Universal enhancement of superconductivity in two dimensional semiconductors at low doping by electron-electron interaction.

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In two-dimensional multivalley semiconductors, at low doping, even a moderate electron-electron interaction enhances the response to any perturbation inducing a valley polarization. If the valley polarization is due to the electron-phonon coupling, the electron-electron interaction results in an enhancement of the superconducting critical temperature. By performing first principles calculations beyond density functional theory, we prove that this effect accounts for the unconventional doping-dependence of the superconducting transition-temperature ($T_c$) and of the magnetic susceptibility measured in $\text{Li}_x\text{ZrNCl}$. By finding the conditions for a maximal $T_c$ enhancement, we show how weakly-doped two-dimensional semiconductors provide a route towards high $T_c$ superconductivity.

The quest for high $T_c$ superconductivity has mainly focused on strongly correlated materials in proximity of electronic instabilities like the Mott transition (cuprates [1]) or fragile magnetic states (iron pnictides [2, 3]). Heavily doped three dimensional (3D) covalently bonded semiconductors, like diamond [4], silicon [5] and SiC [6, 7] have been considered as an alternative, that, however, has lead, so far, to fairly low $T_c$ (< 10 K). In 3D, the density of states at the Fermi level slowly grows with doping. As $T_c$ increases with the density of states [8], a large number of carriers has to be introduced to achieve a large $T_c$. This demanding requirement could be released in two dimensional (2D) semiconductors, such as transition metal dichalcogenides [9–12], clorinonitriles [13, 14] or other layered materials with massive Dirac fermions, where the doping can be controlled by intercalation [13, 14] or field-effect [11, 12, 15]. Indeed, in 2D, the density of states is a constant function of the Fermi energy and, in principle, $T_c$ is expected to be insensitive on doping. Surprisingly, measurements on $\text{Li}_x\text{ZrNCl}$ [13, 14, 16], a weakly-doped multivalley 2D semiconductor, revealed that $T_c$ not only does not increase with doping but even decreases. Here we show that the e-e interaction is responsible for such a puzzling behavior. In particular, in a weakly-doped 2D multivalley semiconductor, e-e manybody effects enhance the response to any perturbation inducing a valley polarization. If the valley polarization is due to the electron-phonon coupling, the e-e interaction will lead to a large increase of $T_c$. We demonstrate that this effect explains the high $T_c$ in $\text{Li}_x\text{ZrNCl}$ and its unconventional behavior [16] as a function of doping. Finally, by finding the conditions for a maximal $T_c$ enhancement, we show how weakly-doped two-dimensional semiconductors are an alternative route towards high $T_c$ superconductivity.

The electronic structure of multivalley semiconductors has minima (maxima) in the conduction (valence) band that are named valleys. In the low doping limit, the equivalent $g_v$ valleys are occupied by few electrons or holes and the electronic structure is described by the effective mass theory. The resulting model Hamiltonian is that of a multicomponent electron gas of mass $m^*$ and density $n$ where the valley index plays the role of a pseudo-spin. Since at low doping the Fermi momentum $k_F$, as measured from the valley bottom, is much smaller than the valley separation, the intravalley e-e interaction dominates over the intervalley one, and (for an isotropic mass tensor) the manybody Hamiltonian has $\text{SU}(2g_v)$ symmetry in valley and spin indexes [5, 17, 19, 20]. In 2D the intravalley Coulomb interactions is $2\pi/\epsilon_M q$, where $q$ is the exchanged momentum, and $\epsilon_M$ the environmental dielectric constant. The strength of e-e scattering is measured by the parameter $r_s = 1/(a_B \sqrt{\pi n})$ where $a_B = \epsilon_M \hbar^2/(m^* e^2)$.

The magnetic properties of a doped semiconductor are described by the interacting spin susceptibility, $\chi_s$, that is related to the derivative of the total spin magnetization $M$ with respect to an applied magnetic field $B_{\text{ext}}$, namely:

$$\chi_s = \frac{\partial M}{\partial B_{\text{ext}}}$$  \hspace{1cm} (1)

The non-interacting spin susceptibility is doping independent, namely $\chi_{0s} = \mu_S^2 N(0)$, where $\mu_S$ is the electron-spin magnetic moment and $N(0) = g_e m^*/(\pi \hbar^2)$ the density of states at the Fermi level. Manybody e-e effects increase the spin susceptibility with respect to its non-interacting value $\chi_{0s}$ and can possibly lead to a magnetic state. Indeed the e-e energy is lower in the spin-polarized state, since electrons with same spin and valley cannot occupy same spatial position because of the Pauli exclusion principle. The enhancement $\chi_s/\chi_{0s}$ increases with increasing $r_s$ (as the relative contribution of exchange to the total energy increases) and it is significant already at moderate correlations, i. e. $r_s \approx 1$ [4, 19, 20, 22, 23].

