Modulation of the Octahedral Structure and Potential Superconductivity of La$_3$Ni$_2$O$_7$ at Ambient Pressure by Compressive Strain

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Abstract: Superconductivity at T_c = 80 K has recently been reported above 14 GPa in La$_3$Ni$_2$O$_7$, which thus introduces a new family of high-temperature superconductors. Using a first-principles calculation with Coulomb repulsion, we unveil a surprising new route to obtain superconductivity in La$_3$Ni$_2$O$_7$ at ambient pressure by introducing compressive strain along the [001] direction. The shape of the NiO$_6$ octahedra affect the Ni-3d_{z^2} density of states (DOS) at Fermi level, and it can be modulated by applying compressive strain instead of hydrostatic pressure. Notably, when the octahedral regularity parameter defined herein is $R \approx 4\%$, La$_3$Ni$_2$O$_7$ acquires a high Ni-3d_{z^2} DOS and hole Fermi pocket. Our study thus indicates a path for obtaining superconductivity in La$_3$Ni$_2$O$_7$ at ambient pressure and elucidates the relationship between structural properties and superconductivity.

The discovery of superconductors with high critical temperatures (high-T_c superconductors) has been a long-standing hot topic in the scientific community. Recently, Sun *et al.* reported the signature of superconductivity with T_c = 80 K above 14 GPa in the bilayer Ruddlesden–Popper phase of $La_3Ni_2O_7$ [1]. This finding has introduced a new family of high-T_c superconductors in addition to the cuprates [2-6] and iron-based [7-12] superconductors. The $La_3Ni_2O_7$ undergoes a structural transition from the ambient-pressure phase *Amam* to the *Fmmm* phase above about 15 GPa. Density-functional theory calculations show that additional Ni-3d_{z^2} orbitals emerge near the Fermi level (E_F) that are vitally important for the high T_c of $La_3Ni_2O_7$.

Subsequent experimental investigations by different groups have confirmed the presence of high-T_c superconductivity in $La_3Ni_2O_7$ [13-16], and the mechanism of the superconductivity has been widely discussed [17-28]. It has been suggested that the pairing symmetry of the *Fmmm* phase is s$_\pm$ and that the dominant pairing occurs in the interlayer between the Ni-3d_{z^2} orbitals. The emergence of a hole pocket around the Γ point under pressure plays a crucial role in the pairing mechanism. Additionally, the consequences of replacing La with other rare-earth (R) elements have also been explored theoretically. It has been reported that the T_c of *Fmmm*-$R_3Ni_2O_7$ can be expected to decrease as the radius of the rare-earth ion decreases [29]. Interestingly, $Tb_3Ni_2O_7$ has been suggested to be a candidate for superconductivity at ambient pressure due to its higher density of states (DOS) at E_F and to its Fermi surface being similar to that of *Fmmm*-$La_3Ni_2O_7$ [30].

Strain engineering is a well-known and effective methodology for designing materials with bespoke properties and for controlling the properties of materials at the atomic level [31-33]. For example, the T_c of crystalline Sr_2RuO_4 can be enhanced from 1.5 to 3.4 K by applying a uniaxial strain through a strain cell [34, 35]. Uniaxial strain has also been suggested for controlling the competing orders in the Y–Ba–Cu–O system [36]. Strain engineering is thus an important method for the study of superconductivity.

Here, we tune the crystal structures and electronic properties of $La_3Ni_2O_7$ via strain engineering. Interestingly, the Ni-3 d_{z^2} DOS at E_F of the *Amam*-$La_3Ni_2O_7$ is significantly increased by applying a compressive strain along the [001] direction, making this phase a candidate superconductor at ambient pressure. Further analysis has shown that the compressive strain modulates the shape of the NiO_6 octahedra to affect the Ni-3d_{z^2} DOS.

The structure of $La_3Ni_2O_7$ has an orthorhombic symmetry (space group: *Amam*) at ambient pressure (Fig. S1(a) of Supplemental Material (SM)). This can be considered as the inter-growth of two planes of NiO_6 octahedra and of a La–O fluorite-type layer stacked along the c directions. The in-plane Ni–O bonds exhibit two different bond lengths of 1.93 Å and 1.91 Å, while the two out-of-plane Ni–O bonds have various lengths, with 2.3 Å for the outer and 1.97 Å for the inner apical Ni–O bonds. To describe the shape of the NiO_6 octahedra, we use the octahedral-regularity parameter R [37], which we define as follows:

$$R = \frac{d_z - d_{x,y}}{d_z + d_{x,y}},$$

where $d_{x,y}$ is the average in-plane O–Ni–O distance, and d_z is the average out-of-plane O–Ni–O distance. This parameter can be used to measure the apical versus basal extension of the octahedra.

We have determined the stress responses of the *Amam* phase to anisotropic compression along the [100], [010], and [001] directions at ambient pressure (Fig. S3(a) of SM). The slope of the stress–strain curve along different directions is almost constant, indicating that the *Amam* phase does not undergo plastic deformation in the range of compressive strain ε that we studied. We calculated the Ni-3d_{z^2} DOS at E_F of the *Amam* phase as a function of strain, as shown in Fig. S3(b) of SM. Note that the evolution of the Ni-3d_{z^2} DOS is similar along the [100] and [010] directions but is different along the [001] direction. We therefore focused on the [100] and [001] directions to investigate the strain effect.

