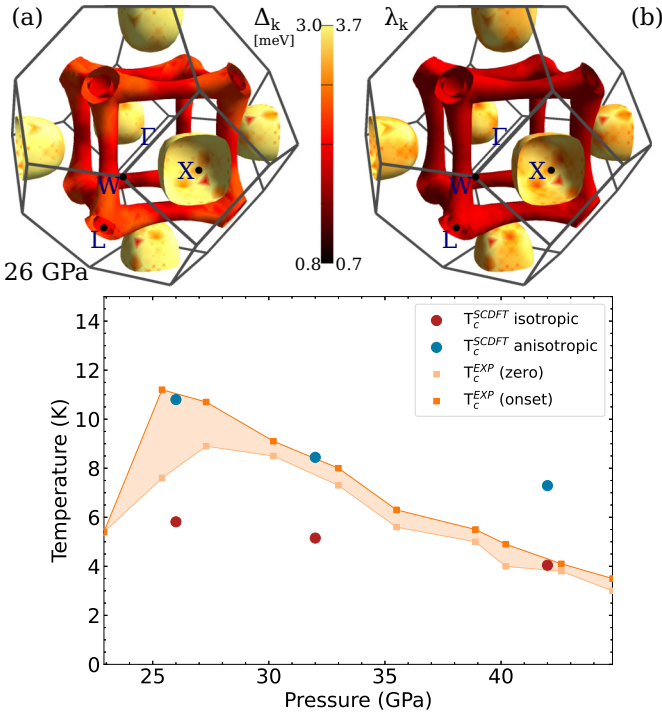


FIG. 5. Fermi surfaces of RS-HgS system. The color bar represents the magnitude of the SCDFT gap (a), and the k -resolved electron-phonon coupling (b). In the lower panel we report the superconducting critical temperature as a function of pressure estimated from the SCDFT isotropic (red) and anisotropic (blue) calculations. The shaded orange region highlights the experimental range between the T_c onset and zero resistivity temperature [3].

in HgS, in analogy with that observed in MgB_2 that exhibits comparable λ [40]. In fact, multigap superconductivity can arise in materials where multiple distinct bands contribute to the formation of the superconducting state. Each band, associated with a different Fermi surface sheet, can exhibit its own superconducting gap, which may vary in magnitude and phase depending on the interactions within and between the bands and in general can enhance the superconducting critical temperature with respect to the isotropic superconducting phase.

V. MULTIGAP SUPERCONDUCTIVITY

In Fig. 4 (blue-gradient histograms) we present the results of the anisotropic solution of the SCDFT gap equation as a function of the temperature. An explicit *ab initio* analysis of the screened Coulomb interaction and its impact on T_c has been performed and is discussed in Appendix F. The multigap nature of the superconducting state in RS-HgS is clearly visible: At $T = 2$ K, two distinct peaks appear at 1.7 meV and approximately 2.7 meV. These two superconducting gaps are associated with the two disconnected sheets of the Fermi surface [see Fig. 5(a)], which exhibit different orbital characters. In particular, the larger gap originates from the electron-like band at the X point, while the smaller gap is associated with the holelike Fermi-surface sheet. Additionally, a tiny isolated peak is observed around 3.3 meV, originating from the incipient electron pocket at the Γ point; however, its contribution

to the superconducting critical temperature is negligible due to the very low density of states (see Appendix G for more details).

To further substantiate the physical origin of the multigap superconducting state, we explicitly analyze the electron-phonon coupling λ_{nk} projected onto the Fermi surface [see Fig. 5(b)]. The resulting Fermi-surface-resolved map reveals a pronounced differentiation of λ_{nk} among the distinct Fermi surface sheets. In particular, the electron-like pockets and the holelike sheets display markedly different coupling strengths, providing direct evidence that the superconducting pairing is band selective.

Notably, the superconducting critical temperature, defined as the point where both the superconducting gaps reach zero, yields a $T_c = 10.8$ K. The predicted critical temperature is now in excellent agreement with experimental value showing that, as for MgB_2 , the multigap physics is responsible for the sizable increase of the superconducting critical temperature.