In a multivalley electron gas, an external perturbation can induce a valley polarization. The existence of such a valley polarization in 2D systems is at the heart of recent developments in the field of valleytronics [10], the valley analogue of spintronics. Any perturbation inducing an asymmetry in the population of the different valleys can
then be seen as an external pseudo magnetic field. In analogy with the magnetic case, a valley susceptibility $\chi_v$ is defined as the first derivative of the valley magnetization ($\mu_s$ times the valley-population difference) with respect to the external pseudo magnetic field.

In the low doping limit, because of the SU(2)$_\mu$ valley-spin symmetry of the model Hamiltonian [5, 19, 20], the valley susceptibility $\chi_v$ is equal to the spin susceptibility $\chi_s$. This equality was experimentally verified in measurements of both spin and valley susceptibility in AIAs quantum wells [24] where the pseudo magnetic field was generated by a strain deformation. Similarly to the strain case in AIAs, an intervalley phonon can also act as a pseudo magnetic field by inducing a valley splitting and a valley polarization via the electron-phonon interaction. As a consequence, the many-body enhancement of the valley susceptibility can result in an augmentation of the superconducting critical temperature ($T_c$) at low doping, as we show it happens in Li$_x$ZrNCl.

ZrNCl is a layered large gap semiconductor, with an extremely weak interlayer coupling ($t_{\perp} < 1.5$ meV) and two equivalent valleys with isotropic mass tensors in the conduction band (see Fig. 1 (a)) at the special points $\mathbf{K}$ and $\mathbf{K}' = 2\mathbf{K}$. The Li intercalation acts as a rigid filling of the conduction band with $x$ electrons [11]. The bands are almost parabolic with $m^* = 0.57$ (in units of the electron mass) for doping $x \leq 2/9$ (see Fig. 1 (a)). Li$_x$ZrNCl is then the physical realization of a 2D two-valley electron-gas. Upon Li intercalation, the system stays insulating due to an Anderson localization ($x \leq 0.05$) and then becomes superconducting at larger doping [13]. The spin-susceptibility $\chi_s$ increases as doping is reduced, as shown in Fig. 2 (top-panel). As the non-interacting $\chi_{0s}$ is doping independent in 2D, the increase can only be due to exchange-correlation effects. The superconducting $T_c$ behaves similarly to $\chi_s$ as it increases from 11.5 K to 15 K for $x$ decreasing from 0.3 to 0.05 (see Fig. 2 bottom panel and Ref. [16]), suggesting that the two effects are related.

In order to evaluate the interacting $\chi_s$, we consider a 2D two valley electron-gas with a finite thickness equal to that of the ZrN layer and environmental dielectric constant $\epsilon_M = 5.59$, as calculated in linear response density functional theory for the parent insulating compound $\beta$-ZrNCl [26]. We obtain the $\chi_s/\chi_{0s}$ enhancement in the random-phase approximation (RPA) approximation [17]. The RPA closely reproduces the quantum Monte-Carlo results [4, 19, 22], for $r_s$ values relevant for Li$_x$ZrNCl ($r_s < 1.5$). As it can be seen in Fig. 2 central panel, the enhancement is already large at these intermediate values of $r_s$, meaning that a substantial renormalization of the intervalley coupling is expected. In order to validate our calculated susceptibility against experiment, we add a doping-independent constant to the theoretical $\chi_s$. Our $\chi_s$ closely reproduces the dependence on doping measured in experiments [1, 17].

To gain insight on the pairing interaction in Li$_x$ZrNCl, we evaluate the phonon spectrum and the electron-phonon interaction using density functional theory [28]. In a general Fermi liquid approach, the electron-phonon coupling parameter of a mode $\nu$ at a phonon-momentum $\mathbf{q}$ is given by:

$$\lambda_{\nu\mathbf{q}} = \frac{2}{\omega_{\nu\mathbf{q}}^2 N(0) N_k} \sum_{\mathbf{k}} \left| d^{\nu}_{\mathbf{k},\mathbf{k}+\mathbf{q}} \right|^2 \delta(\epsilon_{\mathbf{k}}) \delta(\epsilon_{\mathbf{k}+\mathbf{q}})$$

(2)

where the tilde indicates that the quantities are fully screened by all kind of exchange-correlation interaction (charge, spin and valley). The quasiparticle energies (no band index is present as only one band contributes in Li$_x$ZrNCl) are $\epsilon_{\mathbf{k}}$ and $d^{\nu}_{\mathbf{k},\mathbf{k}+\mathbf{q}} = \langle \mathbf{k} | \tilde{V} \delta \mathbf{u}_{\nu\mathbf{q}} | \mathbf{k} + \mathbf{q} \rangle$, with $\tilde{V}$ being the screened [7] single-particle potential that includes, at the mean-field level, the e-e interaction [30]. Moreover $u_{\nu\mathbf{q}}$ and $\omega_{\nu\mathbf{q}}$ are the amplitude of the phonon displacement and the phonon frequency, respectively. In GGA or LDA functionals the exchange-correlation energy depends explicitly on charge densities and spin polarization, but not on valley polarizations. As a consequence, in the small doping limit, the SU(4) spin and valley symmetry of the manybody Hamiltonian is broken. Then the matrix elements in Eq. 2 do not include any enhancement due to intervalley exchange-correlation [17] and, for this reason, they are undressed (bare) with respect to intervalley exchange-correlation interaction. We label them as $d^{\nu}_{\mathbf{k},\mathbf{k}+\mathbf{q}}$ and $\lambda_{\nu\mathbf{q}}$ without the tilde. In the Hartree-Fock (HF) approximation, the matrix elements do include a intervalley exchange-correlation enhancement, that is, however, severely overestimated with
respect to Quantum Monte Carlo or RPA results [19]. For this reason, hybrid functional calculations [31] lead to matrix elements $\tilde{d}_{\nu}^{\alpha}$ that crucially depends on the amount of HF exchange included.

