What Are the Roles of Hydrogen in Infinite-Layer Nickelates?

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(Received 14 April 2023; accepted manuscript online 20 April 2023)

DOI: 10.1088/0256-307X/40/5/057403

Even after more than 30 years of intensive effort, the understanding of physical origin accounting for the high-temperature superconductivity in cuprates remains the open question in condensed matter physics. A possible way to solve this long-standing question is to find other cuprate-analogous structures. In 2019, the long-awaited superconductivity was observed in infinite-layer hole-doped nickelates, i.e., (Nd,Sr)NiO_2, potentially bringing us to the new age of nickelate superconductors.[1] Besides superconductivity, many other interesting properties have been observed, e.g., short-range antiferromagnetic excitations[2] and charge-density waves.[3] Because nickelates show many similarities to cuprates in terms of structures and electronic band structures, it was expected that both nickelates and cuprates have a similar physical origin for the superconductivity. However, there is a big difference between nickelates and cuprates: the superconductivity in nickelates can only be observed in thin-films grown on certain substrates and only a small number of experimental groups in the world can successfully produce the superconductivity; on the other hand, the superconductivity can exist in both bulk and powder-synthesized cuprate samples that are widely produced in many different experimental groups. This puzzle has seriously prevented the rapid development of superconductive nickelates in the community.

Because thin films of nickelate are epitaxially synthesized by a topotactic reaction using the reagent of CaH_2, naturally it is thought that hydrogen may exist in nickelates after the growth process. However, the signal of hydrogen is not observed at all in the nickelates using the advanced transmission electron microscope (TEM), in contrast to the fact that hydrogen can be detected using TEM in Iron-based superconductors.[4] Therefore, the question is still open, i.e., does H really exist in nickelates?

Recently, a joint experimental and theoretical study makes a key step towards solving the hydrogen problem in nickelates.[5] Instead of using the TEM technology, Ding *et al.* used the ultra-sensitive secondary-ion mass spectroscopy (SIMS) to characterize the elemental distributions in (Nd,Sr)NiO_2. Remarkably, it was clearly demonstrated that the hydrogen atom undisputedly exists in the samples. With the increase of reduction time, the amount of hydrogen concentration in the sample linearly increases. While the SIMS can tell us the existence of hydrogen, it cannot tell us their exact locations. Based on the density-functional calculations, it is found that, although H always prefers to locate at the apical oxygen vacancy (AOV) position, the H atoms are not fully randomly distributed in the $NdNiO_2$ lattice. Instead, there are two basic rules for the H distribution to reach the low-energy configurations: (1) Along the out-of-plane direction, H prefers to form ordered H–Ni–H chain arrangement to maximally recover the local octahedral structure. (2) Along the in-plane direction, H prefers to form a large separation between neighboring H atoms; this is possibly due to the Coulomb repulsion prefers to form the large in-plane H-H separation. In general, H is a unique impurity that can exhibit either $+1$ or -1 charge state in the semiconductors. Based on this H configuration, it is found that H in $NdNiO_2$ exhibits a negative -1 charge state at the interstitial site, holding a different location in iron-based superconductors.[4]

Surprisingly, the superconducting transitions are strongly correlated with the H concentration x. It demonstrates a very small superconducting dome with a narrow range of optimal H doping, $0.22 \leq x \leq 0.28$. Both under- and over-doped samples show weakly insulating behavior. The phase diagram shows a striking resemblance to that of the Sr-doped $Nd_{1-x}Sr_xNiO_2$ and demonstrates that, in addition to Sr dopant, the hidden H in the sample may play a critical role to the observed superconductivity. This may also explain the challenge of film synthesis, that is, H content must fall into a narrow window to achieve superconductivity. However, how to understand this interesting H-induced superconductivity is a great challenge. The theoretical team proposed a possible scenario.[5] The existence of AOV can induce interisial s (IIS) orbital.[6] Starting from the non-doped (Nd,Sr)NiO_2, there are sizeable hybridizations among IIS, O $2p$, Nd $5d$ and Ni $3d_{x^2-y^2}$ orbitals that lead to more 3D-like electronic structures. H doping blocks the interlayer hopping related to IIS orbitals rendering the electronic structure to be more quasi-2D-like. On further H doping, the local crystal field and strong orbital coupling readjust the $3d_{x^2-y^2}$–$3d_{z^2}$ orbital polarization, that is, the increased orbital mixing transforms again the electronic structure back to being more 3D-like. In a small middle region with the optimal H doping, the system behaves as the most 2D-like electronic structure that mimics the situation in cuprates and may facilitate superconductivity.

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In the future, there are several important issues related to H in nickelates that need to be addressed: (1) What is the role of H for the observed charge-density wave in nickelates? There is a strong debate on the origin of charge-density waves observed in nickelates.[3,7] Since H can modulate the electronic band structure around Fermi level and e–ph coupling strength in the system, it may further module the charge-density-wave formation. (2) What is the role of H for the observed magnetic excitation? Now, the antiferromagnetic short-range correction is mostly observed in $NdNiO_2$ with a capping layer.[2] Since the magnetic-magnetic interaction may be influenced by IIS state,[6] where H can locally kill the IIS state, it is expected that H may also influence the magnetic excitation in nickelates.

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