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Anatomy of the band structure of the newest apparent near-ambient superconductor $\mathrm{LuH_{3-x}N_x}$

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Introduction. The discovery of high temperature superconductivity under high pressure around 100–250 GPa with T_c about 203 K in a hydrogen-containing $\mathrm{H_3S}$ system [1] gave rise to a flow of experimental and theoretical works (see reviews [2–7]). The subsequent discovery of near-room temperature superconductivity in hydrides brings us back to the classical electron-phonon superconducting pairing, very likely consistent with the Bardeen–Cooper–Schriefer (BCS) theory. Remarkably, there appeared many different classes of hydrides under pressure and band structure calculations (density functional theory – DFT) have shown the ability to predict crystal structures and T_c values for many of those hydrides (for review see [7]).

Here we address the issue of superconductivity in the recently discovered nitrogen-doped lutetium hydride $\mathrm{LuH_xN_y}$ where $T_c = 294\,\mathrm{K}$ was claimed to occur at 10 kbar [8]. This result has sparked intensive theoretical and experimental research. In this paper we performed $\mathrm{DFT+U}$ band structure calculations for both parent $\mathrm{LuH_3}$ and nitrogen doped $\mathrm{LuH_{2.75}N_{0.25}}$. In particular, our analysis reveals the contribution of nitrogen bands to the density of states at the Fermi level which might facilitate formation of superconducting state. We also provide simple BCS-analysis of T_c for materials under consideration.

Computational details. The calculations were performed within the $\mathrm{DFT+U}$ approximation in the VASP software package [9]. The generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [10] was employed. The strong onsite Coulomb repulsion of Lu-$4f$ electrons was described with the DFT+U scheme with the Dudarev approach [11] ($U = 5.0\,\mathrm{eV}$).

We consider $\mathrm{LuH_3}$ and nitrogen doped $\mathrm{LuH_{2.75}N_{0.25}}$ (spatial symmetry group $Fm\bar{3}m$) [8] at ambient pressure. The H atoms are located in positions with tetrahedral $(0.25, 0.25, 0.25)$ and octahedral $(0.5, 0, 0)$ surroundings of Lu atoms. The Lu atoms are located at the point of origin, $(0, 0, 0)$. To get $\mathrm{LuH_{2.75}N_{0.25}}$ only one of the four hydrogen atoms is replaced by the nitrogen atom, since, such substitution, as shown in [8], leads to a metal. The ion relaxation was done for $\mathrm{LuH_{2.75}N_{0.25}}$. Wannier functions were obtained using the Wannier90 [12] package with projection onto H-1s in octahedral environment and N-2p orbitals.

Results. The comparison of GGA+U total densities of states (DOS) and band dispersions between $\mathrm{LuH_3}$ and $\mathrm{LuH_{2.75}N_{0.25}}$ is shown on Fig. 1.

Nitrogen doping leads to formation of a wide peak in the total DOS just below the Fermi level, in contrast to the case of stoichiometric $\mathrm{LuH_3}$. The most important is that the total DOS at the Fermi level increases almost by a factor of two in $\mathrm{LuH_{2.75}N_{0.25}}$, from 1.5 to 2.6 states/eV/u.c. (left panel of Fig. 1). Substitution of hydrogen atom by nitrogen one gives four additional holes per unit cell which leads to ~ 1.8 eV lowering of the Fermi level in $\mathrm{LuH_{2.75}N_{0.25}}$ as compared to $\mathrm{LuH_3}$. Although the bands can not be superposed by their simple shift, some features are quite similar for both systems.

In the case of $\mathrm{LuH_{2.75}N_{0.25}}$, several bands cross the Fermi level at each high-symmetry direction, while for $\mathrm{LuH_3}$ only couple of bands near Γ-point cross the Fermi level. For $\mathrm{LuH_{2.75}N_{0.25}}$ at the Fermi level there are pronounced flat band regions in the vicinity of R and X points, which are missing for $\mathrm{LuH_3}$.