We extended the calculation to the whole pressure range in which the superconducting phase was measured [3], reporting the calculated T_c compared to the experimental measurements in Fig. 5(c) (we report a rough estimation of both the on-set temperature and the “zero resistivity” temperature as graphically extracted from Fig. 3(c) of Ref. [3]). The analysis of electronic, dynamical, and superconducting properties of the system at higher pressures are presented in Appendix H. The experimental superconducting critical temperature is maximum at pressures close to the structural phase transition and then decreases almost linearly. Our calculations confirm this trend with a good agreement up to about 33 GPa, Fig. 5(c). However, as we can see, the agreement between theoretical predictions and experimental results at higher pressure worsens. Interestingly, for the high-pressure region the isotropic solution seems to agree better with the measured T_c 's. At the moment, we do not have a physical explanation for this behavior, but we underline how the calculation of the critical temperature was performed using the state-of-the-art methodology and, if this evidence will be experimentally confirmed, it would pose a theoretical challenge. In particular, we do not reveal any discontinuities in both the repulsive Coulomb electron-electron interaction and attractive electron-phonon one as a function of pressure (see Appendix F and Appendix H for the pressure evolution of the electron-electron matrix elements as a function of the energy and of α^2F , respectively). However, given the sensitivity of multigap superconductors to interband scattering caused by impurities [41–44], a plausible hypothesis could be related to the experimental difficulties in maintaining sample purity (defect free) at elevated pressures. The presence of structural defects could increase the interband coupling averaging the gap over the different bands and thus decreasing the multiband character, eventually lowering the critical temperature.

VI. CONCLUSIONS

In conclusion, in this study we have provided a comprehensive theoretical investigation into the pressure-dependent phase diagram and superconducting properties of mercury sulfide. Our theoretical work predicts the HgS transition from its ambient pressure cinnabar phase to the metallic RS

structure in line with experimental observations. Furthermore, our exploration of the phonon dynamics revealed key insights into the modes driving the structural transition, with implications for superconductivity. We reveal the multigap superconducting nature of the RS phase with predicted critical temperatures resembling the experimental observations in a wide range of pressures. However, at high pressures ($\gtrsim 40$ GPa), the multigap solution overestimates T_c and the experiments seem to be explained by the isotropic solution, probably due to the emergence of pressure-induced defects. We also note that additional effects, such as anharmonic phonon renormalization and possible plasmon-mediated contributions to the pairing interaction, may become relevant under pressure and could further influence the superconducting properties. These aspects represent a promising direction for future theoretical and experimental investigations. We call for further experiments to better clarify these aspects.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX A: TRANSITION FROM CINNABAR TO ROCK SALT

The cinnabar structure is characterized by a threefold helical chains arranged in a hexagonal crystal structure [see Figs. 6(a) and 6(b)], with atoms located in $(u, u, 0)$, $(0, 1 - u, 2/3)$, and $(1 - u, 0, 1/3)$ for mercury and $(1 - v, 1 - v, 1/2)$, $(0, v, 1/6)$, and $(v, 0, 5/6)$ for sulfur.

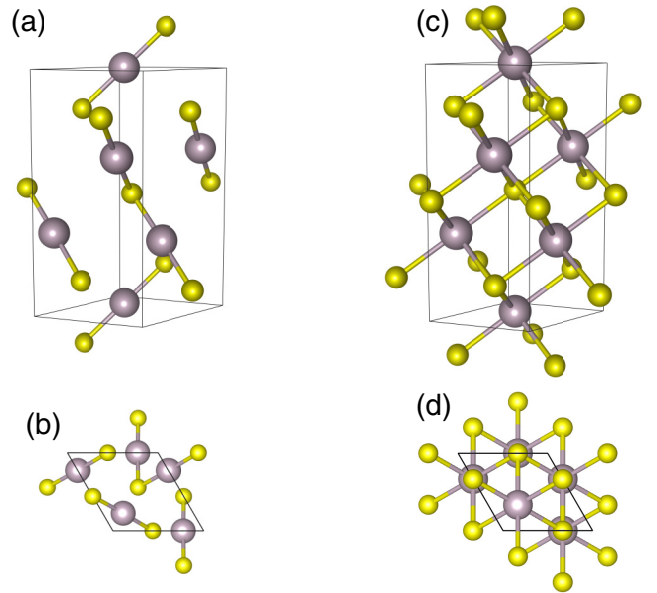


FIG. 6. Crystal structures of HgS: (a) Side view of ambient pressure cinnabar phase; (b) top view of ambient pressure cinnabar structure; (c) side view of RS structure at 26 GPa; (d) top view of RS structure at 26 GPa.

As shown in Fig. 7, as a function of pressure, HgS exhibits a transition to a RS structure [reported in Figs. 6(c) and 6(d)] in which the helical chains are broken: This transition is characterized by the u and v values of $1/3$ and $2/3$ respectively and a c/a ratio of $\sqrt{6}$ [13].

