Origin of the critical temperature discontinuity in superconducting sulfur under high pressure

M. Monni, F. Bernardini, A. Sanna, G. Profeta, and S. Massidda

1 CNR-IOM (UOS Cagliari) and Dipartimento Fisica, Università degli Studi di Cagliari, I-09042 Monserrato (CA), Italy
2 Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany
3 CNR-SPIN and Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell’Aquila, Via Vetoio 10, I-67100 Coppito (L’Aquila) Italy

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Elemental sulfur shows a superconducting phase at high pressure (above 100 GPa), with critical temperatures that rise up to 20 K [Phys. Rev. B 65, 064504 (2002); Nature (London) 525, 73 (2015)] and presenting a jump at about 160 GPa, close to a structural phase transition to the \(\beta\)-Po phase. In this work we present a theoretical and fully \textit{ab initio} characterization of sulfur based on superconducting density functional theory (SCDFT), focusing in the pressure range from 100 to 200 GPa. Calculations result in very good agreement with available experiments and point out that the origin of the critical temperature discontinuity is not related to the structural phase transition but induced by an electronic Lifshitz transition. This brings a strongly (interband) coupled electron pocket available for the superconducting condensation.

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The extraordinary discovery of superconductivity at \(\approx 200\) K in sulfur hydride at high pressure by Drodzov \textit{et al.} [1] has revived the interest of the scientific community on electron-phonon coupling as the driving force for the superconducting condensation, able to lead to a Cooper pairing stronger than any known unconventional mechanism. It is remarkable that the prediction of a possible high-temperature superconducting phase in sulfur hydride was done by an \textit{ab initio} investigation earlier than experimental confirmation, both in SH\(_2\) [2] and SH\(_3\) [3]. This is a strong indication of the predictive power of modern theoretical and computational methods in studying crystal structures, and electronic, dynamical, and superconducting properties of new materials in different thermodynamic conditions.

The experiment of Drodzov \textit{et al.}, moreover, has demonstrated the decomposition of SH\(_2\) under pressure and coexistence with elemental sulfur, via the reaction \(3\text{H}_2\text{S} \rightarrow 2\text{H}_3\text{S} + \text{S}\) [4]. As a confirmation of this, in Ref. [1] the authors reported the superconducting critical temperature of pure sulfur as a function of pressure up to 250 GPa, finding a critical temperature as high as 20 K. This represents a relevant result on its own, considering the peculiarities of the sulfur phase diagram under high pressure.

The high-pressure superconducting properties of pure sulfur were already known. Indeed, it was considered [5] the element with the highest critical temperature, 17 K, under pressure. The high-pressure phase diagram of sulfur, like other group-IV elements, is characterized by a series of phase transitions from open and insulating structures, to more compact and metallic ones. Phase I, stable at low pressure, is formed by eight-ring structures. It transforms at 1.5 GPa in a trigonal chainlike structure (phase II). The tetragonal phase, phase III, is stable starting from 36 GPa up to 83 GPa. From 83 to 153 GPa, the structure of S is body centered monoclinic (bcm) with two atoms in the primitive cell [6–10]. Above 153 and up to 212 GPa [11] S presents a rhombohedral \(\beta\) – Po structure (shown in Fig. 1). Superconductivity has been measured within the range of stability of the bcm structure [7] coexisting with a charge density wave (CDW) phase characterized by an \textit{incommensurate} periodic modulation on the primitive structure which is present up to 135 GPa. The coexistence of the CDW phase with superconductivity is recognized as a peculiar feature of sulfur phase diagram [12] since CDW often competes with the superconducting phase. Magnetic measurements show that the superconducting transition temperature increases with pressure and abruptly jumps from 14.2 to 16.5 K at 155 \pm 7 GPa [13], close to the transition from the bcm to the \(\beta\)-Po (\(P \approx 153\) GPa) [7,13]. This effect was recently confirmed by resistivity measurements under pressure performed by Drozdov \textit{et al.} [1] even if not explicitly noted. The origin of this jump still awaits a complete explanation which we address in this work, where we revisit the superconducting phase diagram of pure sulfur by means of \textit{ab initio} computational approach, not relying on any semiempirical parameters and investigating a wide pressure range which includes both the bcm and the \(\beta\)-Po phases.

