A proposal to improve Ni-based superconductors

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Recently discovered superconductivity in hole-doped nickelate Nd$_{0.8}$Sr$_{0.2}$NiO$_{2}$ caught intensive attention in the field. An immediate question is how to improve its superconducting properties. Guided by the key characteristics of electronic structures of the cuprates and the nickelates, we propose that nickel chalcogenides with a similar lattice structure should be a promising family of materials. Using NdNiS$_2$ as an example, we find this particular crystal structure a stable one, through first-principle structural optimization and phonon calculation. We justify our proposal by comparing with CaCuO$_2$ and NdNiO$_2$ the strength of the charge-transfer characteristics and the trend in their low-energy many-body effective Hamiltonians of doped hole carriers. These analysis indicates that nickel chalcogenides host low-energy physics closer to that of the cuprates, with stronger magnetic interaction than the nickelates, and thus deserve further experimental exploration. Our proposal also opens up the possibility of a wide range of parameter tuning through ligand substitution among chalcogenides, to further improve superconducting properties.

Hole doped nickelate, Nd$_{1-x}$Sr$_x$NiO$_2$ [1, 2], as a first Ni-based high-temperature superconductor, has recently attracted great attention in condensed matter physics recently. It displays type-II superconductivity, dome-shaped superconducting phase [2] and strange metal (linear resistivity) behavior in its normal state [1]. All of these characteristics suggest that this material represents a new family of unconventional superconductors. Meanwhile, their strong temperature and doping dependent hall coefficient [2], negative magnetoresistance [3], absence of long-range magnetic order [4, 5] in the parent compound, and increasing normal-state resistivity in the overdoped regime [2, 6] also indicate rich underlying physics in this new superconductor that might be absent in the cuprates [7–10]. Obviously, these nickelate superconductors are of a promising family to help unravel the long-standing puzzles of high-temperature superconductivity and even to find higher transition temperature $T_c$ beyond the cuprates.

So far within limited attempts, the highest $T_c$ of nickelates is only about 12K [2, 6], one order of magnitude lower than the best cuprates [10, 11]. Furthermore, at present, superconductivity is only found in thin films but not in bulk samples [3], for reasons yet to be understood. Significant experimental progress is thus expected upon improvement of sample quality. On the other hand, it is of equal importance to seek other approaches to improve the superconducting properties besides the sample quality.

Here we address this timely issue by first comparing the high-energy electronic structure of the cuprates and nickelates to identify their key characteristics being the strength of charge transfer. Based on this, we propose a new family of material, nickel chalcogenides, as a promising candidate to improve the superconducting properties. Taking NdNiS$_2$ as an example, through density functional structure optimization and phonon calculation, we first demonstrate that this compound is stable under the same crystal structure as NdNiO$_2$. The corresponding high-energy electronic structure confirms our expectation of an enhanced charge-transfer characteris-

To identify the key difference between the cuprates and nickelates, we compare their high-energy electronic structure using density functional theory (DFT). Since both the cuprates and nickelates host strong antiferromagnetic (AFM) correlation [13, 14] inherited from the unfrustrated square lattice of spin 1/2 local moment [15], we calculate the band structures under AFM order within the LDA+$U$ approximation [16–18].

![FIG. 1. Comparison of LDA+$U$ band structures of CaCuO$_2$, NdNiS$_2$ and NdNiO$_2$ under AFM order, unfolded in the one-Cu/Ni Brillouin zone. The red, blue and green colors represent the weights of Cu/Ni, Ca/Nd and O/S orbitals, and Nd f-orbitals are set transparent. The lower panel shows the magnified band structure of the purple dashed boxes in the upper panel. Notice the trend in the relative energies of O/S and Cu/Ni orbitals.](cond-mat.supr-con)
and unfold them to the one-Ni unit cell for a simpler visualization [19]. Fig. 1(a)(c) show that compared with NdNiO$_2$, the main difference of CaCuO$_2$ at the large energy scale is the much lower energy of its $d$-orbitals (in red) relative to the $p$-orbitals (in green), reflecting a much stronger charge-transfer nature well known to the community [20]. Given that both families are doped spin $1/2$ systems, it is reasonable to expect that promoting such a charge transfer characteristic should improve significantly the superconducting properties, due to various considerations of low-energy physics such as enhanced super-exchange interaction [15] and renormalized kinetic energy. Since there is no chemical way to further lower the orbital energy of Ni (other than replacing it by Cu), we are left with no choice but to raise the energy of the ligand $p$-orbitals, for example by substituting O with S or Se.