In order to evaluate the bare quantity $\lambda_{\vec{q}\nu}$ as a function of doping, we use density functional perturbation theory [9] and Wannier interpolation [7] (see [17] for other doping). We find a marked softening of an intervalley phonon having $\approx 59$ meV phonon-energy at $x = 1/18$ in a region of radius $2\kappa_F$ around $\mathbf{K}$ (Fig. 3). As the softening $\Delta\omega_{\nu\vec{q}}$ is essentially constant in this region, we conclude that $|d_{\nu}^{\alpha_{\mathbf{k+q}}}| \approx |d_{\nu}^{\alpha_{\mathbf{2K+q}}}|$. Indeed, under this assumption the phonon softening at $\mathbf{q}$ close to $\mathbf{K}$ is $\Delta\omega_{\nu\vec{q}} \approx -\chi_0(\mathbf{q})|d_{\nu}^{\alpha_{\mathbf{2K+q}}}|^2/(2\omega_{\nu\vec{q}})$ [17]. Here $\chi_0(\mathbf{q})$ is the bare finite-momentum response-function, which is constant and doping independent in 2D for $|\mathbf{q} - \mathbf{K}| < 2\kappa_F$ [17, 34].

The average electron-phonon coupling $\lambda$ as a function of doping is shown in Tab. I. We further decompose $\lambda$ in inter- and intra-valley contributions finding that at low doping (i) the intravalley contribution is suppressed for $x$ going to zero and (ii) the intervalley contribution is almost doping independent and dominant, as shown in Fig. 3 and in [17]. In the Eliashberg function at $x = 1/18$ most of the coupling arises from intervalley phonons at $\approx 59$ and $24.5$ meV, (Fig. 3). These phonons have large phonon linewidths $\gamma_{\nu\vec{q}} = \pi N(0)\omega_{\nu\vec{q}}^2\lambda_{\nu\vec{q}}$, as shown by the red bars in Fig. 3. Finally, both the average electron-phonon coupling and the logarithmic average of the phonon frequencies are roughly constant (see Tab. I), so that $T_c$ as obtained from McMillan equation [35] slightly increases with doping, in agreement with previous calculations at higher doping [11, 12], but in qualitative disagreement with experimental data (see Fig. 2 bottom panel).

Assuming a constant intravalley electron-phonon matrix element ($|d_{\nu}^{\alpha_{\mathbf{k+q}}}| \approx |d_{\nu}^{\alpha_{\mathbf{2K+q}}}|$), we can derive an effective Hamiltonian where the presence of a small phonon displacement $u_{\mathbf{K}+\nu\vec{q}}$ is described as an external pseudo magnetic field $B_{\nu\text{ext}} = |d_{\nu}^{\alpha_{\mathbf{2K+q}}}| |K_{\nu}| / \mu_S$. Indeed, if we define a two-component spinor using as basis the states $|\mathbf{K} + \nu\vec{q}|$ and $|2\mathbf{K} + \nu\vec{q}|$, where $\nu = \mathbf{k} - \mathbf{K}$, we obtain the following form of the one-body part of the Hamiltonian:

$$H'_{\nu} = \frac{\hbar^2 \gamma^2}{2m^*} I + B'_{\nu\text{ext}} \mu_S \sigma_z,$$  

(3)

where $I$ and $\sigma_z$ are the $2 \times 2$ identity and the Pauli matrix along the x-direction, respectively. We explicitly verify the accuracy of such Hamiltonian by performing a DFT electronic structure calculations on a $\sqrt{3} \times \sqrt{3}$ supercell with AA stacking. In this supercell, the two valleys at $\mathbf{K}$ and $2\mathbf{K}$ in the unit cell, are folded at the zone center. As shown in Fig. 4, by displacing the atoms from the equilibrium, the intervalley phonon splits the two valleys by a constant amount equal to $2B'_{\nu\text{ext}} \mu_S$, as predicted by the model Hamiltonian. The intervalley phonons induce a valley polarization and act as a pseudo magnetic field.

