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Classic rock revival

1. **High pressure floating-zone growth of perovskite nickelate $LaNiO_3$ single crystals**
   Authors: Junjie Zhang, Hong Zheng, Yang Renb and J. F. Mitchell
   arXiv:1705.00570
2. **$LaNiO_3$ - a highly metallic and antiferromagnetic strongly correlated transition metal oxide**
   Authors: Z. W. Li, H. Guo, Z. Hu, L. Zhao, C.-Y. Kuo, W. Schmidt, A. Piovano, T. W. Pi, D. I. Khomskii, L. H. Tjeng and A. C. Komarek
   arXiv:1705.02589

Recommended with a Commentary by Leon Balents, Kavli Institute of Theoretical Physics, UCSB

The rare earth nickelates, with the chemical formula $RNiO_3$ and the perovskite structure based on the cubic lattice, are one of the paradigmatic families of materials undergoing metal-insulator transitions (MITs). They are prominently featured in the authoritative reivew from 1998 on Mott MITs by Imada, Fujimori, and Tokura[1]. With increasing ionic radius of the rare earth element R, the nickelates become increasingly metallic, and in the standard phase diagram, a line of finite temperature MITs terminates at a zero temperature MIT lying between R=Pr, with an antiferromagnetic insulating ground state and the end member, R=La, with a paramagnetic metallic ground state. This phase diagram has probably been reproduced hundreds of times in the literature. In the intervening decades the nickelates have re-risen periodically as prominent research subjects for diverse reasons.

It might be surprising to learn that, despite the fact that the nickelates were an established topic already in the 1990s, this classic rock (mineral) $LaNiO_3$ (LNO) did not actually exist, at least in single crystal form. All the work on LNO was carried out on polycrystalline powders and thin films. Single crystals are not necessarily better than the former, but they are often different, and usually studying them is clarifying. Rather remarkably, as explained in the two featured papers above, after all this time, this year two groups have managed to produce single crystals of LNO, using the floating zone technique with high oxygen pressure.

Both group's crystals are rhombohedral, with $R\bar{3}c$ symmetry, as expected from polycrystal studies. They display a broad maximum of magnetic susceptibility somewhat above 200K, and show metallic behavior down to the lowest measured temperatures, both features consistent with the standard phase diagram. However, a major surprise occurred in the study by Li et al (paper 2) who observed an antiferromagnetic ordering transition at 135K.

Neutron diffraction showed clear peaks at the wavevector $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ in pseudocubic notation, which is the same type of antiferromagnetic order found in the low temperature phase of all the other nickelates (R=Pr,Nd etc.). Thus according to this study the ground state of LNO is *not* a paramagnetic but an antiferromagnetic metal! A transition is not observed in paper 1 above, but I would note that the residual resistivity (zero temperature limit of the resistivity) in paper 1 is about $14\mu\Omega$-cm, about 36 times larger than the $0.38\mu\Omega$-cm found in paper 2, which may indicate that extreme purity is required to realize the antiferromagnetic state.

Assuming the result holds up, what do we learn from this revision of the nickelate phase diagram? It has bearing on a long-standing debate in the literature on the driving force behind the MIT and antiferromagnetism in these compounds. For the more insulating nickelates, R=Sm and smaller rare earths, two transitions occur on lowering temperature. The first transition coming from high temperature is the MIT one, and occurs without magnetic ordering. It is characterized by a symmetry lowering from orthorhombic to monoclinic, driven by an alternating contraction and expansion of NiO_6 octahedra around every other Ni site. At lower temperature, antiferromagnetic order at the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ wavevector develops. Partly based on these observations, a view that the non-magnetic structural changes drive the MIT and the antiferromagnetism was proposed. Initially thought of as “charge ordering” of differently charged nickel ions, this has also been deemed “charge disproportionation” (I will use this name for concreteness) and most recently a “site selective Mott transition”, viewed through the lens of Dynamical Mean Field Theory (DMFT). In the Nd and Pr compounds, the structural and magnetic transitions occur together, leaving open the chicken and egg question of whether charge disproportionation or magnetism are the driving force here. DMFT studies seem to support the continuing importance of charge disproportionation[2], while other work advocated for a magnetic mechanism[3].

At least for LNO, the new work points to a clear answer, since antiferromagnetism occurs in the metallic state. A preliminary search by the authors did not reveal any structural or electronic changes associated with charge disproportionation, though it remains possible that the effect is simply very small. Antiferromagnetism seems to be in the drivers seat in LNO. It would be natural to think then that in the nearby materials $PrNiO_3$ and $NdNiO_3$, antiferromagnetism might again also be a driving factor. There one does observe charge disproportionation, but in fact it follows on symmetry grounds: in an underlying orthorhombic crystal (which these are), charge disproportionation is always induced by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ antiferromagnetism as a secondary order parameter[4]. This is not true for rhombohedral symmetry, consistent with the absence of charge disproportionation in antiferromagnetic LNO.

Many prior experimental and theoretical results should be revisited in light of these findings. Very narrow atomic scale superlattices of LNO, found to display an antiferromagnetic metallic state[5], might be stabilizing the inherent three-dimensional order of the crystals. A pseudogap observed in tunneling measurements of LNO films[6] might be indicative of local formation of the antiferromagnetic state. More generally it is inspiring to see previously “impossible” crystals grown using modern machines, and we may hope to enjoy the fruits of these labors more broadly across interesting electronic materials.

References

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