FIG 1. Evolution of R, d_{xy}, and d_z of the *Amam* phase at ambient pressure as functions of the compressive strain along (a) the [100] and (b) the [001] directions. The electronic properties of the *Amam* phase at ambient pressure with $\varepsilon = 0$ and 0.02 (c) along the [100] and (d) along the [001] directions. The horizontal gray dashed line represents the Fermi level.

When a compressive strain is applied along the [100] direction in the *Amam* phase, d_{xy} is shortened, and d_z is enlarged (Fig. 1(a)), increasing R from 5.3% to 6% in the range of strains 0–0.03. In Fig. 1(c), we compare the band structure and DOS of the *Amam* phase at $\varepsilon = 0$ and 0.02. For $\varepsilon = 0$, the electronic states of the Ni-t$_{2g}$ and 3d_{z^2} orbitals are located almost totally below E_F, while the Ni-3$d_{x^2-y^2}$ and O-2p orbitals dominate across E_F, which is consistent with previous work [1, 30, 38]. For $\varepsilon = 0.02$, however, the Ni-3d_{z^2} band deviates away from E_F, and the Ni-3d_{z^2} DOS at E_F correspondingly decreases from 0.39 to 0.34 states eV^{-1} f.u.$^{-1}$. We also calculated the electronic properties at different strains and found that the Ni-3d_{z^2} DOS decreases

slightly with increasing strain, as shown in Fig. S3(b) of SM. Compressive strain along the [100] direction, therefore, reduces the Ni-$3d_{z^2}$ DOS at E_F, which is not beneficial for superconductivity.

When compressive strain is applied along the [001] direction, d_z decreases while d_{xy} increases (Fig. 1(b)). Note that R decreases as the strain increases, and it is down to 3.9% at $\varepsilon = 0.02$, which is similar to its value in the $Fmmm$ phase at 30 GPa ($R = 4.0\%$). Interestingly, the Ni-$3d_{z^2}$ band crosses E_F at $\varepsilon = 0.02$, and its fractional charge is transferred to the Ni-$3d_{x^2-y^2}$ bands, causing a small "self-doping" hole Fermi pocket to emerge around the Γ point (Fig. 1(d)). The Ni-$3d_{z^2}$ DOS at E_F is 2.03 states eV^{-1} f.u.$^{-1}$, which is comparable to that of the $Fmmm$ phase at 30 GPa (2.64 states eV^{-1} f.u.$^{-1}$). We also found that the Ni-$3d_{z^2}$ DOS increases abruptly, and the hole Fermi pocket emerges around the Γ point when the strain exceeds 0.005 (Figs. S3(b) and S8–10 of SM). The high DOS at E_F and the existence of the hole Fermi pocket around the Γ point thus make the $Amam$ phase with compressive strain along the [001] direction a candidate superconductor at ambient pressure.

FIG 2. Evolution of R, d_{xy}, and d_z for the $Fmmm$ phase at 30 GPa as functions of the compressive strain along (a) the [100] and (b) the [001] directions. The electronic properties of the $Fmmm$ phase at 30 GPa with $\varepsilon = 0$ and 0.02 are shown (c) along the [100] and (d) along the [001] directions. The horizontal gray dashed line represents the Fermi level.

We then calculated the stress response of the $Fmmm$ phase at 30 GPa, and we obtained the stress–strain relation shown in Fig. S35 of SM. The constant slope indicates that the $Fmmm$ phase does not undergo plastic deformation in the range of compressive strain we studied. When a compressive strain is applied along the [100] direction, $d_{x,y}$ shrinks and d_z elongates, resulting in an increase in R (Fig. 2(a)). It is worth noting that $R = 5.1\%$ at $\varepsilon = 0.02$, which is similar to that of the $Amam$ phase at

ambient pressure ($R = 5.3\%$). Fig. 2(c) shows the electronic properties of the *Fmmm* phase along the [100] direction at $\varepsilon = 0.02$. We find that the energy of the Ni-3d_{z^2} band decreases around E_F, inducing the disappearance of the hole pocket around the Γ point. The corresponding Ni-3d_{z^2} DOS at E_F is 0.42 states eV^{-1} f.u.$^{-1}$, which is much lower than in the case without strain.

We also investigated the effect of strain on the *Fmmm* phase along the [001] direction. The compressive strain elongates $d_{x,y}$ and shortens d_z, resulting in a decrease in R. In addition, the strain lifts the Ni-3d_{z^2} band upward, inducing a Ni-3d_{z^2} DOS peak far away from E_F (Fig. 2(d)). For example, the Ni-3d_{z^2} DOS at E_F decreases from 2.64 to 1.03 states eV^{-1} f.u.$^{-1}$ at $\varepsilon = 0.02$. Hence, the application of compressive stress along either the [100] or the [001] direction is not beneficial for the superconductivity of the *Fmmm* phase.

