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High $T_c$ superconductivity in weakly electron-doped HfNCl

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We investigate magnetic and superconducting properties in electron-doped Li$_x$HfNCl. HfNCl is a band insulator that undergoes an insulator to superconductor transition upon doping at $x \approx 0.13$. The persistence of the insulating state for $x < 0.13$ is due to an Anderson transition probably related to Li disorder. In the metallic and superconducting phase, Li$_x$HfNCl is a prototype two-dimensional two-valley electron gas with parabolic bands. By performing a model random phase approximation approach as well as first-principles range-separated HSE06 calculations, we find that the spin susceptibility $\chi_s$ is strongly enhanced in the low-doping regime by the electron-electron interaction. Furthermore, in the low-doping limit, the exchange interaction renormalizes the intervalley electron-phonon coupling and results in a strong increase of the superconducting critical temperature for $x < 0.15$. On the contrary, for $x > 0.15$, $T_c$ is approximately constant, in agreement with experiments. At $x = 0.055$ we found that $T_c$ can be as large as 40 K, suggesting that the synthesis of cleaner samples of Li$_x$HfNCl could remove the Anderson insulating state competing with superconductivity and generate a high $T_c$ superconductor.

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I. INTRODUCTION

The low-doping limit of multivalley semiconductors has recently been proposed as an alternative route to achieve high $T_c$ superconductivity.1,2 Transition metal dichalcogenides, ternary transition-metal dinitrides, and cloronitrides have been reported to achieve fairly high $T_c$ upon doping. It is possible to dope multivalley semiconductors up to electron densities of $n \sim 10^{14}$ cm$^{-2}$ via field-effect doping.1,4,5,11–13 The doping of these materials can be also be achieved and controlled by intercalation.9,10,14–17 However, reaching the low-doping limit can be difficult as disorder and the consequent Anderson transition can suppress superconductivity.

In a two-dimensional, and quasi two-dimensional (2D) semiconductors, in the weakly-doped regime, the density of states (DOS) is constant. This is different from 3D semiconductors with parabolic bands, where generally the density of states increases as $\sqrt{\varepsilon_F}$, as the number of electrons increases, $\varepsilon_F$ being the Fermi level. Therefore, in 3D semiconductors, a large number of carriers is needed to achieve a sizeable density of states at the Fermi level $N(0)$. As in a phonon-mediated mechanism, $T_c \sim N(0)$, in a 2D semiconductor, $T_c$ is expected to be constant because of the constant DOS, as long as the phonon spectrum is weakly affected by doping. However, in the weakly doped regime of transition-metal chloronitrides, the $T_c$ increases with decreasing doping.9,10,14. This unexpected behavior resulted in a search for a theoretical understanding of the physics of superconductivity in 2D semiconductors.10,26

In previous works, it has been shown that in 2D multivalley semiconductors, at low doping, the electron-electron interaction enhances the intervalley electron-phonon coupling, explaining the behavior of $T_c$.25,26 The enhancement of the $T_c$ is linked to the enhancement of the spin susceptibility, $\chi_s$. Furthermore, a systematic study of electronic, magnetic, and vibrational properties of Li$_x$ZrNCl has been performed using density functional theory (DFT) with hybrid functionals with exact exchange and range separation, and this study shows that the exact exchange component leads to a similar enhancement in spin susceptibility and electron-phonon interaction.20 This effect on the enhancement of $T_c$ should be quite general as it only requires basic ingredients such as a 2D multivalley (ideally two-valley) semiconductor and large enough electron-gas parameter, $r_s = 1/a_B\sqrt{n}$ with $a_B = \epsilon_M\hbar^2/(m^*e^2)$ where $n$ is the electron density per unit area (linked to the doping per formula unit, $x$, per area $\Omega$ of 2 formula units for Li$_x$ZrNCl: $n = 2x/\Omega$, $\epsilon_M$ is the environmental dielectric constant (i.e. the dielectric constant of the undoped semiconductor), and $m^*$ the effective mass of the electronic band.22 Therefore, it is natural to search for high $T_c$ superconductivity in other materials with either larger $\epsilon_M$ or with lower $n$ and $m^*$.