I. METHOD

We performed first-principles density functional theory (DFT) calculations of the normal state properties of pure S under external isotropic pressure. We used the plane wave basis within the ultrasoft pseudopotential approximation [14] for the solution of the Kohn-Sham equation using the generalized gradient approximation (GGA-PBE) [15] for the exchange correlation energy. The phase diagram of S under pressure was obtained through stress minimization with the Parrinello-Rahman method. Dynamical properties and electron-phonon coupling constants were calculated by density functional perturbation theory [14,16]. The bcm (distorted with an incommensurate wave vector) structure (see below) was simulated adopting the \(\beta\)-Po phase, which represents a good approximation of the actual bcm structure within the pressure range studied. Indeed, the primitive cell of the \(\beta\)-Po structure is a subunit of the bcm structure, provided that the lattice parameters \(a_m, b_m, c_m\) and the angle \(\beta\) of the bcm structure satisfy the following relations: \(a_m = a_r(3 + 6 \cos \alpha_r)^{1/2}\), \(b_m = a_r(2 - 2 \cos \alpha_r)^{1/2}\), \(c_m = a_r\).
obtained with this approach. The isotropic approximation is applied in most of the calculations based on the solution of the Eliashberg equations or using the McMillan equation to estimate \( T_c \), because it is the computationally less expensive method to compute \( T_c \). Although useful as a first estimation of the critical temperature, this methodology has the drawback that it does not allow to preserve the anisotropic features of the superconducting gap, which in multiband systems, MgB\(_2\) above the others, has dramatic consequences. The second approach is named “multiband” because the average of the el-ph coupling and Coulomb screening matrix elements is performed over different groups of bands without retaining the full \( k \) dependence of the el-ph matrix elements. We label thereafter as \( T^{(\text{multi})} \) the critical temperature obtained with this approach.

The matrix elements of the Coulomb interaction screened with a static dielectric matrix, within the random phase approximation (RPA), were calculated on a mesh of \( 8^3 \times 8^3 \) \( k \) and \( k' \) points.

II. RESULTS AND DISCUSSION

The calculated lattice constants of sulfur in the \( \beta\)-Po phase in the studied pressure range (\( \beta\)-Po phase) are in perfect agreement with previous first-principles calculations in Ref. [12].

The CDW phase is confirmed by the calculation of vibrational properties which reveal the presence of structural instability at an incommensurate wave vector. In Fig. 1, we plot the sulfur phonon dispersion along the high symmetry directions of the Brillouin zone (BZ) at 100, 180, and 200 GPa. The presence of a soft mode is evident along the \( \Gamma^-\text{F} \) direction at 100 GPa, underlining the presence of a modulated structure [12]. In the literature CDW instabilities are often discussed in terms of FS nesting. This point of view has been challenged by Johannes et al. [36] for NbSe\(_2\), where no nesting was found at the CDW vector. The situation here is rather similar: At \( \mathbf{q}_{\text{CDW}} \) we find a peak for both the electron-phonon coupling \( \lambda_{q,j} \) and the phonon linewidth \( \gamma_{q,j} \), but not for the (so-called) nesting function proportional to the charge susceptibility.

Increasing the pressure, the dynamical instability disappears and we obtain positive phonon frequencies at a pressure slightly lower than 140 GPa. Thus, the experimental reported CDW phase transition, in agreement with the interpretation given in Ref. [12], can be interpreted as originating from the dynamical instability of a single phonon mode.