As it happens in the magnetic case, the response to the pseudo magnetic field is enhanced by the intervalley exchange-correlation (which is however absent in our DFT calculation, as shown in [17]). As the total magnetization due to the pseudo magnetic field $B'_{\nu\text{ext}}$ is written either as $M = \chi_s B'_{\nu\text{ext}}$ or as $M = \chi_{0s} B'_{\nu}$, where now $B'_{\nu}$ is the total magnetic field, sum of the external plus the exchange-correlation field, we have [17],

$$\frac{B'_{\nu}}{B'_{\nu\text{ext}}} = \frac{|d_{\nu}^{\alpha_{\mathbf{2K+q}}}|}{|d_{\nu}^{\alpha_{\mathbf{2K}}}|} = \frac{\chi_s}{\chi_{0s}},$$  

(4)

namely the electron-phonon coupling at $\mathbf{q} = \mathbf{K}$ is renormalized by intervalley correlation effects exactly in the same way as the spin susceptibility with an enhancement that is independent from the phonon index $\nu$. Assuming again a constant intervalley matrix element we have that:

$$\chi_{\text{inter}} = \left(\frac{\chi_s}{\chi_{0s}}\right)^2 \chi_{\text{inter}},$$  

(5)
so that \( \tilde{\lambda} = \lambda^{\text{intra}} + \tilde{\lambda}^{\text{inter}} \). We use the \( \chi_{s}/\chi_{0s} \) enhancement in Fig. 2 (central panel) to evaluate \( \tilde{\lambda} \), the renormalized Eliashberg function and \( T_c \) using McMillan equation [35]. The results are shown in Fig. 2 (bottom panel). We now find that the doping dependence of the superconducting critical temperature is in excellent agreement with experimental data and both the value of \( T_c \) as well as its dependence on doping are correctly reproduced. Intervalley exchange-correlation is the mechanism responsible for the enhancement of \( T_c \) at low doping in Li\(_{1/3}\)ZrNCl.

In this work we have shown that at low doping of a multivalley two dimensional semiconductor the intervalley exchange-correlation enhances \( T_c \) for any pairing mechanism inducing a valley polarization. We have shown a detailed calculation for Li\(_{1/3}\)ZrNCl and the case of phonon mediated pairing, but the results of our work are universal and provide a general guideline to realize a superconducting state in a doped semiconductor. First of all the system should be strongly two dimensional. In this case the density of states is doping independent and constant down to very low doping, where Anderson localization occurs. In three dimensional multivalley doped semiconductors, the enhancement of the valley susceptibility due to manybody effects still occurs, but the density of states has a square root dependence on the Fermi energy, so that at low doping the number of carriers tends to zero and \( T_c \) is suppressed. Indeed, in three dimensional multivalley doped semiconductors like diamond, Si or SiC [4–7], \( T_c \) increases with doping, in stark contrast with the Li\(_{1/3}\)ZrNCl case. Furthermore, in order for the enhancement to occur, a multivalley electronic structure is needed. However, the enhancement is smaller as the number of valleys increases and ultimately tends to one in the limit of infinite number of valleys. Two is then the optimal number of valleys. Finally, the \( T_c \) enhancement is larger, the larger the \( r_s \) parameter. A larger \( r_s \) parameter can be obtained reducing the density (or doping), reducing the dielectric constant of the spacers (\( \epsilon_M \)) or increasing the effective mass of the band (\( m^* \)). At fixed \( \epsilon_M \) and \( m^* \), the largest enhancement should be found in the proximity of the band insulating or semiconducting state. In the very low doping limit, in the absence of disorder, the enhancement of \( T_c \) can be so large to induce high \( T_c \) superconductivity. However, in this limit, disorder and the resulting Anderson localization tend to suppress superconductivity. Thus, high \( T_c \) superconductivity will only be seen in very clean samples. Finally, it is worth to recall than the pairing mechanism does not need to be necessary the electron-phonon interaction. Indeed, any mechanism (e.g. spin-fluctuations) inducing a valley polarization will experience an enhancement of \( T_c \) due to intervalley exchange-correlation.

**TABLE I.** Values of \( \epsilon_F \), \( \omega_{\log} \), \( \lambda \), \( \lambda^{\text{intra}} \), \( \lambda^{\text{inter}} \), \( \chi_{\log} \), \( \chi_{0\log} \), \( \chi_{\log}/\chi_{0\log} \) and \( \lambda \) from density functional perturbation theory[9] and Wannier interpolation [7]. All energies are in meV. The enhancement \( \chi_{s}/\chi_{0s} \) is calculated in the RPA approximation. The couplings \( \tilde{\lambda}^{\text{inter}} \) and \( \tilde{\lambda} \) are obtained via Eq. 5.