An interesting system with these features can be intercalated HfNCl. Superconductivity has been observed with Li-intercalated $\beta$-HfNCl with $T_c = 20$ K, and with co-intercalated Li$_{0.48}$(THF)$_2$HfNCl with $T_c = 25.5$ K.10,15. As $\beta$-ZrNCl, $\beta$-HfNCl is a two dimensional two-valley semiconductor with almost perfect parabolic conduction band and constant DOS. Moreover, in $\beta$-HfNCl, $\epsilon_M = 4.93$ is slightly smaller than in the case of $\beta$-ZrNCl ($\epsilon_M = 5.59$). Thus, it is natural to expect that a similar enhancement in the $T_c$ at low doping occurs also
in Li$_2$HfNCl. However, the $T_c$ in Li$_2$HfNCl is surprisingly flat in the weakly-doped regime, and the Anderson transition occurs at almost three times larger doping ($x \approx 0.15$) with respect to Li$_2$ZrNCl. It is then possible that the Anderson transition prevents the enhancement of the $T_c$ at low doping, or alternatively, the reported doping is indeed nominal doping and not the real electron doping occurring in the sample. More experimental insight into the low-doping regime can also be obtained by field-effect doping. In this work, we follow the method introduced in References 15, 23, and 27 to explore the behavior in Li$_2$HfNCl. We propose that clean samples at sufficiently low doping can achieve higher $T_c$ without the need of further intercalation.

II. COMPUTATIONAL DETAILS

Calculations are performed using the QUANTUM ESPRESSO \textit{ab initio} method\textsuperscript{22} with the generalized gradient approximation (GGA) as implemented in the PBE functional\textsuperscript{29} with ultrasoft norm conserving pseudopotentials and plane wave basis sets. The doping of the semiconductor is simulated by changing the number of electrons and adding a compensating jellium background, which has been previously shown to give accurate results\textsuperscript{20,24}. The atomic coordinates are relaxed with lattice parameters fixed at the experimental values from Reference 15. For the energy convergence, a threshold on the change in total energy of $10^{-10}$ Ry is used for all calculations. A Methfessel-Paxton smearing of 0.01 Ry with an electron-momentum grid of $48 \times 48 \times 48$ are used for the relaxation of the internal coordinates and calculating the electronic band structure. The density of states is calculated using a Gaussian smearing of 0.01 Ry.

Furthermore, we have performed calculations with the HSE06\textsuperscript{28} functional that has exact exchange and range separation components, using the CRYSTAL code\textsuperscript{30} with Gaussian type triple-$\zeta$ valence polarized basis set orbitals\textsuperscript{31,32} where the diffuse Gaussian functions of the Hf basis are reoptimized. A Fermi-Dirac smearing of 0.0025 Ha, electron-momentum grid of $48 \times 48 \times 16$, energy convergence threshold of $10^{-9}$ Ha, real space integration tolerances of 8-12-8-30-60, with 6th order multipolar expansion are used for the HSE06 calculations.

The effective mass, $m^*$ is calculated from the curvature of a 4th order polynomial fit to the region between the Fermi energy and the conduction band minimum around the special point $K$, assuming that the mass tensor is isotropic.

Electron-phonon coupling and phonon frequencies are calculated with the PBE functional with a Methfessel-Paxton smearing of 0.02 Ry, electron-momentum grid of $12 \times 12 \times 4$, Wannierization\textsuperscript{28} of the electronic bands with an electron-momentum grid of $6 \times 6 \times 2$, correspondingly, a phonon-momentum grid of $6 \times 6 \times 2$, and a Wannier interpolation scheme of electron-phonon coupling with a grid of $40 \times 40 \times 64$.