APPENDIX B: ENERGY GAP EVOLUTION AS A FUNCTION OF PRESSURE

In Fig. 8, we present the experimental electronic band gap as a function of pressure, alongside our computed (minimum) Kohn-Sham gaps obtained using the PBE, PBE + vdW correction, and r^2 SCAN exchange-correlation functionals. Notably, all functionals exhibit a clear change of the energy

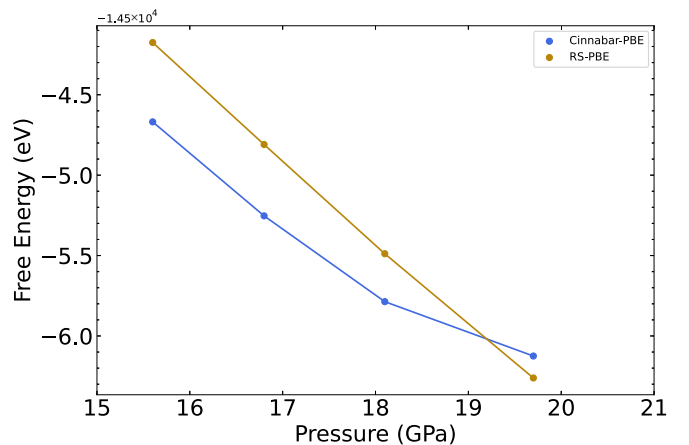


FIG. 7. Free energy as a function of pressure for the cinnabar (blue) and RS (gold) phases calculated using the PBE functional. The intersection between the curves at ~ 19 GPa indicates the phase transition.

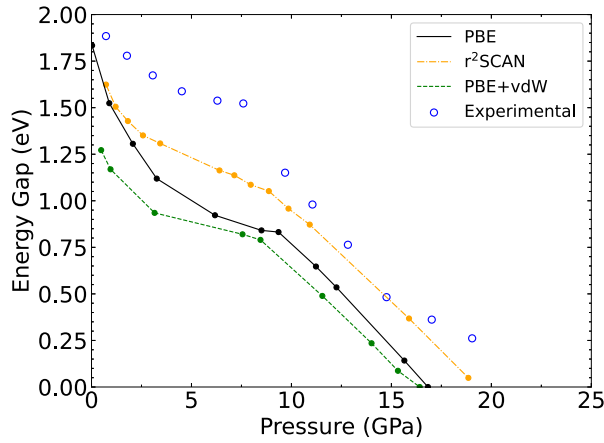


FIG. 8. Energy gap of the cinnabar HgS as a function of pressure. In black are shown the theoretical gaps obtained using the PBE exchange-correlation functional, in green the ones calculated with the PBE + vdW corrections and in orange the ones calculated using the r^2 SCAN exchange-correlation functional. The blue circles represent the experimental data observed by Zhang *et al.* [3].

gap as a function of pressure, in particular in the slope (above ~ 8 GPa). This behavior is linked to a modification in the nature of the band gap: Below 8–9 GPa, the system exhibits an indirect band gap, with the conduction band minimum at the Γ point and the valence band maximum situated along the Γ -A path in the Brillouin zone. Above this pressure range, the gap remains indirect, but the conduction band minimum shifts to the high-symmetry M point (see Fig. 9).

As shown in Fig. 8, metallization occurs approximately 4 GPa before the structural phase transition, regardless of the functional used. The r^2 SCAN functional improves the prediction of the band gap with respect to the PBE-based functionals.

The effect of electronic temperature on transition pressure

A larger electronic temperature (smearing parameter in DFT calculations) accelerates the metallization process (see Fig. 10).

Although this aspect may seem like a technicality, the issue is deeper and is related to the semiconductor-to-metal crossover that precedes the structural phase transition, leading to a lower critical pressure. This issue does not affect too much the r^2 SCAN results due to the larger band gap predicted by this functional. Ultimately, employing a smaller smearing parameter ensures an overall qualitative agreement in the transition pressure across all functionals.

In the study of the effects of electronic smearing on the electronic gap closure, it should be noted that the computational parameters (smearing and k -point grid) are converged for the smallest smearing value used in the calculations ($\sigma = 0.05$ eV). Then the smearing parameter is increased while keeping the k -point grid unchanged, which therefore remains “overconverged” for such large smearings. In this way, we are able to isolate the role of the electronic temperature on the electronic gap closure in pressure.