Taking NdNiS$_2$ as an example, we first examine the stability of this compound under the same crystal structure [c.f. Fig. 2(a)] as the nickelates. Our structure optimization calculation [18] gives lattice constants $a = b = 4.505\text{Å}$ and $c = 3.703\text{Å}$. With these structural parameters, further phonon calculation finds that phonon frequencies are all positive, as shown in Fig. 2(b). This confirms a stable structure realizable in the lab.

Next, we verify the enhanced charge-transfer characteristic of this material. Fig. 1(b) shows the similar unfolded band structure of AFM NdNiS$_2$. As expected from above chemical intuition, substituting O by S raises the energy of the $p$-orbitals (in green) quite significantly, thereby enhancing the charge-transfer nature. The density of state (DOS) plots in Fig. 3 illustrate a similar trend. Right below the Fermi energy, the relative weight of the most relevant ligand $p_p$-orbitals (in green) to the $d_{z^2}$-orbital (in red) grows systematically from NdNiO$_2$ to NdNiS$_2$ and CaCuO$_2$. (Here, $p_p$ refers to O/S $p$-orbitals pointing toward nearest Cu/Ni atoms.) Indeed, substituting O by S enhances the charge-transfer nature and brings nickel chalcogenides closer to the cuprates.

To reveal the physical benefits of a stronger charge-transfer characteristic, we proceed to investigate the low-energy effective Hamiltonian using well-established approaches for the cuprates [12, 18, 21, 22]. Using DFT-parameterized high-energy many-body Hamiltonian, we calculate the local many-body ground state via exact diagonalization. The ground state with a doped hole is a spin-singlet state similar to the well-known Zhang-Rice singlet [22] with (self-)doped hole mostly residing in the ligand $p$-orbitals.

Note that such a strong singlet formation introduces an important correction to Fig. 1 and 3: it pulls the energy of $x^2 − y^2$ orbital closest to the chemical potential, even beyond the $3\xi^2 − r^2$ orbital. This effect, however, will still respect the above mentioned trend concerning the relative energies of O/S orbitals and Cu/Ni orbitals.

Using this singlet state as basis, the low-energy Hamiltonian of hole carriers resembles the well-known $t$-$J$ model: (The subspace spanned by this singlet state form the basis for the low-energy effective Hamiltonian, upon integrating out the rest of the Hilbert space perturbatively.)

$$H = \sum_{i\nu} t_{i\nu} \tilde{c}^\dagger_{i\nu} \tilde{c}_{i\nu} + \sum_{<i,j>} JS_i \cdot S_j,$$

where $\tilde{c}^\dagger_{i\nu}$ create a dressed hole at site $i$ of spin $\nu$. $S_i = \sum_{\nu} \tilde{c}^\dagger_{i\nu} \sigma_{\nu,\nu'} \tilde{c}_{i\nu'}$ denotes the spin operator and $\sigma_{\nu,\nu'}$ is the vector of Pauli matrices.