III. RESULTS AND DISCUSSION

A. Electronic structure

The primitive unit cell of HfNCl has rhombohedral structure (space group $R\bar{3}m$, number 166) with 2 formula units per unit cell. It can also be constructed by a conventional cell of hexagonal structure with 6 formula units per cell with ABC stacking. Instead of using the rhombohedral unit cell, we take advantage of the weak interlayer interaction\textsuperscript{20,24,25,35,36}, which makes the stacking order negligible, and we adopt a hexagonal HfNCl structure with AAA stacking. This is equivalent to the hexagonal structure with the space group $P\bar{3}m1$ (space group number 164), with 2 formula units in the unit cell.

To confirm the assumption that the stacking order does not play a significant role in the conduction band, we compare the electronic bands and the density of states of hexagonal and rhombohedral structures for the doping $x = 0.11$ in Figure 1. The electronic structure is not affected by the stacking difference.

![FIG. 1. Electronic structure and density of states (DOS) of Li$_2$HfNCl calculated with the PBE functional. The hexagonal structure (H) with AAA stacking is compared to the rhombohedral structure (R) with ABC stacking for the doping $x = 0.11$. For the hexagonal structure with AAA stacking, the electronic structure of the doping $x = 0.11$ is compared to that of the doping $x = 0.31$. The DOS is given in units of states/eV per 2 formula units of each unit cell.](image)

This layered system can be considered as the prototype of 2D two-valley electron gas. Indeed the bottom of the conduction band of HfNCl is composed of two perfectly parabolic bands at points $K$ and $K^\prime = 2K$ in the Brillouin zone. The conduction band is a simple parabola, with a minimum at the $K$-point of the Brillouin zone. And the density of states is essentially constant along the parabolic part of the conduction band. The curvature of the rhombohedral structure is slightly smaller, hence the
The Fermi energy is slightly lower, than the hexagonal structure. This difference also would lead to slightly larger effective mass calculated with the rhombohedral structure. The rest of the calculations are performed with the hexagonal structure.

Upon Li intercalation, Li atoms are placed between the HfNCl layers. Li acts as a donor and gives electrons to the Hf-N layers. The density of states stays almost constant as shown in our virtual crystal calculation for Li$_x$HfNCl in Figure 1. The semiconducting state is lost with doping and superconductivity emerges. While it is well-established that in Li$_x$ZrNCl the superconducting state is enhanced at low doping, there is no evidence of this enhancement in experiments with Li$_x$HfNCl.

Table I. The fundamental band gap, $E_g$, between the valence band maximum at the $\Gamma$ point and the conduction band minimum at the $K$ point, effective mass, $m^*$, and density of states at the Fermi level, $N(0)$, of each doping calculated with the PBE and HSE06 functionals.