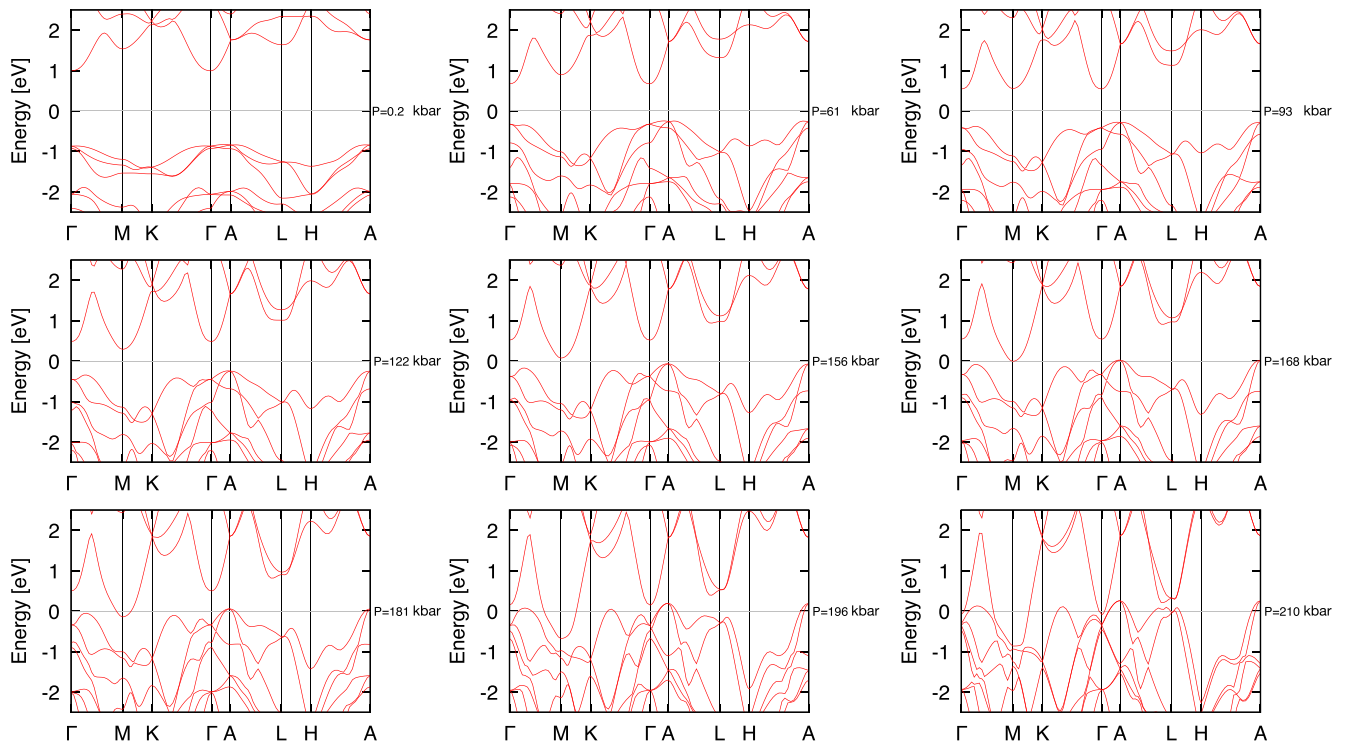


FIG. 9. Electronic band structures as a function of pressure for the cinnabar phase spanning from ambient pressure up to 21 GPa.

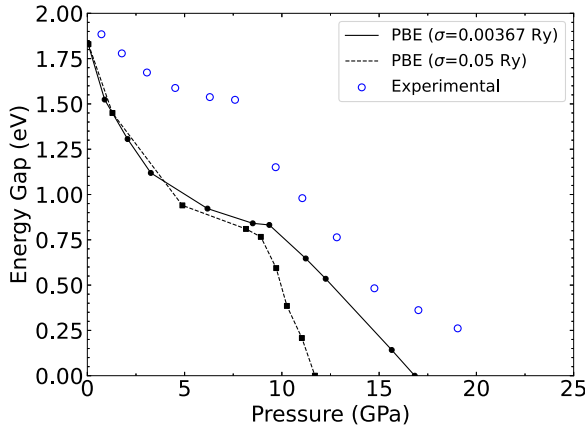


FIG. 10. Energy gap of the HgS cinnabar system as a function of the pressure. Black circles (solid line) are the theoretical gaps obtained using the PBE exchange-correlation functional with a gaussian smearing of $\sigma = 0.00367$ Ry, while black squares (dashed line) are the ones calculated using the same exchange-correlation functional but with an higher smearing of $\sigma = 0.05$ Ry. The blue circles represent the experimental data observed by Zhang *et al.* [3].