Table I shows our resulting nearest neighbor hopping parameters $t_{i\nu}$ and super-exchange parameters $J$ for the three materials. Despite the larger lattice constant in NdNiS$_2$, $t_{i\nu}$ turns out to be similar in all three materials owing to the larger radius of S $p$-orbitals. In contrast, $J$ is systematically enhanced from NdNiO$_2$, to NdNiS$_2$ and CaCuO$_2$. This is because a stronger charge-transfer nature (higher $p$-orbital energy) gives a reduced charge-transfer gap $\Delta_{CT}$ (approximate energy to return an electron from the $p_p$-orbital back to Cu/Ni $d_{z^2}$-orbital.) With the intra-atomic repulsion roughly the same in Cu and Ni, this in turn enhances the super-exchange processes ($\propto \Delta_{CT}^{-1}$) [12, 23]. We stress that despite the simplicity of such an estimation, the qualitative trend among these materials is robust.

The enhanced $J$ is likely very important for the superconducting properties. It would not only lead to a stronger magnetic correlation that dominates the low-energy physical Hilbert space, but also give rise to a larger renormalized kinetic energy [10, 24]. In other words, a larger $J$ can stretch
the energy scale of all the low-energy physics, effectively producing a larger temperature scale in the phase diagram. One can therefore expect that NdNiS$_2$ should have better superconducting properties than the nickelates.

An interesting feature of NdNiS$_2$ is that the possible electron-carrier density in the parent compound will increase as a result of higher-energy $p$-orbitals (c.f. Fig. 1 and 3). On the one hand, since the electron carriers are shown to be nearly decoupled from the hole carriers [12] in the nickelates (and the same is found in NdNiS$_2$ [18]), their existence should not interfere much with the hole superconductivity. On the other hand, these weakly correlated electron carriers might introduce additional physical effects absent in the cuprates (for example, strengthening the essential superconducting phase stiffness.) Further experimental investigation of the nickel chalcogenides will prove highly illuminating.

Finally, we note that it is not just S that has a good $p$-orbital energy. Se having a similar chemical orbital energy and NdNiS$_2$ should have better superconducting properties. Taking NdNiS$_2$ as an example, we find this compound stable under the desired crystal structure and thus realizable in laboratory. The resulting high-energy electronic structure displays the anticipated enhancement of the charge-transfer nature. We then reveal the physical benefits of a stronger charge-transfer characteristic via derivation of low-energy effective Hamiltonian. The resulting Hamiltonian encapsulates a stronger super-exchange spin-interaction, implying a higher temperature scale for all low-energy physics, including superconductivity. Our study paves the way to discover more nickel-based superconductors in nickel chalcogenides with improved superconducting properties, for examples NdNiS$_2$–O$_x$ and NdNiS$_2$–Se$_y$. Further experimental exploitation of the wide range of tunability through ligand substitution would likely make significant contribution to the resolution of the long-standing puzzles of high-temperature superconductivity.

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**TABLE I.** Comparison of energy difference of $d_{x^2-y^2}$ and $p_f$, $\Delta_{pd} = \varepsilon_{pf} - \varepsilon_{d_{x^2-y^2}}$; estimated charge transfer gap, $\Delta_{CT}$; hybridization between $d_{x^2-y^2}$ and $p_f$ orbitals, $t_{pd}$; nearest neighbor hopping $t$ and exchange parameter $J$ in one band $t-J$ model and $T_c$ [2, 25] for three different materials, CaCuO$_2$, NdNiS$_2$, and NdNiO$_2$.

| Material      | $\Delta_{pd}$ | $\Delta_{CT}$ | $t_{pd}$ | $t$ | $J$ | $T_c$ |
|---------------|---------------|---------------|----------|-----|-----|-------|
| CaCuO$_2$     | 3.7           | ~ 3.5         | 1.3      | 0.3 | ~ 0.3 | > 50K |
| NdNiS$_2$     | 5.7           | ~ 4.0         | 1.2      | 0.3 | ~ 0.13 | ?     |
| NdNiO$_2$     | 8.9           | ~ 6.0         | 1.3      | 0.3 | ~ 0.07 | ~ 12K |

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