We point out that the presence of a structural instability related to the soft phonon mode below 140 GPa makes calculations of the superconducting coupling less reliable with decreasing pressure. This is because we are neglecting the phase transition to the distorted (uncommensurated) \( bcm \) structure which experimentally takes place at \( P \approx 153 \) GPa [7]. However to mimic the effect of the CDW we perform the following action: (a) We cut from the calculation of the coupling the soft modes which appear for pressure below 140 GPa. Physically, this can justified considering that this mode would not contribute to the coupling due to the opening up of a CDW-type gap corresponding to their momentum transfer. (b) We (partially) consider the reduction of the electronic DOS due to the CDW distortion [12] by rescaling...
interactions contributing to the superconducting instability. We stress that the SCDFT approach ensures that all the relevant parameters for the two “bands” which are used in multiband SCDFT: the DOS at the Fermi level, the el-ph coupling constants ($\lambda$), and the (averaged) Coulomb matrix element ($\mu$).

A first inspection of Table I reveals that, because of the prevalent $sp$ character of the FS’s, most of the coupling come from the intraband $sp$ channel: $\lambda_{sp,sp}\gg\lambda_{sp,d}$.

This is highlighted by the Eliashberg functions involving $sp$ bands, which shows a relevant coupling within all the frequency range when compared with the phonon DOS (see Fig. 4). The sheets with $d$ character have a small intraband coupling due to the absence of small $q$ optical phonons, which allow intraband scattering within the (small) Fermi surface. On the other hands, interband coupling with $sp$ FS is strongly enhanced: $\lambda_{d,sp}\gg\lambda_{d,d}$. This last channel represents the most coupled (in particular for low-energy phonons) (see Fig. 4).

FIG. 2. Electronic band structure of sulfur in the $\beta$-Po phase at 100 (black dashed line) and 180 GPa (colored thick line). The sidebar represents the orbital character scale from blue ($sp$ character) to green ($d$ character).

FIG. 3. Fermi surface of S in the $\beta$-Po phase at 180 GPa. The two panels show the FS centered at the $\Gamma$ point (left) and centered at the $Z$ point (right). The pockets with $d$ character are located around the $Z$ point.

FIG. 4. Band-resolved Eliashberg functions $\alpha^2 F_{ij}(\omega)$ with $i,j = sp,d$ at 180 GPa compared with the phonon density of states (filled gray curve).
TABLE I. Density of states (states/eV/spin) at the Fermi level for sp FS sheets (DOS FS\textsubscript{sp}) and for d FS sheets (DOS FS\textsubscript{d}). Electron-phonon coupling constant: mean (\bar{\lambda}), mediated over different FS sheets (\lambda i,j(i\neq j) with i,j = sp,d). Average Coulomb matrix element over the FS times the DOS at the Fermi energy (\mu).

<table>
<thead>
<tr>
<th>P</th>
<th>DOS FS\textsubscript{sp}</th>
<th>DOS FS\textsubscript{d}</th>
<th>\bar{\lambda}</th>
<th>\lambda(iFS\textsubscript{d} - FS\textsubscript{d})</th>
<th>\lambda(iFS\textsubscript{d} - FS\textsubscript{sp})</th>
<th>\lambda(iFS\textsubscript{sp} - FS\textsubscript{sp})</th>
<th>\mu</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.148</td>
<td>0.0</td>
<td>0.642</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.202</td>
</tr>
<tr>
<td>120</td>
<td>0.142</td>
<td>0.0</td>
<td>0.630</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.192</td>
</tr>
<tr>
<td>130</td>
<td>0.143</td>
<td>0.0</td>
<td>0.597</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.193</td>
</tr>
<tr>
<td>140</td>
<td>0.138</td>
<td>0.0047</td>
<td>0.713</td>
<td>0.040</td>
<td>1.539</td>
<td>0.618</td>
<td>0.194</td>
</tr>
<tr>
<td>160</td>
<td>0.135</td>
<td>0.0086</td>
<td>0.742</td>
<td>0.055</td>
<td>1.421</td>
<td>0.604</td>
<td>0.194</td>
</tr>
<tr>
<td>180</td>
<td>0.134</td>
<td>0.0118</td>
<td>0.704</td>
<td>0.050</td>
<td>1.217</td>
<td>0.556</td>
<td>0.196</td>
</tr>
<tr>
<td>200</td>
<td>0.134</td>
<td>0.0118</td>
<td>0.654</td>
<td>0.048</td>
<td>1.052</td>
<td>0.520</td>
<td>0.200</td>
</tr>
</tbody>
</table>