APPENDIX C: COMPUTATIONAL METHODS

Structural, electronic, and dynamical properties calculations were performed using the plane-wave pseudopotential DFT QUANTUM-ESPRESSO package [30–32]. We used optimized norm-conserving Vanderbilt pseudopotential [45–47] and the GGA-PBE approximation for the exchange-correlation functional, with an energy cutoff of 80 Ry. Integrations over the BZ of the HgS RS structure were carried out using a uniform $32 \times 32 \times 32$ grid and a $\sigma = 0.05$ eV Gaussian smearing. For the HgS cinnabar structure we used a $10 \times 10 \times 4$ grid to have the same density in sampling the Brillouin zone.

To ensure the convergence on the calculated pressure a 10^{-3} (a.u.) threshold on the forces has been used and the energy cutoff was enhanced to 100 Ry.

Van der Waals interactions were also applied with a semiempirical correction (Grimme-D3 [48]) to the PBE functional.

To perform calculation with the r^2 SCAN [49] we employed the projector augmented-wave pseudopotential method [50,51] as implemented in the Vienna Ab-initio Simulation Package (VASP) [52–55]. An energy cutoff of 650 eV for the plane wave basis was used with the same Gaussian smearing and k -point grids used with QUANTUM-ESPRESSO.

Phonon frequencies were calculated, for the HgS RS phase, at the harmonic level, using the linear response theory [30–32], on a $8 \times 8 \times 8$ phonon grid wave vectors corresponding to 29 irreducible q -points and a $32 \times 32 \times 32$ mesh for the electronic wave vectors.

The SCDFT [33,34] was used for the calculation of superconducting properties.

In SCDFT the superconducting properties are obtained by solving an effective gap equation as a function of temperature. While the gap equation is mathematically similar to a BCS equation the equation's kernel is defined as the functional derivative of an exchange correlation energy functional. The

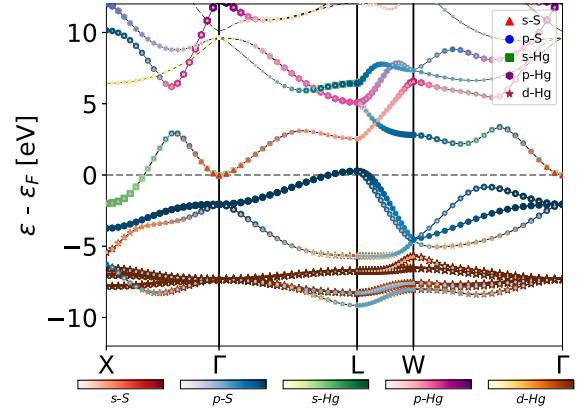


FIG. 11. Electronic band structure of the HgS in the RS-phase at 26 GPa, calculated with VASP at PBE level. Different symbols and colors' gradient represent the character of the eigenvalues (see legends).

functional we use in this work is derived in Ref. [56]. Since the gap equation only provides information on the values of the Kohn-Sham gap, the true mean body gap function is computed by using a supplementary functional, which is discussed in Refs. [56,57]. Therefore, in this work, when discussing the superconducting gap, we always refer to physical excitations rather than the fictitious Kohn-Sham gap. A precise introduction to the SCDFT formalism as used in this work can be found in Ref. [57]. To accurately describe the anisotropy (momentum dependence) of the superconducting gap we use a Monte Carlo approach, the algorithm was detailed in Refs. [33,34] as well as in the more recent Ref. [58]. The key parameter which determines the calculation quality is the number of Monte Carlo k -points accumulated on the Fermi surface. In this work we use 50 000 k -points, with a skin depth of 20 meV (which sets the region in energy space which is more densely sampled).

APPENDIX D: ROCK-SALT BAND STRUCTURE

The electronic band structure of the RS phase is shown and discussed in Fig. 2 of the main text. In Fig. 11 the projections of the atomic orbitals of the electronic bands are shown. The bands near the Fermi level exhibit significant contributions from Hg s , S p , and S s orbitals, with Hg- p states high in energy with respect to the Fermi level. The pronounced orbital separation of the states crossing the Fermi energy highlights the multiorbital nature of the low-energy electronic structure, which is a key factor in determining the superconducting behavior of RS-HgS.