In order to define the minimal orbital basis set for $\mathrm{LuH_{2.75}N_{0.25}}$, needed to reproduce electronic bands near the Fermi level we performed the projection onto Wannier functions. The orbital character of the bands built

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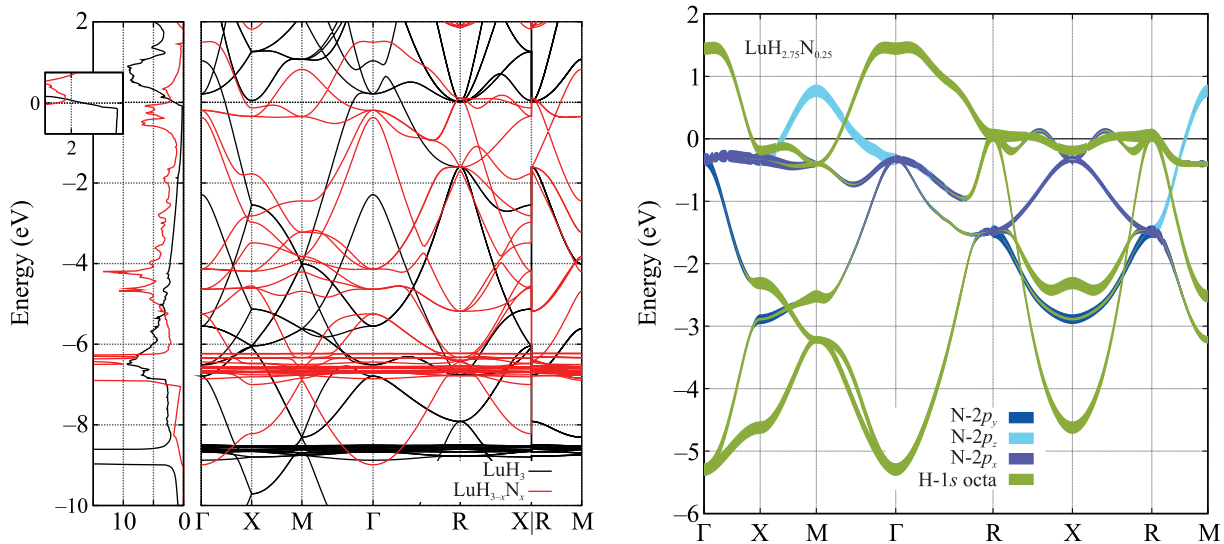
Fig. 1. (Color online) Left panel: GGA + U total DOS (right side) and band dispersions of LuH_3 (black lines), $LuH_{2.75}N_{0.25}$ (red lines on the right side). The inset (left panel) shows DOS near the Fermi level $[-0.5; 0.5]$ eV. Right panel: The bands projected on Wannier function with linewidth showing contributions of H-1s octahedral and N-2p states

on the projected Wannier functions are presented in Fig. 1.

The most important parameter of superconducting materials is its critical superconducting temperature T_c. To get its simplest rough theoretical estimate, we use the well known BSC equation $T_c = 1.14\,\omega_D\exp(-1/\lambda)$. We employ $T_c^{LuH3} = 62\,K$ value [13] obtained with anisotropic Migdal–Eliashberg formalism with $\omega_D = 19.3$ meV $= 220$ K. With the values we can exclude the pairing constant g from BCS equation and then estimate T_c^{LuHN} value for nitrogen doped material, assuming that ω_D and g do not change significantly. The increase of DOS at the Fermi level gives $T_c \sim 111$ K for $LuH_{2.75}N_{0.25}$.

Conclusion. Our findings suggest that nitrogen doping of LuH_3 can significantly alter the electronic properties of the material (bringing light elements N-2p and H-1s states at the Fermi level), facilitating the occurrence of superconductivity. In particular, nitrogen doping doubles the value of DOS at the Fermi level. Simple BCS analysis suggests that for $LuH_{2.75}N_{0.25}$ the critical temperature might exceed 100 K, and one can even increase it with further hole doping by nitrogen up to 180 K.

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