<table>
<thead>
<tr>
<th>$x$</th>
<th>XC</th>
<th>$E_g$ (eV)</th>
<th>$m^*$ (m$_e$)</th>
<th>$N(0)$ (states/eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>PBE</td>
<td>2.203</td>
<td>0.615</td>
<td></td>
</tr>
<tr>
<td>0.055</td>
<td>PBE</td>
<td>2.195</td>
<td>0.599</td>
<td>0.587</td>
</tr>
<tr>
<td>0.11</td>
<td>PBE</td>
<td>2.171</td>
<td>0.585</td>
<td>0.632</td>
</tr>
<tr>
<td>0.13</td>
<td>PBE</td>
<td>2.168</td>
<td>0.580</td>
<td>0.639</td>
</tr>
<tr>
<td>0.16</td>
<td>PBE</td>
<td>2.164</td>
<td>0.572</td>
<td>0.654</td>
</tr>
<tr>
<td>0.18</td>
<td>PBE</td>
<td>2.156</td>
<td>0.568</td>
<td>0.666</td>
</tr>
<tr>
<td>0.20</td>
<td>PBE</td>
<td>2.153</td>
<td>0.564</td>
<td>0.680</td>
</tr>
<tr>
<td>0.31</td>
<td>PBE</td>
<td>2.130</td>
<td>0.540</td>
<td>0.833</td>
</tr>
<tr>
<td>0</td>
<td>HSE06</td>
<td>3.330</td>
<td>0.522</td>
<td></td>
</tr>
<tr>
<td>0.055</td>
<td>HSE06</td>
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<td>0.496</td>
<td>0.511</td>
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<tr>
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<td>HSE06</td>
<td>3.148</td>
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<tr>
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<td>HSE06</td>
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<td>0.466</td>
<td>0.545</td>
</tr>
<tr>
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<td>HSE06</td>
<td>3.084</td>
<td>0.456</td>
<td>0.556</td>
</tr>
<tr>
<td>0.18</td>
<td>HSE06</td>
<td>3.055</td>
<td>0.451</td>
<td>0.565</td>
</tr>
<tr>
<td>0.20</td>
<td>HSE06</td>
<td>3.031</td>
<td>0.446</td>
<td>0.577</td>
</tr>
<tr>
<td>0.31</td>
<td>HSE06</td>
<td>2.908</td>
<td>0.425</td>
<td>0.723</td>
</tr>
</tbody>
</table>

In Table I we present the band gap, $E_g$, effective mass, $m^*$, and density of states, $N(0)$ of each doping with the PBE and HSE06 functionals. The band gap, $E_g$ decreases with increased doping for both functionals. As the doping increases, the $m^*$ decreases, and this trend is similar in ZrNCl. However, in general, the effective mass of HfNCl is slightly larger than that of ZrNCl. Similarly, the $N(0)$ is larger in HfNCl than ZrNCl for all doping.

B. Spin susceptibility

Similar to the $T_c$, the magnetic spin susceptibility is enhanced in Li$_x$ZrNCl at low doping, whereas there are no experiments of spin susceptibility as a function of doping for Li$_x$HfNCl. Spin susceptibility is the response of the spin magnetization to an applied magnetic field:

$$\chi_s = \left( \frac{\partial^2 E}{\partial M^2} \right)^{-1},$$  \hspace{1cm} (1)

where $E$ and $M$ are the total energy and magnetization, respectively. The non interacting spin susceptibility, $\chi_{0s}$, is obtained by neglecting the electron-electron interaction of the conducting electrons. For perfectly parabolic bands, the non interacting spin susceptibility is doping independent and equal to

$$\chi_{0s} = \mu_s N(0) = \frac{g_s m^*}{\pi \hbar^2},$$  \hspace{1cm} (2)

where $\mu_s$ is the Bohr magneton, $g_s$ is the valley degeneracy (2 in our case) and $m^*$ the band effective mass. We calculate $\chi_{0s}$ from the density of states of the undoped compound, and by extrapolating the $N(0)$ of the desired doping. Our calculations show that $\chi_{0s}$ is not enhanced at the low-doping limit. As $N(0)$ is larger in HfNCl, the $\chi_{0s}$ is also larger in HfNCl than ZrNCl.