APPENDIX E: PHONON PROPERTIES AT THE L POINT VERSUS PRESSURE

In this section, we analyze the dynamical properties of the RS-HgS system under pressure, calculated with the PBE functional, with special focus to the two phonon modes at the L point of the Brillouin zone in the 80–120 cm^{-1} frequency range. These modes display eigenvectors predominantly associated with either Hg or S displacements. Notably, the S-dominated mode, which are characterized by S moving

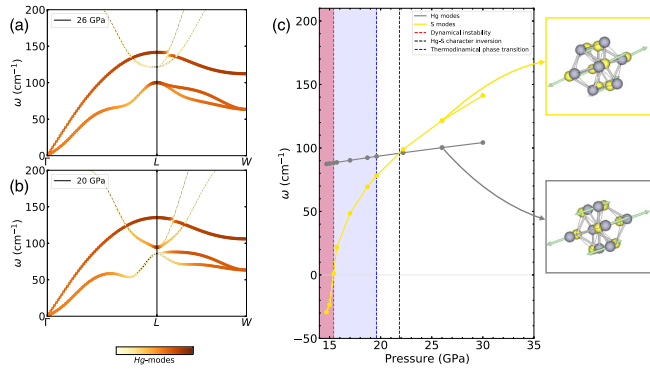


FIG. 12. Phonon frequencies along the Γ -L-W path of RS-HgS at 26 GPa (a) and 20 GPa (b). The color gradient indicates the Hg character of the modes. (c) Frequencies of pure Hg (gray) and S (yellow) modes at the L point as a function of pressure. The vertical dashed lines indicate the onset of dynamical instability at 15.4 GPa (red), the thermodynamic phase transition at 19.6 GPa (blue), and the character inversion around 22 GPa (black). Insets illustrate the eigenvectors of the two modes, with green arrows representing the displacements of the atoms.

in the planes perpendicular to the [111] direction, exhibits a pronounced softening and acts as the primary instability that drives the structural phase transition from the RS to the cinnabar phase around 15 GPa. The evolution of the Hg and S mode frequencies is shown in Figs. 12(a)–12(c), where a crossing occurs at around 22 GPa.

These modes undergo a pressure-driven inversion of character, reflecting a nontrivial mixing of vibrational states. As the pressure decreases, the branches maximum (minimum) at L moves upward (downward). Around 22 GPa these two branches become degenerate at the L point and, beyond this pressure, the bands split, but with inverted character. This band inversion is remarkably similar to the band inversion observed in the electronic structure of topological insulators, where the conduction and valence band characters are exchanged, giving rise to a topological gap [1,2].

The RS phase exhibits dynamical instability at a pressure roughly 4 GPa below the thermodynamic transition point, suggesting that it can persist as a metastable structure down to pressures below 19 GPa.

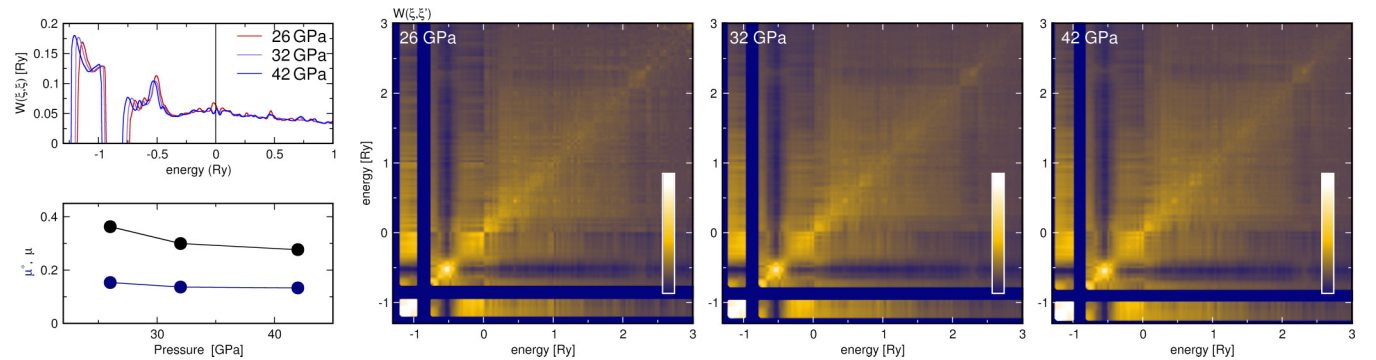


FIG. 13. Pressure dependence of the *ab initio* calculated Coulomb interaction. The two panels on the left show the pressure dependence of μ and μ^* . The three panels on the right show the function $W(\xi, \xi')$, as computed in the random-phase approximation for the dielectric screening. The color scale goes from zero to 0.15 Ry.

APPENDIX F: COULOMB INTERACTION

The Coulomb interaction in conventional superconductors reduces the binding within the Cooper pairs. We denote by $W_{k,k'}$ the matrix elements of the screened Coulomb interaction with respect to the Kohn-Sham orbitals,

$$W_{k,k'} = 4\pi \sum_{\mathbf{G}, \mathbf{G}'} \epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}) \times \frac{\langle k' | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | k \rangle \langle k | e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | k' \rangle}{|\mathbf{q} + \mathbf{G}| |\mathbf{q} + \mathbf{G}'|}, \quad (\text{F1})$$

where $k = (\mathbf{k}, n)$ is a combined momentum and band index, $\mathbf{G}$ are reciprocal lattice vectors and we have assumed the static approximation for the dielectric matrix $\epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q})$.

