Understanding and control of the metallic state in epitaxial NdNiO3

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Summary

The story of perovskite rare-earth (RE) nickelates ($RENiO_3$) began in 1977 when a series of ceramic samples, including RE=Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, were firstly synthesized by Gerard Demazeau $et\ al.$ under ultra-high oxygen pressure However, despite these extreme synthesis conditions, only polycrystalline samples could be obtained, severely limiting the study and application of this materials family. Therefore, they almost vanished from the view of researchers for more than 20 years. However, $RENiO_3$ have regained interests since the 90's of last century. These renewed interest in nickelates was motivated by the development of new techniques (i.e. Molecular Beam Epitaxy (MBE), Pulsed Laser Deposition (PLD) and Magnetron sputtering) for growing high-quality single crystalline oxide thin films and also the pursuit of new compounds with high-T_c superconductivity apart from the cuprates.

Indeed, as oxides with strong electron correlations, $RENiO_3$ with a heterostructure share many common features with the cuprates and were predicted to enable robust superconductivity without the need of doping Today, after having been studied for half a century, and when this thesis was half-way, $RENiO_3$ eventually proved themselves as an ideal parent compound for superconducting infinite-layer nickelate. However, the discovery of superconductivity, despite being the dream for many researchers in this field, is not the end of the story for nickelates. Instead, it is a new start. This is not only because of their promising applications in memristors, resistivity switching devices, and neuromorphic computing, but also due to the possibility of clarifying many concerns in condensed matter physics by employing this material as model system.

Perovskite $RENiO_3$ are quantum materials in the family of strongly electron-correlated systems, which usually show puzzling metallic properties that cannot be well explained by the conventional theories. Among these properties, a metal-insulator transition (MIT) driven by electronic interactions is particular important.

In $RENiO_3$, most of the materials (except for the bulk $LaNiO_3$) display a characteristic MIT. A full understanding of its origin and the nature of their insulating state has attracted most of the interest of researchers in this field. Several scenarios, like the Mott-Hubbard model (insulating state caused by Coulomb repulsion), charge ordering ($Ni^{3+\delta}$ and $Ni^{3-\delta}$ coexisting in the insulating state), and negative charge transfer (charge transfer between the Ni $3d$ band and O $2p$ band), were successively proposed with the advance of both calculations and experiments.

Unfortunately, less attention was paid to their metallic state. Unlike the diverse properties of the insulating state, $RENiO_3$ in their metallic state were considered to possess uniform Ni-O bonds and therefore, display a "boring" metal-like behaviour. However, several recent works and also the works discussed in this thesis have revealed that the tunable electronic properties in the metallic state of nickelates are far from being fully understood. Getting insight into this behaviour is the main purpose of this thesis work.

Since these materials were not previously investigated in our lab, in chapter 3 we demonstrate that we are able to grow atomically flat thin films whose properties can be systematically and reproducibly tuned by changing the RE ion, the substrate lattice parameter and orientation and the film thickness. We compare the observed trends with those reported in the literature and, while there is mostly agreement with the existing understanding on the basic behaviour, these prepare us with a reliable material base for an in-depth investigation of the electronic properties of nickelates and a study on the underlying physics.

In chapter 4, a systematic work in studying the combined effect of epitaxial strain and disorder were performed on the $NdNiO_3$ films with various thickness and grown on different substrates. We found the electrical properties, including metal-insulator transition, resistivity, and resistivity exponent (the scaling of resistivity with temperature that is generally used to determine the nature of electron interactions), of $NdNiO_3$ films show a clear dependence with epitaxial strain. Thin films under low strain conditions show a linear dependence of the resistivity *versus* temperature. In addition, the apparent temperature exponent, n, can be tuned with the epitaxial strain between n= 1 and n= 3. We also discussed the critical role played by quenched random disorder in the value of n. Our work shows that the assignment of Fermi/Non-Fermi liquid behaviour based on experimentally obtained resistivity exponents needs to be reconsidered as it requires an in-depth analysis of the degree of disorder in the material.

Among the origin of disorders, oxygen vacancies are commonly observed in epitaxial nickelate thin films. To decouple the effect of disorder from the strain in epitaxial films, the concentration of oxygen vacancies in the same sample were tuned by thermal annealing in Chapter 5. We found that heavily oxygen deficient $NdNiO_3$ films, which are insulating due to electron localization, contain pristine regions that

undergo a hidden metal-insulator transition. Increasing oxygen content increases the connectivity of the metallic regions and the metal-insulator transition is first revealed, upon reaching the percolation threshold, by the presence of hysteresis, while the slope of the resistivity still shows an overall insulating character. Only upon further oxygenation is the global metallic state (with a change in the resistivity slope) eventually achieved. It is shown that sufficient oxygenation leads to linear temperature dependence of resistivity in the metallic state, with a scattering rate directly proportional to temperature, like in the cuprates. Despite the known difficulties to establish the proportionality constant, the experiments are consistent with a relationship $1/\tau = \alpha k_B T/\hbar$, with α not far from unity, which would add the nickelates in the class of Planckian metals.

In Chapter 6, we performed an unconventional measurement of resistivity from 5 K to 700 K. We unveiled that the cuprate-like linear-T-resistivity is maintained in the NNO films over a wide temperature range (100-550 K); while the resistivity shows a clear deviation from the linear trend at higher temperature, consistent with the addition of a parallel saturation channel. Moreover, the resistivity saturation (ρ_{SAT}) is shown to present a dramatic increase in the thinner films, manifesting that interfacial effects are at play. Detailed analysis of the structural and electrical properties reveals that the resistivity of pristine NNO films (pure phase, low strain constraint, and weak interfacial effects) obey the Mott-Ioffe-Regel scenario (it saturates before the electron mean free path becomes smaller than the interatomic distance), lacking the signatures of bad metal behaviour, which had been proposed in previous works. We show that nickelates belong to a class of intermediate-correlated metals, an distinct regime between conventional metals and strongly correlated metals, that explains the combination of strange metallicity and conventional behaviour observed in these systems.

In summary, this thesis reports a systematic analysis on the epitaxial nickelate thin films. As oxides with strong electron-lattice coupling, the electrical properties of nickelate thin films can be tuned by many factors that are often inter-twinned. By separating the contributions of these different factors, we unveil that in pristine nickelate films, a linear-temperature-resistivity, following a near Planckian dissipation, can be achieved in a wide temperature range (100- 500 K) with no signatures of bad metal behaviour (chapter 6). By comparing with other electron correlated systems, we show that there is a class of systems with strength of electron interactions intermediate between those normal and strongly correlated metals. On the other hand, both the increase of strain and disorder exert significant effects on their electrical performance, including the metal-insulator transition (chapter 3 and 5) and resistivity-temperature scaling (chapter 4). These tunable properties benefit their applications, however, the study of underlying physics on this material should be more careful and accompanied by a detailed characterization of the microstructure.