We note that the band anisotropy of the el-ph is not very large: The average value of the el-ph coupling on FS \(\bar{\lambda}\) (which represents the average electron-phonon coupling) is only 10% less than the maximum eigenvalue of the \(\lambda\) matrix, which determines \(T_c\) in the multiband BCS theory of superconductivity [39]. As a last consideration, we stress that while the el-ph coupling varies strongly with pressure, the Coulomb interaction is nearly constant over the investigated pressure range as shown in Table I.

Figure 5 reports the evolution of the calculated (full red squares) superconducting critical temperature as a function of pressure. In the same graph, we report also the critical temperature of the pressure compared with available experimental data.

For \(P \leq 130\) GPa, the d electron pockets are empty and do not contribute to the electron-phonon coupling. For \(P \geq 140\) GPa, \(T_c^{\text{(multi)}}\) is always greater than \(T_c^{\text{(iso)}}\) by 1–2 K (depending on the pressure). As shown in Table I the leading contribution to superconductivity above 140 GPa comes from the d-band coupling to \(sp\) band through to the interband channel \(\lambda_d,sp\) giving rise to sizable off-diagonal terms of the coupling. The anisotropy of the el-ph interaction within the interband channel alone gives only a limited effect on \(T_c\), resulting in a relatively small gain of \(T_c^{\text{(multi)}}\) over \(T_c^{\text{(iso)}}\).

The overall theoretical picture fits reasonably well with the existing experimental data considering the intrinsic error bar of \textit{ab initio} methods (DFT and SCDFT functionals). In addition, we must consider that differences between the two sets of measurements exist in the critical pressure as well as in the pressure behavior (especially at high pressure). This can be surely due to the differences in the measurements (magnetic versus resistivity), to the (possible) formation of metastable phases at high pressure and in the error bar in the pressure measurement.

These results indicate that the observed jump in the critical temperature of sulfur can not be ascribed to the disappearance of a CDW phase and the corresponding effect on the DOS, but it is induced by the crossing of a new electronic band with d character and strongly coupled with phonons. This band adds a sizable contribution to the total coupling and leads to a discontinuous jump in critical temperature. This statement can be verified by a computational experiment performed artificially removing the effect of the d pocket from the coupling, that is, setting to zero all the scattering matrix elements involving this pocket. The calculated critical temperatures are significantly lower as shown in Fig. 5 (orange stars) and decreasing as a function of the pressure.

III. CONCLUSIONS

In conclusion, we have performed first-principles calculations of the electronic and dynamical properties of the high-pressure phase of sulfur reproducing the disappearance of the CDW phase at high pressure which has been considered as the main reason for the jump in the superconducting critical temperature across the transition. However, by means of extensive \textit{ab initio} calculations of the electron-phonon coupling and superconducting critical temperature, we have shown that...
another event affects the superconducting condensation: the crossing at the Fermi level of a new electronic band, with strong \( d \) character and significant phononic coupling. This occurrence leads to a jump in the critical temperature that compares well with the experimental evidence and that occurs at the same pressure at which the phase transition is predicted. This effect highlights the role of the Lifshitz transition in enhancing the superconducting critical temperature due to the strong coupling between phonons and directional \( d \) states. At the same time, we explain the origin of the high-temperature superconducting phase of sulfur, in which the disappearance of the CDW phase is concomitant with the change of the Fermi surface topology allowing new (highly) coupled scattering channels.

[37] The reduction is about 15% at 100 GPa and goes to zero at the \( \beta\)-Po to \( bcm \) transition that is reported to be nearly second order, involving an almost continuous distortion of the \( \beta\)-Po structure [7]. This approximation appears to be a good compromise between the numerical feasibility and the physical accuracy of the calculation.