In the isotropic approximation [57] Eq. (F1) is averaged over surfaces of constant energy (ε) in k -space, i.e.,

$$W(\xi, \xi') = \frac{1}{N(\varepsilon)N(\xi')} \sum_{k,k'} W_{k,k'} \delta(\xi_k - \xi) \delta(\xi_{k'} - \xi'), \quad (\text{F2})$$

where $N(\xi) = \sum_k \delta(\xi_k - \xi)$ is the density of states. The value of T_c is mostly affected by the Coulomb repulsion at the Fermi level. This is usually expressed by the parameter μ ,

$$\mu = N(0)W(0, 0), \quad (\text{F3})$$

defined as the average on the Fermi surface of the electron-electron matrix elements times the density of states at the Fermi level. In simple superconductors with a good metallic screening W can be computed reasonably accurately in the random-phase approximation and μ typically acquires values within the range 0.2-0.4.

In Fig. 13 we report the pressure dependence of $W(\xi, \xi')$ and μ as computed with the *elk*-FLAPW code.

In conventional Migdal-Eliashberg theory one does not use the full Coulomb interaction as we do but an adjustable Coulomb parameter μ^* which can be either fitted to experiments or constructed from Morel-Anderson's theory, under the assumption of W and N being energy independent. However, we can rigorously redefine μ^* as that constant Coulomb coupling which, when used in the McMillan-Allen-Dynes equation, gives the same T_c as obtained by solving the Eliashberg equations with the full Coulomb interaction W . These values of μ^* are reported in Fig. 13 and show a slowly decreasing trend in pressure.

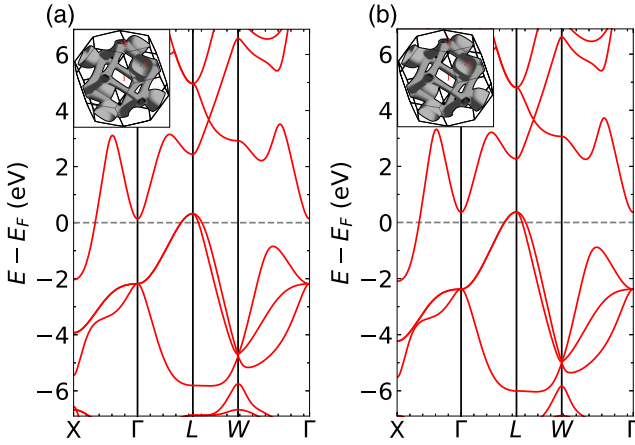


FIG. 14. Electronic band structure of HgS in the RS phase at 32 GPa (a) and 42 GPa (b) calculated at PBE level. Energies are referred to the Fermi level. The inset displays the Fermi surface of the system.

APPENDIX G: CONTRIBUTION OF THE ELECTRONIC POCKET AT Γ

In the system at 26 GPa, to estimate the contribution of the small electron pocket at Γ to the total density of states at the Fermi level, we approximate the DFT band dispersion near the band minimum by a parabolic (effective-mass) model. Since the electron pocket at Γ is s -like in a cubic (fcc) crystal, the effective mass tensor at Γ is expected to be essentially isotropic, which is confirmed by our electronic structure calculation near Γ along all the high symmetry directions. The effective mass m^* is obtained by fitting the DFT band along a high-symmetry line for small k :

$$E(k) \approx E_{\Gamma} + \frac{\hbar^2 k^2}{2m^*} = E_{\Gamma} + \alpha k^2, \quad (\text{G1})$$

where E_{Γ} is the energy at the center of the Brillouin zone, i.e., the minimum of the parabola.

For a three-dimensional, non-spin-polarized, parabolic band, the density of states per unit volume is

$$g(E) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E - E_{\Gamma}} \Theta(E - E_{\Gamma}). \quad (\text{G2})$$

Evaluating this equation at $E = E_F$ gives the DOS per volume of the pocket.

The density of states at E_F associated with the pocket, in units of states/eV per unit cell, is then $g_{\text{pocket}}(E_F) = 6 \times 10^{-4}$ states/eV, while from DFT a total density of states at the Fermi level of $g_{\text{tot}}(E_F) = 0.8187$ states/eV is obtained. The relative contribution of the Γ pocket to the density of states at the Fermi level is thus 0.07%, an absolutely negligible contribution.