We calculate the spin susceptibility with the HSE06 hybrid functional by calculating the total energy at fixed magnetization and then using equation 1 to obtain $\chi_s$. We choose the HSE06 functional, because it can reproduce the $\chi_s/\chi_{0s}$ of ZrNCl. We also compare our results with those obtained by a model based on RPA. The model is appropriate in the low-doping limit where $|k_F - K| \ll K$, a condition necessary to have the intravalley electron-electron scattering dominating over the intervalley one, as explained in the supplementary material of Reference 25. This model assumes a 2D two-valley electron gas with no intervalley Coulomb scattering. Therefore, only the intravalley electron-electron interaction remains and the RPA susceptibility can be calculated analytically, by using the PBE effective mass of undoped HfNCl and the environmental dielectric constant, $\epsilon_M = 4.93$. This value is smaller in HfNCl than ZrNCl ($\epsilon_M = 5.59$).
In a 2D two-valley electron gas, the reduction of doping implies an increase of the $r_s$ electron-gas parameter, and, consequently, of the electron-electron interaction\textsuperscript{25}. The effective mass of β-HfNCl as calculated by the PBE functional is larger (0.615 m$_e$) than β-ZrNCl (0.57 m$_e$)\textsuperscript{25}. Therefore, both the larger $m^*$ and the smaller $\epsilon_M$ of HfNCl lead to larger $r_s$ as compared to ZrNCl, at similar low-doping regime\textsuperscript{25}. This implies that the electron-electron interaction is larger in HfNCl, and hence the spin susceptibility enhancement is also larger in HfNCl. While the spin susceptibility enhancement at low doping is present for both calculations with the RPA and the HSE06 functional, as presented in Figure 2, it is milder with the HSE06 functional than the RPA calculation.

C. Electron-phonon interaction

The electron-phonon coupling of a mode $\nu$ at a phonon-momentum $\mathbf{q}$ is defined as

$$
\tilde{\lambda}_{\mathbf{q}\nu} = \frac{2}{\omega^2_{\mathbf{q}\nu}} N(0) \Lambda \sum_{\mathbf{k}} |d_{\mathbf{k},\mathbf{k}+\mathbf{q}}|^2 \delta(\epsilon_{\mathbf{k}}) \delta(\epsilon_{\mathbf{k}+\mathbf{q}}),
$$

where $\epsilon_{\mathbf{k}}$ is the quasiparticle energy and the electron-phonon matrix elements are defined such that $d_{\mathbf{k},\mathbf{k}+\mathbf{q}} = \langle \mathbf{k} | i \partial V / \partial u_{\mathbf{q} \nu} | \mathbf{k} + \mathbf{q} \rangle$, $u_{\mathbf{q} \nu}$ is the phonon displacement of the mode $\omega_{\mathbf{q} \nu}$, and $V$ is the single particle potential that is fully screened by charge, spin, and valley exchange and correlation effects (see Eq. 2 in Reference 25 for more details). We first calculate the non-interacting $\lambda_{\mathbf{q}\nu}$ with the PBE functional, that does not have the valley polarization dependence, using the Wannier interpolation method\textsuperscript{24}.

In Figure 3 we show the phonon dispersion along the high symmetry directions, and the Eliashberg function, $\alpha^2 F(\omega)$ and the electron-phonon coupling, $\lambda(\omega)$ for the doping $x = 0.055$. The Eliashberg function has two distinct peaks that are dominated by the modes with large phonon linewidths, $\gamma_{\mathbf{q} \nu}$, at the $\mathbf{K}$-point of the Brillouin zone at the energies $\sim 19$ meV and $\sim 59$ meV. To analyze the contribution to the electron-phonon coupling, we separate it into the inter- and intra-valley components. The intervalley electron-phonon coupling, $\lambda_{\text{inter}}$, is defined such that the modes contributing to the coupling are in the vicinity of the $\mathbf{K}$ and $2\mathbf{K}$ points such that, in equation 3 $\mathbf{k} \in I(\mathbf{K})$ and $\mathbf{k} + \mathbf{q} \in I(2\mathbf{K})$; or $\mathbf{k} \in I(2\mathbf{K})$ and $\mathbf{k} + \mathbf{q} \in I(\mathbf{K})$. The rest of the coupling is attributed to the intravalley electron-phonon coupling, $\lambda_{\text{intra}}$. Also shown in Figure 3 that these modes at the $\mathbf{K}$-point contribute significantly to intervalley component of the Eliashberg function and have a large intervalley electron-phonon coupling $\lambda_{\text{inter}}$. Therefore, they induce a valley polarization in this system\textsuperscript{25}.

