YEAR IN REVIEW

HIGHLIGHTS OF 2020

The dawn of the nickel age of superconductivity

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Whereas high-temperature superconductivity in cuprates has been studied for 30 years, during the past year it has been reported in nickelates. This raises new questions for physicists and chemists about the mechanism of superconductivity — despite the electronic similarities of Cu and Ni, it seems that nickelate superconductivity requires consideration of a second orbital.

Not long after the discovery of high-temperature superconductivity in cuprates in the early 1990s, it was suggested that isostructural nickelates might have similar properties. After all, Ni borders Cu in the periodic table, with its Ni^{1+} ion being isoelectronic (d^9) with the Cu^{2+} ion. Three decades lapsed with substantial study of nickelates, but with no fruit borne. The drought ended last year with the announcement of T_c up to 15 K in a nickelate, $NdNiO_2$ (REF.[1]) and the confirmation of the discovery[2] earlier this year. But old and now new questions remain to be answered.

The discovery of superconductivity in a nickelate compound is anticipated to clarify the underlying mechanism(s) of superconductivity in their sister cuprate materials. One of the most prominent questions is whether they are two sides of the same coin, given the same structure and similar valence, or whether they involve fundamentally different electronic behaviour.

Besides the factor-of-seven larger T_c achieved so far in the cuprate[3], there are several differences between the compounds, including different lattice constants (atomic sizes). Noted by several theory groups is that Nd (or La, which is an often used substitute because it has no open $4f$ shell) has a $5d$ band that contributes electronic carriers. Another difference is that the interlayer Nd^{3+} ion provides a different Madelung potential and crystal field on the metal ion compared to the Ca^{2+} ion. The primary effects are that the metal d_{z^2} orbital becomes active in $NdNiO_2$ whereas it is a bystander in the cuprate, and the $2p$ states in O are more tightly bound by ≈ 1 eV or more in the nickelate relative to the cuprate[4].

This dichotomy of viewpoint had appeared already two decades earlier in comparisons of $LaNiO_2$ and $CaCuO_2$. A 1999 study[5] emphasized the similarities. Besides structure and metal ion valence d^9 configuration, the position and bandwidth of the crucial $d_{x^2-y^2}$ band is similar. Yet there are qualitative differences in the properties of the undoped materials. $CaCuO_2$ is an insulating antiferromagnet whereas $NdNiO_2$ displays no magnetic order and is conducting — albeit weakly so — like so many other oxide 'bad metals', several of which superconduct. A 2004 study[6] pointed out two further substantial differences. The tripositive rare earth $5d$ orbitals in $LaNiO_2$ become partially occupied, thereby hole-doping the Ni $3d$ bands already at stoichiometry, and providing screening of Ni moments as well as competing itinerant magnetic exchange processes. An additional difference is the substantial role played by the Ni d_{z^2} orbital in the Fermi level region.

This unusual involvement of the Ni d_{z^2} orbital introduces new physics. This interference can be traced to two factors. First, in the infinite-layer structure (FIG. 1), the missing oxygen layer results in a 15% decrease of the $\hat{c}$ lattice parameter relative to cubic perovskite. As a result, the d_{z^2} orbital is less isolated concerning interlayer coupling, but this aspect should be similar in the cuprate and nickelate. In addition, the rare earth (Nd, or La) $5d$ orbital is larger than the $3d$ orbital of Ca. The result is enhanced $\hat{c}$ axis coupling, but also interference by the rare earth ion in the behaviour of the e_g orbitals of the metal ion. The interference is via crystal field, $\hat{c}$-axis coupling, and by providing $5d$ carriers that interact with the Ni moments.

In both materials the d_{z^2} orbital is essentially degenerate with the t_{2g} orbitals, but in the nickelate its separation from the $d_{x^2-y^2}$ energy is only 70% as large[4]. These numbers are obtained from density functional calculations used for weakly correlated materials, which serve as the accepted 'underlying electronic structure' of quantum materials. A point of wide agreement is that intra-atomic Ni interaction effects (as in the cuprate) will be important in the calculations, these being the Coulomb repulsion, U, between electrons and Hund's coupling, J, between parallel spin electrons, in the $3d$ shell. Values of U in the 3-9 eV range are being used in various theoretical treatments, and the actual value seems to be a more important issue in the nickelate than in the cuprate. An aspect of uncertainty is the degree of screening by the charged carriers and its effect on the two e_g orbitals.

An open question concerns the status of the configuration of the Ni^{1+} ion. In the cuprates, the d^9 state in the Cu^{1+} ion, with spin $S = 1/2$ in the $d_{x^2-y^2}$ orbital, is the unambiguous reference state. In doped cuprate samples, the d^8 state becomes relevant, and hybridization with p_σ orbitals on the four neighbouring O ions must be considered. Although Ni^{1+} ion appears analogous to the Cu^{1+} ion, hybridization is reduced and the supporting players upon doping have been suggested to be different.

One suggestion, based on an interacting cluster model, is that the d^8 configuration, such as Ni^{2+}, comes more strongly into play[7]. This ion can assume either the prosaic and symmetric $S = 0$ state, or the conventional

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Key advances

- Extraction of layers of oxygen ions from thin films of perovskite structure (Nd,Sr) NiO_2 has led to emergence of the long sought nickelate superconductivity.

- Comparison of the nickelate with the isostructural and isovalent, high temperature superconducting, cuprate has framed the main debate on the importance of their obvious similarities and less evident differences.