APPENDIX H: HIGHER PRESSURE RESULTS

In this appendix we provide a detailed analysis of the electronic structure, phonon density of states, and superconducting properties of RS-HgS at approximately 32 and 42 GPa. The purpose of this comparison is to elucidate the

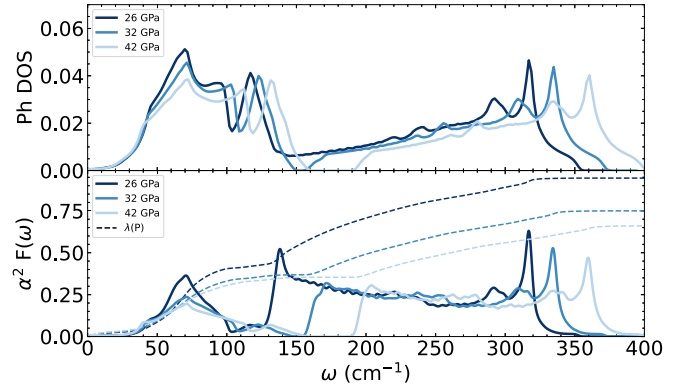


FIG. 15. Phonon density of states (top) and Eliashberg spectral function (bottom) at different pressure of the HgS RS system. The dashed lines in the bottom panel represent the electron-phonon coupling parameter as a function of frequency.

mechanisms through which external pressure modulates the electronic bandwidth, lattice dynamics, and ultimately the superconducting response of the system.

We start with the electronic properties, presenting, In Fig. 14, the electronic band structures of the system at 32 and 42 GPa showing only moderate changes. In particular, a redistribution of spectral weight is observed, with a small charge transfer from the electron-like band at the X point of the BZ toward the holelike bands at L .

The behavior of the phonon spectrum is shown in Fig. 15. We find that the relatively rigid Hg-dominated modes show only minor shifts under pressure. On the contrary, as already shown in Appendix E, the S-dominated phonon mode at the L point of the Brillouin zone is strongly pressure dependent and exhibits a pronounced soft character. This mode undergoes significant hardening with increasing pressure, while at lower pressures it approaches a dynamical

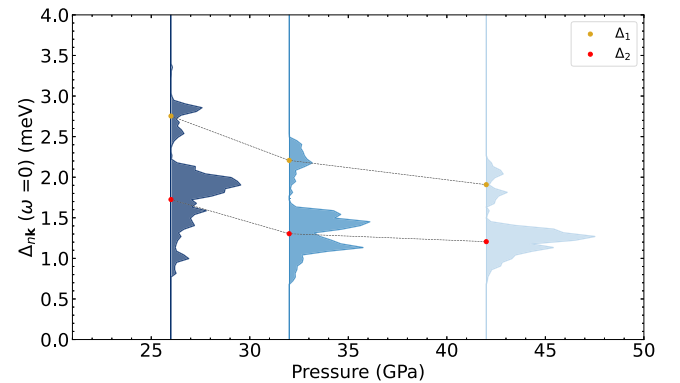


FIG. 16. Solution of the SCDFT anisotropic equation for the k -resolved superconducting gap at fixed temperature of 2 K as a function of pressure. A histogram shows the distribution of the superconducting gap as a function of the energy for each pressure. Red (Δ_2) and gold (Δ_1) points represent the "averaged" gaps at each pressure, obtained through a weighted average of the histograms in the two branches, and the dashed black-line connecting them is a guide for the eyes.

instability. Together, these effects lead to the progressive opening of a gap in the phonon density of states as pressure increases.

The evolution of the superconducting properties are discussed in terms of the Eliashberg spectral function in Fig. 15. The discussed shift of the S-dominated mode toward higher frequencies also impacts the Eliashberg spectral function $\alpha^2F(\omega)$ and the electron-phonon coupling, which loses contributions from the intermediate-frequency region and consequently decreases with increasing pressure. Finally, we analyze the pressure dependence of the k -resolved

superconducting gap, reporting in Fig. 16 its distribution at 2 K for the considered pressures.

A clear evolution of both the magnitude and anisotropy of the superconducting gap is observed as a function of pressure. At lower pressure, the gap distribution is broader, reflecting a stronger anisotropy of the pairing interaction. Upon increasing pressure, the distribution progressively narrows and shifts toward lower energies, indicating a reduction of both the overall pairing strength and its anisotropic character. As a consequence, the superconducting state evolves toward a weaker and more isotropic pairing regime at higher pressures.

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