FIG 3. Two-dimensional Fermi surface of the *Amam* phase at ambient pressure (a) without strain, (b) with $\varepsilon = 0.02$ along the [100] direction, and (c) with $\varepsilon = 0.02$ along the [001] direction. The calculated two-dimensional Fermi surface of the *Fmmm* phase at 30 GPa (d) without strain, (e) with $\varepsilon = 0.02$ along the [100] direction, and (f) with $\varepsilon = 0.02$ along the [001] direction. Different colors represent different bands. See text for additional discussion of these figures.

Next, we calculated the two-dimensional Fermi surface of the *Amam* phase at ambient pressure (Fig. 3(a–c)) and of the *Fmmm* phase at 30 GPa with $\varepsilon = 0$ and 0.02 (Fig. 3 (d–f)). The *Amam* phase with $\varepsilon = 0.02$ along the [100] direction exhibits a Fermi surface topology similar to that without strain. In contrast, the application of a compressive strain along the [001] direction causes a Lifshitz transition to occur and a hole Fermi pocket to emerge at the Fermi surface around the Γ point, inducing a Fermi-surface topology that is similar to that of the *Fmmm* phase without strain. For the *Fmmm*

phase with a compressive strain applied along the [100] direction, the hole pocket around the Γ point disappears, and the Fermi-surface topology becomes similar to that of the *Amam* phase at ambient pressure without strain. When a compressive strain is applied along the [001] direction, additional hole pockets emerge along the Γ–X and Γ–Y directions.

To investigate further the relationship between R and the electronic properties of $La_3Ni_2O_7$, we plotted the evolution of the Ni-$3d_{z^2}$ DOS at 0, 5, 15, and 30 GPa as a function of R (Fig. 4). For the *Amam* phase at ambient pressure, $R = 5.3\%$ without strain (the star symbol), corresponding to a Ni-$3d_{z^2}$ DOS of 0.39 states eV^{-1} f.u.$^{-1}$. As R increases (the open-square symbols corresponding to strain along the [100] direction), the Ni-$3d_{z^2}$ DOS decreases, and when R decreases (the solid-square symbols corresponding to strain along the [001] direction), the Ni-$3d_{z^2}$ DOS increases, reaching its maximum value of 2.03 states eV^{-1} f.u.$^{-1}$ at $R \approx 4\%$, after which it decreases again. For the *Amam* phase at 5 GPa, the relationship between R and the Ni-$3d_{z^2}$ DOS is similar to that at ambient pressure. For the *Fmmm* phase at 15 GPa without strain (the star symbol), $R = 4.1\%$, and the Ni-$3d_{z^2}$ DOS is 2.9 states eV^{-1} f.u.$^{-1}$, which is consistent with the experimental observation of the emergence of superconductivity at pressures above 14 GPa [1, 13-16]. Whether R increases or decreases from this value, the Ni-$3d_{z^2}$ DOS decreases. For the *Fmmm* phase at 30 GPa, the relationship between R and the Ni-$3d_{z^2}$ DOS is similar to that at 15 GPa. Without strain, R decreases from 5.3% to 4.0% when the pressure is increased from 0 to 30 GPa. Thus, hydrostatic pressure modulates the maximum value of the Ni-$3d_{z^2}$ DOS.

As discussed above, R modulates the Ni-$3d_{z^2}$ DOS at E_F significantly. When R is about 4%, $La_3Ni_2O_7$ exhibits a high Ni-$3d_{z^2}$ DOS at E_F, leading to potential superconductivity. Both hydrostatic pressure and compressive strain can alter the regularity R of the NiO_6 octahedra, modulate the Ni-$3d_{z^2}$ DOS at E_F, and finally, affect the superconductivity of $La_3Ni_2O_7$. We, therefore, expect that compressive strain can be used to achieve superconductivity in $La_3Ni_2O_7$ at ambient pressure.

FIG 4. Evolution of the Ni-$3d_{z^2}$ DOS at the Fermi level as a function of R. The star symbols represent R in the absence of strain. The solid and open symbols correspond to the application of compressive strain along the [001] and [100] directions, respectively.

In summary, we have performed a first-principles calculation, which includes Coulomb repulsion, of the structures and electronic properties of $La_3Ni_2O_7$ via strain engineering. The results show that the application of a compressive strain along the [001] direction makes the *Amam* phase of $La_3Ni_2O_7$ a potential superconductor at ambient pressure. Significantly, the Ni-$3d_{z^2}$ DOS at E_F is closely related to the shape of the NiO_6 octahedra. Just like hydrostatic pressure, compressive strain also provides an important method for modulating R and further tuning the Ni-$3d_{z^2}$ DOS. Our results thus provide a potential scheme for obtaining superconductivity in $La_3Ni_2O_7$ at ambient pressure, and they demonstrate the relationship between superconductivity and crystal structure.

See Supplemental Material for band structures, DOS, in-plane O-Ni-O average distance, out-plane O-Ni-O average distance, the octahedral regularity parameter R and structural information of $La_3Ni_2O_7$ under various compressive.

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