| \( x \) | \( \epsilon_F \) | \( \omega_{\log} \) | \( \lambda \) | \( \lambda^{\text{intra}} \) | \( \lambda^{\text{inter}} \) | \( \chi_{\log}/\chi_{0\log} \) | \( \lambda \) |
|----|----|----|----|----|----|----|----|
| 1/18 | 246 | 43.9 | 0.48 | 48.0 | 0.10 | 42.8 | 0.38 | 1.37 | 0.72 | 0.82 |
| 1/9 | 448 | 44.8 | 0.51 | 47.6 | 0.11 | 43.9 | 0.39 | 1.27 | 0.62 | 0.74 |
| 1/6 | 622 | 44.6 | 0.52 | 45.5 | 0.16 | 44.3 | 0.36 | 1.21 | 0.53 | 0.69 |
| 2/9 | 790 | 43.3 | 0.55 | 42.9 | 0.20 | 43.4 | 0.35 | 1.18 | 0.49 | 0.69 |

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The results reported in the present paper were obtained from first-principles density functional theory in the linear response as implemented in the QUANTUM-ESPRESSO [9] package. Converged phonon dispersion and electron-phonon interaction were obtained by using Wannier interpolation [7]. Li intercalation was simulated by changing the number of electrons and adding a lithium compensating background [11]. All the structures considered were obtained by using the experimental lattice parameters and performing optimization of internal coordinates. More details in [17].
Supplementary Materials of
Universal enhancement of superconductivity in two dimensional semiconductors at low doping by electron-electron interaction.

Spin susceptibility from experiments

In Ref. [1] (see, in particular, the discussion in the supplementary information of Ref. [1]) all possible diamagnetic contributions were subtracted from the measured susceptibility $\chi$, namely:

$$\chi_s = \chi - \chi_{\text{Li}^+}^{\text{core}} - \chi_{\text{ZrNCl}}^{\text{core}} - \chi_L - \chi_{\text{orb}}$$

(6)

where $\chi_{\text{core}}^{\text{Li}^+}$ and $\chi_{\text{core}}^{\text{ZrNCl}}$ are the core diamagnetic susceptibility from Li ion and pristine $\beta -$ZrNCl, respectively. The quantities $\chi_L$ and $\chi_{\text{orb}}$ are the Landau diamagnetic and orbital susceptibilities, respectively. The $\chi_{\text{core}}^{\text{Li}^+}$ and $\chi_{\text{core}}^{\text{ZrNCl}}$ susceptibilities are doping independent. The orbital susceptibility $\chi_{\text{orb}}$ was considered zero for a magnetic field applied along the c direction. Finally, in Ref. [1] the Landau susceptibility $\chi_L$ was assumed to be

$$\chi_L = -\frac{1}{3m^*}\chi_s$$

(7)

where $m^*$ is the band effective mass in units of the electron mass ($m^* = 0.66$ in [1]). This last assumption is not correct. Indeed, in a 2D electron gas with parabolic bands:

$$\chi_{0L} = -\frac{1}{3(m^*)^2}\chi_{0s}$$

(8)

where $\chi_{0L}$ is the non interacting Landau susceptibility. Moreover, it has been shown that many-body effects strongly renormalize the spin susceptibility, while the Landau susceptibility is only weakly renormalized [2, 3]. For the doping regime considered here we can assume that $\chi_{0L} = \chi_L$. Thus Eq. 7 should be replaced by:

$$\chi_L = -\frac{1}{3(m^*)^2}\chi_{0s} = -\frac{\mu_S^2}{3(m^*)^2}N(0).$$

(9)

Since we are only interested in the variation of the susceptibility with doping, and $\chi_{0s}$ is doping independent, we add back to the experimental data the negative quantity, erroneously removed with Eq. 7. This is done by multiplying the susceptibilities presented in Fig. 4 of Ref. [1] by a $[1 - 1/(3m^*)] = 0.495$ factor. The results are reported in Fig. 2 in our main paper as measured data.

Spin susceptibility in the random phase approximation

We compute the interacting spin susceptibility of a multivalley 2D electron gas in the random phase approximation. We integrate numerically the expression given by [4], which (after correcting few typos) reads:

$$\frac{\chi_{0s}}{\chi_s} = 1 - \frac{2\alpha r_s}{\pi} \int_0^1 dx \frac{xF(x)}{\sqrt{1-x^2}} + \frac{\sqrt{2}\alpha r_s}{\pi} \int_0^\infty x^2 F(x)dx \int_0^\infty du \left[ \frac{1}{\epsilon(x, iu)} - 1 \right]$$

$$\times \left( A\sqrt{1+A/R} - B\sqrt{1-A/R} \right) R^{-5/2}$$

(10)

where $\alpha = \sqrt{g_v g_s/4}$ with $g_v$ ($g_s$) being the valley (spin) degeneracy, $x=q/2k_F$, $A=x^4-x^2-u^2$, $B=2x^2u$, $R=\sqrt{A^2+B^2}$ and $u=\omega/(4\epsilon_F)$. The imaginary frequency dielectric function $\epsilon(x, iu)$ is defined as:

$$\epsilon(x, iu) = 1 + \alpha r_s g_v g_s F(x) \left[ \frac{1}{2x} - \sqrt{A+R/(2^{3/2}x^3)} \right]$$