- Several observations — electronic, magnetic, and structural — point toward a new frontier Ni d_{z^2} orbital, with its role in interlayer coupling, in addition to the $d_{x^2-y^2}$ orbital that has dominated the discussion in cuprate superconductivity.
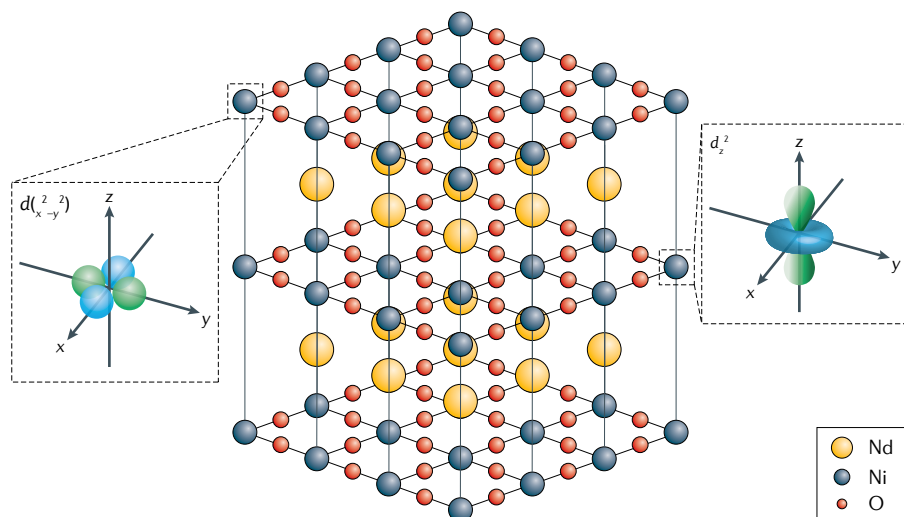
Fig. 1 | **Infinite layer nickelate, NdNiO₂.** A schematic showing the structure of an infinite layer nickelate, illustrating also the two active Ni orbitals. Red spheres indicate oxygen, gold spheres are Nd. The sample used in REF.[1] was synthesized in thin film form by chemically extracting layers of oxygen atoms from a layer-by-layer synthesized thin perovskite film. The most evident effect of the synthesis technique was that it stabilized an 'infinite layer' structure in which the layer of oxygen atoms linking CuO_2 layers in most cuprates is missing. Hole-doped (Nd,Sr) NiO_2 seems to mimic isostructural and isovalent $(Ca,Sr)_{1-x}CuO_2$, which superconducts when hole-doped up to 110 K (REF.[3]).

Hund's rule $S=1$ state, which has been proposed as nearby in energy. The non-magnetic $S=0$ configuration has the pd_o-bonding $d_{x^2-y^2}$ orbital of both spins occupied (or unoccupied, depending on viewpoint), and minimizes spin physics to the extent it is involved. $S=1$ contributions would enrich the 'spin physics'. These issues impact the follow-up dynamical theory, which with all relevant degrees of freedom (yet to be agreed on) should contain the real physics of nickelates.

A further possibility in this local-ion ansatz is the distinctive inter-orbital $S^*=0$ 'off-diagonal singlet' with electrons (or holes) of opposite spins in each of the e_g orbitals — the $d_{x^2-y^2}^{\uparrow} d_{z^2}^{\downarrow}$ configuration — giving a spin singlet with internal orbital structure and anisotropic interorbital coupling. This possibility seems radical as it violates Hund's first rule. The S^* singlet was found already in one of the early studies[6] but at an interaction strength, U, thought to be unphysically large. Unlike the cuprate, even at unrealistically large values of U, the nickelate never becomes insulating (pure d^9) (REF.[6]). This off-diagonal singlet does at least neighbour the physical range of the doped nickelate, in which case it would enter theories treating the dynamics.

Given the unsettled nature of the electronic structure of $(Nd,Sr)NiO_2$, it is pertinent

to note the recently synthesized[8] (under pressure) d^8 compound $Ba_2NiO_2(AgSe)_2$ (BNOAS). Its structure has a NiO_2 'infinite layer' interspersed with an insulating AgSe spacer layer, separated by a Ba^{2+} layer. Other compounds with a similar $Ni^{2+}O_2$ layer are nonmagnetic[8]. BNOAS shows no Curie–Weiss moment in susceptibility, yet displays a magnetic transition (also in susceptibility) around 130 K. Calculations using two different codes[9] obtain a small gap insulating state for BNOAS, with the same $S^*=0$ singlet as the ground state of the d^8 ion — spin-polarized internally but with no net moment. This unanticipated state is further evidence that the off-diagonal singlet discussed above is 'near' in energy to the Ni ground state in doped $NdNiO_2$.

Dynamical treatment of the Ni intra-atomic repulsion, U, is required to address spectroscopic data more directly. Several such studies from single band to six band models, which differ in methods and in choices of U, do not arrive at a consensus on several spectroscopic features. They do generally concur that the d^9 configuration is dominant, somewhat at odds with the cluster calculation[7] and correlated band result[9] that suggest the importance of d^8 ($S=0$ or $S^*=0$ singlets). At stoichiometry, the correlated Fermi surface remains the same as in density functional theory

calculations and the low energy band structure is renormalized. At physical doping levels and for binding energy larger than 1 eV the excitations become incoherent (ill-defined).

A crucial question is why bulk-prepared $Nd_{0.8}Sr_{0.2}NiO_2$ is not superconducting[10] whereas the thin films are. The most evident difference, a 3% larger c-axis lattice constant, provides additional evidence of the involvement and sensitivity of the Ni d_{z^2} orbital, which provides a new frontier orbital that is active for nickelate superconductivity.

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Competing interests
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