Consequently, the spin susceptibility enhancement is directly linked to the enhancement in the electron-phonon coupling due to the intervalley interaction\textsuperscript{25,26}. The intervalley electron-phonon coupling is enhanced similarly to $\chi_s / \chi_{0s}$ such that

$$
\frac{\tilde{\lambda}_{\text{inter}}}{\lambda_{\text{inter}}} = \left( \frac{\chi_s}{\chi_{0s}} \right)^2.
$$

Following the previously developed methodology\textsuperscript{25,26} we first calculate the bare intervalley electron-phonon coupling $\lambda$ with the PBE functional, and use the spin susceptibility enhancement of RPA or HSE06 to obtain the corresponding fully dressed coupling $\tilde{\lambda}$.

In Table II we present the bare electron-phonon coupling $\lambda$, and its intra- and inter-valley components, $\lambda_{\text{intra}}$, $\lambda_{\text{inter}}$ calculated with the PBE functional, as well as the fully-interacting electron-phonon coupling for the RPA and the HSE06 calculations, $\lambda_{\text{RPA}}$, $\lambda_{\text{HSE06}}$ and their corresponding $\omega_\lambda$ values.

D. Superconductivity and $T_c$ enhancement

Finally, we calculate the superconducting critical temperature $T_c$ using the McMillan-Allen-Dynes equation\textsuperscript{41,42}:

$$
T_c = \frac{\omega_{\log}}{1.20} \exp \left( \frac{-1.04(1 + \tilde{\lambda})}{\lambda - \mu^* - \mu(1 + 0.62\lambda)} \right),
$$

where $\mu^* = \mu [1 + \mu \log(\epsilon_F / \omega_D)]$ is the screened Coulomb pseudopotential, with $\epsilon_F$ and $\omega_D = 900$ meV being Fermi and Debye energy respectively. We set the unscreened
TABLE II. For each doping, the bare electron-phonon coupling $\lambda$ and its intravally $\lambda^{\text{intra}}$ and intervally $\lambda^{\text{inter}}$ components as calculated by the PBE functional; the fully-interacting electron-phonon coupling for the RPA and the HSE06 functionals, $\hat{\lambda}^{\text{RPA}}$ and $\hat{\lambda}^{\text{HSE06}}$; the PBE functional values of $\omega^{\log}_{\text{PBE}}$ with the intra- and intervally components, $\omega_{\log}^{\text{PBE intr}}$ and $\omega_{\log}^{\text{PBE inter}}$; and the rescaled $\omega_{\log}^{\text{RPA}}$ and $\omega_{\log}^{\text{HSE06}}$ in meV. The screened Coulomb pseudopotential $\mu^{*}$ and the $T_c$ values calculated by the RPA and HSE06 functional are also given.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\lambda$</th>
<th>$\lambda^{\text{intra}}$</th>
<th>$\lambda^{\text{inter}}$</th>
<th>$\hat{\lambda}^{\text{RPA}}$</th>
<th>$\hat{\lambda}^{\text{HSE06}}$</th>
<th>$\omega^{\log}_{\text{PBE}}$</th>
<th>$\omega_{\log}^{\text{PBE intr}}$</th>
<th>$\omega_{\log}^{\text{PBE inter}}$</th>
<th>$\omega^{\log}_{\text{RPA}}$</th>
<th>$\omega^{\log}_{\text{HSE06}}$</th>
<th>$\mu^{*}$</th>
<th>$T_c^{\text{RPA}}$</th>
<th>$T_c^{\text{HSE06}}$</th>
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<tr>
<td>0.055</td>
<td>0.861</td>
<td>0.133</td>
<td>0.728</td>
<td>6.730</td>
<td>2.578</td>
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<td>33.325</td>
<td>0.276</td>
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<td>1.628</td>
<td>32.593</td>
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<td>33.325</td>
<td>33.235</td>
<td>0.276</td>
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</tr>
<tr>
<td>0.13</td>
<td>0.803</td>
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<td>0.621</td>
<td>1.959</td>
<td>1.547</td>
<td>31.458</td>
<td>29.026</td>
<td>30.926</td>
<td>30.404</td>
<td>30.325</td>
<td>0.276</td>
<td>38.15</td>
<td>25.18</td>
</tr>
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<td>0.16</td>
<td>0.860</td>
<td>0.208</td>
<td>0.652</td>
<td>1.800</td>
<td>1.523</td>
<td>28.643</td>
<td>26.451</td>
<td>29.380</td>
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<td>0.254</td>
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<td>1.724</td>
<td>1.551</td>
<td>26.781</td>
<td>25.103</td>
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<td>27.066</td>
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<td>0.248</td>
<td>25.69</td>
<td>21.67</td>
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<tr>
<td>0.20</td>
<td>0.932</td>
<td>0.256</td>
<td>0.676</td>
<td>1.688</td>
<td>1.554</td>
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<td>24.686</td>
<td>27.040</td>
<td>26.668</td>
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<td>0.242</td>
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<td>0.31</td>
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<td>0.372</td>
<td>0.601</td>
<td>1.401</td>
<td>1.331</td>
<td>25.915</td>
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<td>25.906</td>
<td>0.222</td>
<td>19.89</td>
<td>18.30</td>
</tr>
</tbody>
</table>