(11)
The wavefunctions of conduction bands are localized on ZrN atoms. We treat each ZrN layer as a 2D electron gas of finite thickness, with a rectangular charge profile of width \( a \). We set \( a = 2.5 \) Å, to mimic the profile of the DFT charge distribution of the conducting electrons. In addition we also consider the perfect (long-range) metallic screening of the adjacent ZrN layers, located at a distance \( d = 10.5 \) Å. We encode this information in the form factor:

\[
F(x) = \frac{2}{qa^*} \left( 1 + \frac{e^{-qa^*} - 1}{qa^*} \right) + \frac{1 - e^{-4qd^*}}{1 + e^{-4qd^*}} + 2e^{-2qd^*} - 1
\]

where \( q = 2 \pi k_F, k_F = 1/(r_s a), a^* = a/a_B, b^* = b/a_B, a_B = (\epsilon_M/m^*)0.529177 \) Å, and we suppose that \( d \gg a \).

In the top panel of Fig. 2 of our main paper, we add a doping independent constant \( C \) to the RPA result for \( \chi_s \) to account for the Landau diamagnetic term, Eq. 9, and for the uncertainties on the estimations of the others diamagnetic (doping independent) terms of the left hand side of Eq 6. The best agreement with experiment is obtained for \( C = -7.77 \times 10^{-6} \) emu/mol. Note that, using a value of \( m^* = 0.57 \) as in the rest of the paper, Eq. 9 gives \( \chi_L = -8.89 \times 10^{-6} \) emu/mol, in close agreement with the value obtained for the constant \( C \).

Model Hamiltonian and SU(2g_v) spin-valley symmetry in the low density limit

In two dimension the Coulomb repulsion is written as

\[
v(q) = \frac{2 \pi e^2}{\epsilon_M q}
\]

where \( q \) is the exchanged momentum beween the two interacting electrons and \( \epsilon_M \) the environmental dielectric constant. We can define two types of electron-electron scattering: i) the intravalley scattering with \( q \sim \kappa_F \) ( \( \kappa_F \) being the Fermi momentum measured from the valley bottom), that does not change the valley index of the electrons, ii) the intervalley scattering with \( q \sim |K - K'| = |K| \) (\( K \) and \( K' = 2K \) being the positions of the valley bottoms in the Brillouin zone), that changes the valley index of the electrons.

In the low doping limit, namely for \( \kappa_F \ll |K - K'| \), because of the divergence of the Coulomb repulsion for \( q \to 0 \), the intravalley scattering is dominant and the intervalley scattering and can be neglected. Under this hypotesis, the valley index (as the spin index) is conserved by the Coulomb interaction, it can be treated as a pseudospin and the manybody Hamiltonian has exact SU(2g_v) spin and valley symmetry, namely

\[
H = \sum_{\kappa \nu \sigma} \frac{\hbar^2 \kappa^2}{2m^*} c_{\kappa \nu \sigma}^\dagger c_{\kappa \nu \sigma} + \sum_{\kappa \nu \sigma \kappa' \nu' \sigma'} \sum_{q} v(q) c_{\kappa \nu \sigma}^\dagger c_{\kappa' \nu' \sigma'}^\dagger c_{\kappa' \nu' \sigma'} c_{\kappa \nu \sigma} - q c_{\kappa \nu \sigma} c_{\kappa \nu \sigma} - q c_{\kappa \nu \sigma} c_{\kappa \nu \sigma}
\]

where \( v, v' = 1, ..., g_v \) are valley indexes and \( \sigma, \sigma' = \pm \) are spin indexes and \( c, c^\dagger \) are creation and destruction operator (see e. g. Eq. 3.35 of Ref. [5]). It follows that:

\[
\chi_v = \chi_s
\]

Spin susceptibility in local spin density functional theory

The total energy in local spin density functional theory in the presence of an external (bare) magnetic field \( B_{ext} \) is written as:

\[
E_{LSD} = T + \int d\mathbf{r} \epsilon_{h,xc}(n, m) - \mu_s \int d\mathbf{r} m(\mathbf{r}) B_{ext}
\]
where $T$ is the kinetic energy functional, $\epsilon_{h,xc}(n,m) = \epsilon_h(n) + \epsilon_{xc}(n,m)$ is the Hartree and exchange and correlation energy per particle, $n(r)$ is the electron density and $m(r) = n_+(r) - n_-(r)$. The Kohn-Sham potential for each spin channel $(\pm)$ is written as

$$V_{KS}^\pm = \frac{\delta \epsilon_{h,xc}}{\delta n(r)} \pm \frac{\delta \epsilon_{h,xc}}{\delta m(r)} \mp \mu_s B_{\text{ext}}.$$  \hspace{1cm} (17)

In a paramagnetic system[6], we have that

$$\frac{\delta \epsilon_{xc}(n,m)}{\delta m} \bigg|_{m=0} = 0$$ \hspace{1cm} (18)

We can then expand at second order $\epsilon_{xc}(n,m)$ in $m$ and obtain

$$V_{KS}^\pm = \frac{\delta \epsilon_{h,xc}}{\delta n(r)} \pm \frac{\delta^2 \epsilon_{xc}}{\delta m(r)^2} m \mp \mu_s B_{\text{ext}}.$$ \hspace{1cm} (19)

We call

$$\tilde{B} = B_{\text{ext}} + B_{xc}$$ \hspace{1cm} (20)

the total (screened by the exchange-correlation) field, where

$$\mu_s B_{xc} = -\frac{\delta^2 \epsilon_{xc}}{\delta m(r)^2} m.$$ \hspace{1cm} (21)

The fields are related to the magnetization by the following two relations:

$$\mu_s m = \chi_{0s} \tilde{B},$$ \hspace{1cm} (22)

$$\mu_s m = \chi_s B_{\text{ext}}.$$ \hspace{1cm} (23)

where $\chi_{0s}$ and $\chi_s$ are the bare and interacting susceptibilities, respectively. Combining Eq.s 20, 21, and 23, we obtain:

$$\tilde{B} = (1 - f \chi_s) B_{\text{ext}}$$ \hspace{1cm} (24)

where $f = \frac{\delta^2 \epsilon_{xc}}{\delta m(r)^2} \frac{1}{\mu_s^2} < 0$. From Eqs. 22 and 23 we have

$$\frac{\tilde{B}}{B_{\text{ext}}} = \frac{\chi_s}{\chi_{0s}}.$$ \hspace{1cm} (25)

meaning that the total magnetic field in the sample is renormalized by exchange-correlation effects exactly as the manybody enhancement of the spin susceptibility.

Replacing Eq. 25 in Eq. 24, we obtain:

$$\frac{\chi_s}{\chi_{0s}} = \frac{1}{1 + f \chi_{0s}}$$ \hspace{1cm} (26)

The relation between the total (screened) magnetic field and the external (bare) one is determined by the function $f$ that is related to the second derivative of the exchange correlation potential with respect to the spin magnetization. If the exchange correlation functional has no dependence on $m$, then $f = 0$ and there is no susceptibility enhancement.

**Absence of valley susceptibility enhancement in local spin density**

In Li$_x$ZrNCl a valley polarization can be induced by the atomic displacements of an intervalley phonon, as shown in Fig. 4 in the main paper. In this case the deformation potential acts as an external (bare) $B_{\text{ext}}' = |d_{K,2K}^\nu| u_{K'}/\mu_S$ pseudo magnetic field.
In an exact many-body treatment, in the low doping limit, the $SU(4)$ spin and valley symmetry is preserved. This is not necessary the case if approximated local exchange and correlation functionals are used. If a 4-component local exchange correlation kernel is adopted in the calculation, namely

$$\epsilon_{xc} = \epsilon_{xc}(n, m, m_v)$$

where $m_v(r) = n_{v=1}(r) - n_{v=2}(r)$ is the valley magnetization and $\epsilon_{xc}(n, m, m_v) = \epsilon_{xc}(n, m_v, m)$, then the $SU(4)$ symmetry can be preserved. The valley exchange-correlation enhancement is written as

$$\chi_s = \frac{1}{1 + f_v \chi_0 s}$$

with $f_v = \frac{2 \epsilon_{xc}}{\delta m_v(r)^2 \mu_s^2} < 0$. Thus if the exchange and correlation energy per particle depends explicitly on $m_v$, there is a valley exchange-correlation enhancement different from 1.

In standard local LDA/GGA functionals, the $SU(4)$ spin valley symmetry is broken and the exchange and correlation energy per particle is assumed to be

$$\epsilon_{xc} = \epsilon_{xc}(n, m)$$

independent of $m_v$. In this case, $f_v = 0$ and the valley exchange-correlation enhancement is exactly one. Thus the valley susceptibility is bare in this case.

Finally, it is important to remark that standard LDA/GGA parametrizations of the electron gas are for the three dimensional case. Thus the exchange-correlation enhancement of spin and valley susceptibilities is taken into account incorrectly.

**Relation between phonon softening and bare susceptibility**

The softening at $q$ in Fermi liquid theory with an effective single particle potential [7] is written as:

$$\Delta \omega_{q,\nu} = \frac{1}{N} \sum_k \frac{|d^\nu_{k+k+q}|^2 f_{k+q} - f_k}{\omega_{q,\nu} \epsilon_{k+q} - \epsilon_k}$$

the tilde means screened with respect to intervalley exchange correlation. Assuming a constant inter-valley matrix element ($|d^\nu_{k,k+K}| \approx |d^\nu_{K,2K}|$), we have for the phonon softening at phonon momentum $q$ close to $K$:

$$\Delta \omega_{q,\nu} = -\frac{|d^\nu_{K,2K}|^2}{2\omega_{q,\nu}} \chi_0(q)$$

where the bare finite-momentum response-function is

$$\chi_0(q) = -\frac{2}{N} \sum_k \frac{f_{k+q} - f_k}{\epsilon_{k+q} - \epsilon_k}$$

For the parabolic 2-valley band-structure of Li$_x$ZrNCl ad $q = K$ we have:

$$\Delta \omega_{K,\nu} = -\frac{|d^\nu_{K,2K}|^2}{2\omega_{K,\nu} \mu_s^2} \chi_0$$

since $\chi_0(K) = \lim_{q \to K} \chi_0(q) = N(0) = \chi_0 / \mu_s^2$.