$\mu = 0.231$ that gives the correct estimate of the experimental $T_c = 19.94$ K at the highest doping of $x = 0.31$ by using the RPA enhanced fully screened electron-phonon coupling, $\lambda$. This is in agreement with the GW estimate of $\mu = 0.237$ at $x = 0.12$. We present the screened Coulomb pseudopotential, $\mu^{*}$ that is used to calculate the $T_c$ for each doping and the final $T_c$ values for the RPA and HSE06 calculations in Table II.

![FIG. 4](image)

FIG. 4. Superconducting critical temperature $T_c$ as a function of doping calculated with the bare electron-phonon coupling, $\lambda_{\text{qu}}$, as calculated by the PBE functional, and with the fully dressed electron-phonon coupling, $\lambda_{\text{qu}}$, using the RPA and HSE06 functional. The experimental data is taken from Reference 12.

With the PBE functional, the superconducting temperature, $T_c$, is reduced in the low-doping limit, in stark disagreement with experiments, as shown in Figure 4. When the dressing of the intervally electron-phonon coupling by the intravally Coulomb interaction is taken into account, the $T_c$ is enhanced in a similar fashion of what happens to the spin susceptibility, i.e. it is enhanced significantly, up to $\sim 70$ K, with RPA, while the enhancement is softer, up to $\sim 40$ K with the HSE06 functional. In addition, the HSE06 functional agrees well with the experimental $T_c$ for the doping between $0.15 < x < 0.20$. We show the details of this scaling for the RPA calculation in A and we present the phonon dispersion, $\omega$, Eliashberg function $\alpha^2F(\omega)$, and electron-phonon coupling $\lambda(\omega)$ for the rest of the dopings in B.

IV. CONCLUSION

We study the electronic, magnetic, and vibrational properties of Li$_2$HfNCl at the low-doping regime. We first calculate the electronic structure and find that the effective mass $m^*$ and the density of states, $N(0)$ are larger in HfNCl as compared to ZrNCl, both for the PBE and the HSE06 functionals.

As there are no experimental data for the spin susceptibility of HfNCl as a function of doping, we calculate the spin susceptibility enhancement using both RPA calculations and the HSE06 functional. Both $m^*$ and $\epsilon_M$ contribute to a larger $r_s$ in HfNCl than ZrNCl. Therefore, the spin susceptibility enhancement is larger in HfNCl than ZrNCl at the low-doping limit and this is visible both in the RPA calculations and the HSE06 calculations of $\chi_s/\lambda_{0s}$.