**First principles calculations: technical details**

The results reported in the present paper were obtained from first-principles density functional theory in the generalized gradient approximation [8]. The QUANTUM-ESPRESSO [9] package was
used with ultrasoft [10] pseudopotentials and a plane-wave cutoff energy of 34 Ry on the kinetic energy and 340 Ry on the charge density. Li intercalation was simulated by changing the number of electrons and adding a jellium compensating background [11]. All the structures considered were obtained by using the experimental lattice parameters and performing optimization of internal coordinates. This choice assures that the interlayer distance is the experimental one.

The phonon dispersion was calculated using linear response [9] on $12\times12\times12$ electron-momentum grid and and $4\times4\times4$ phonon-momentum grid with an Hermite Gaussian smearing of 0.02 Ryd. We then Wannier interpolate [7] the phonon dispersion to any desired phonon momentum in the Brillouin zone, by using a denser $40\times40\times40$ (randomly shifted from the origin) electron-momentum grids and smearing of 0.01 Ryd. For the average $\lambda$ calculation we used the Wannier interpolated phonon frequencies over a $20\times20\times20$ and a similar electron-momentum grid (randomly displaced from the origin) was used for the electronic integration. For the phonon linewidth at a given phonon momentum $\mathbf{q}$ we use a $120\times120\times120$ electron momentum grid (randomly displaced from the origin).

The Eliashberg function $\alpha^2 F(\omega)$ is defined as:

$$\alpha^2 F(\omega) = \frac{1}{N(0)N_\epsilon} \sum_{k,\epsilon,\nu} \frac{|d_k^\nu|^2}{2\omega_{\nu\epsilon}} \delta(\epsilon_k)\delta(\epsilon_{k+\mathbf{q}})\delta(\omega - \omega_{\nu\epsilon})$$

(34)

The total electron-phonon coupling $\lambda(\omega)$ is defined as:

$$\lambda(\omega) = 2 \int_0^\omega d\omega' \frac{\alpha^2 F(\omega')}{\omega'}$$

(35)

The total electron-phonon coupling is $\lambda(\omega \to \infty)$.

**Phonon dispersion in Li$_x$ZrNC1 as a function of doping**

In the case of constant matrix elements, the phonon softening is ruled by the bare response-function $\chi_0(\mathbf{q})$, see Eq. 31. Similarly the phonon linewidth is proportional to the nesting factor $N_f(\mathbf{q}) = \frac{1}{N_\epsilon} \sum_k \delta(\epsilon_k - \epsilon_F)\delta(\epsilon_{k+\mathbf{q}} - \epsilon_F)$. In Fig.5 (left) we plot $\omega_K + \tilde{\Delta}\omega_K$ and the nesting factor (as vertical red bars) for a perfect parabolic 2D electron-gas. In the right panel, we compare these results with the DFT calculations for $x = 1/18$. At this doping, as well for $x = 1/9$ (see Fig. 6) the $2k_F$ area around $\mathbf{K}$ is well separated from that around $\Gamma$.

In the ideal case of constant intervalley matrix elements, the phonon softening is flat in a region of radius $2k_F$ around $\mathbf{K}$. Standard linear response calculations based on Fourier interpolation do not reproduce this fact (see Fig. 5 on the right, black dashed line) as the grid used in the calculation is too coarse. On the contrary the analytical behavior is very nicely captured by our Wannier interpolation scheme [7], as shown in Fig. 5 on the right, red lines. The simple model also accounts for the behavior of the phonon linewidth. In this case the nesting factor as a function of $\mathbf{q}$ of Fig.5 (left) should be compared with the phonon linewidth (red bars in Fig. 3 of the main paper).

The phonon dispersion and the Eliashberg functions for several doping are shown in Fig. 6. The intravalley contribution to the Eliashberg function and its integrated value are plotted on the left panels. As it can be seen the Eliashberg function is composed of two main peaks. The intravalley contribution to the electron-phonon coupling is suppressed for small doping.

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FIG. 5. (Left): Phonon frequency (black line) and line-width (vertical red bars) for a perfect parabolic 2D electron gas with constant electron-phonon matrix element. The phonon wavevector $q$ is measured either with respect to zone center or with respect to $K$. (Right): comparison between Wannier and Fourier interpolated phonon dispersion in Li$_{1/18}$ZrNCl.

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FIG. 6. Wannier interpolated phonon dispersion of Li$_x$ZrNCl as a function of doping. The total Eliashberg function and the Eliashberg function due to intravalley scattering are also plotted on the right panels.