Then, we calculate the phonon dispersion $\omega_{\text{qu}}$, Eliashberg function $\alpha^2F(\omega)$, and the bare electron-phonon coupling $\lambda(\omega)$ using the PBE functional. We further calculate the fully-dressed electron-phonon coupling $\hat{\lambda}$, based on the enhancement in the spin susceptibility.

This enhancement is then directly reflected in the calculated $T_c$. There is no enhancement in the $T_c$ with the PBE functional. On the other hand, we can speculate that depending on the enhancement in the spin susceptibility, high $T_c$ can be reached; ranging from 40 K (with the HSE06 functional) to 70 K (with the RPA calculation). Furthermore, the HSE06 functional gives comparable $T_c$ values to the experiments for dopings $0.15 < x < 0.20$. However, the $T_c$ goes to zero in experiments for the reported doping $x < 0.15$. A possible explanation for this disagreement is that the disorder at
the low-doping limit can lead to Anderson localization. Alternatively, it could be that the reported doping is only a nominal doping. Experiments of field-effect doping can also help to learn more about the low-doping regime. In either case, our results predict that removal of the Anderson transition or better control of doping in Li$_x$HfNCl could lead to emergence of a high $T_c$ superconducting state.

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**Appendix A: Electron-phonon Coupling Scaling**

We present the electron-phonon coupling in equation (5) as a function of doping in Figure 5. The top panel shows the average non-interacting electron-phonon coupling $\lambda$, as well as the inter- and intra-valley components of it.

The second panel shows the total $\omega_{\text{log}}$, also decomposed into inter- and intra-valley components. In addition, we also present how it is rescaled with the RPA calculation, by rescaling of the $\tilde{\lambda}_{\text{inter}}$. Starting with the definition of $\omega_{\text{log}}$:

$$\omega_{\text{log}} = \exp \left[ \frac{2}{\lambda} \int_0^{+\infty} \alpha^2 F(\omega) \frac{\log(\omega)}{\omega} d\omega \right], \quad (A1)$$

we have separated $\omega_{\text{log}}$ into inter- and intra-valley terms. The inter-valley term is

$$\omega_{\text{log}}^{\text{inter}} = \exp \left[ \frac{2}{\lambda_{\text{inter}}} \int_0^{+\infty} \alpha^2 F(\omega)^{\text{inter}} \frac{\log(\omega)}{\omega} d\omega \right], \quad (A2)$$

and intra-valley term is defined similarly. The relation between these two terms hold such that

$$\omega_{\text{log}} = (\omega_{\text{log}}^{\text{inter}})^{\lambda_{\text{inter}}/\lambda} \times (\omega_{\text{log}}^{\text{intra}})^{\lambda_{\text{intra}}/\lambda}. \quad (A3)$$

Therefore, we rescaled it for the RPA calculation by keeping the intravalley $\lambda^{\text{intra}}$ component the same, but rescaling the full-interacting intervalley $\tilde{\lambda}_{\text{inter}}$ and hence the total $\lambda$ electron-phonon coupling elements. These are shown in the third panel of the figure for the RPA calculations.

**Appendix B: Phonon Modes as a Function of Doping**

In this section, we present the phonon dispersion of Li$_x$HfNCl for all doping values. The left panels of Figure 6 show the phonon dispersion with increasing doping. Similarly the right panels show the corresponding Eliashberg function, $\alpha^2 F(\omega)$ and the electron-phonon coupling $\lambda(\omega)$. In all cases, there are two distinct peaks of $\alpha^2 F(\omega)$, and consequently an increase in the $\lambda(\omega)$.
FIG. 6. Left: Phonon dispersion of Li$_x$HfNCl as a function of doping. Right: Total Eliashberg function, $\alpha^2 F(\omega)$ and electron phonon coupling, $\lambda(\omega)$.