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John Goodenough and the many lives of transition-metal oxides

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In honor of John Goodenough's centennial birthday, I discuss some of his insights into magnetism and the role of mixed valence in transition-metal oxides. His ideas form an important part of the continuing evolution of our understanding of these fascinating materials with a wide range of technologically-important functionalities. In particular, will mention connections to phenomena such as colossal magnetoresistance, enhanced thermopower, and high-temperature superconductivity.

I. INTRODUCTION

John B. Goodenough (JBG) shared the 2019 Nobel Prize in Chemistry for this contributions to the development of the Li-ion battery [1]. That achievement was just one part of a long career of studying transition-metal oxide compounds that began with a focus on magnetism [2, 3]. Transition-metal oxides are fascinating materials with a broad range of functionalities of practical importance. To illustrate the impact of JBG's work, I will tell three stories that each start with JBG's research and lead to more recent work. To conclude, I will consider some positive lessons that can be drawn from a long and successful career.

II. FROM SPINELS TO COLOSSAL MAGNETORESISTANCE

JBG's initial important insights were inspired by practical necessity. He was working at MIT Lincoln Laboratory in a team that had a goal of improving the magnets used in the magnetic core memory of the early electronic computers [3]. A calculation suggested that it would be good to switch from ferromagnetic transition-metal alloys to ferrimagnetic transition-metal oxides. There were lots of published results on magnetic properties and structures of a variety of spinels [a crystal structure including the oldest known magnetic material, magnetite (Fe_3O_4)] from Verwey and coworkers at Philips Research, but no systematic interpretation.

JBG set out to make sense of the jumble of results for spinels with various combinations of metal ions. He was trained as a theoretical physicist, and had evaluated the connection between electronic band structure and lattice distortions of simple metals with hexagonal close-packed structure [4]. In considering the oxides, JBG was motivated by Pauling's approach of starting with atomic orbitals and considering the hybridization between orbitals on neighboring atoms [5][6]. JBG intuitively sorted local structure and magnetic interactions according to the approximate integral occupancy of $3d$ states [7]. In doing so, he identified patterns, such as the fact that Cu^{2+} ions prefer a square planar configuration of O neighbors, rather than octahedral coordination; we would now associate that with a symmetry breaking to lift the degeneracy of the two e_g orbitals ($3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$), corresponding to the Jahn-Teller effect.

This approach came in handy for analyzing the neutron diffraction results of Wollan and Koehler [8] on another magnetic system, $La_{1-x}Ca_xMnO_3$ with the perovskite structure. Using his rules connecting exchange and bonding character, JBG was able to explain both the particular antiferromagnetic order of Mn^{3+} ions in undoped $LaMnO_3$ and the ferromagnetic order that occurs when Ca dopants lead to the presence of some Mn^{4+} ions [9]. A few years later, Kanamori interpreted the superexchange rules in terms of interactions between specific $3d$ orbital combinations on neighboring transition-metal ions [10]. Collectively, these results became known as the Goodenough-Kanamori rules for superexchange.

While oxides are important for practical magnetic materials, within condensed matter physics they dropped from significant attention until the discovery of high-temperature superconductivity in a layered-perovskite cuprate, $La_{2-x}Ba_xCuO_4$ three decades later [11] (I will return to the cuprates further on). Manganites came back to prominence after another decade. With the availability of single-crystal samples, a neutron diffraction study [12] of the layered compound $La_{0.5}Sr_{1.5}MnO_4$ revealed magnetic and charge order that were beautifully described by Goodenough's original analysis [9]. This was paralleled by a flood of interest in the perovskite system, $La_{1-x}Ca_xMnO_3$, when transport studies revealed "colossal" magnetoresistance at the transition to the ferromagnetic phase [13, 14].

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To describe the conductivity of the ferromagnetic phase, it is necessary to take account of the "double exchange" mechanism [15], in which the hopping of an electron from one magnetic Mn ion to another tends to align the moments; however, to properly describe the magnitude of the resistivity, it is necessary to include the impact of the electron-phonon coupling associated with the local distortion around a Mn^{3+} but absent around a Mn^{4+} [16], of the type originally identified by JBG [9]. The key to the huge magnetoresistance is the first order character of the transition from the insulating paramagnetic phase to the metallic ferromagnetic phase and its sensitivity to magnetic field; for reviews of a huge amount of theoretical and experimental research, see [17, 18].

III. FROM ANTIFERROMAGNETISM TO LARGE THERMOPOWER

The concept of antiferromagnetic order was first proposed by Néel [19]; it was only with the development of the first research reactor that it became possible to test this possibility, and one of the first examples studied was NiO [20]. NiO was also one of the first compounds for which Mott proposed the importance of strong intraorbital Coulomb interactions, which could frustrate electron hopping and lead to an insulating state [21]. This idea remained controversial for quite some time. There were still arguments about this in the mid '80s. The band picture, supported by calculations using density functional theory, led to a small-but-finite insulating gap of 0.3 eV. Sawatzky and Allen [22] demonstrated spectroscopically that the band gap was large ($\sim$ 4 eV), but the energy difference (Mott gap) between $3d^8$ and $3d^9$ states was even larger; O $2p$ states dominate the valence-band states at the lower edge of the optical gap, so that excitation across the gap involves charge transfer O $2p$ states to Ni $3d$. The crossover in the nature of the gap, from Mott to charge-transfer, was analyzed more generally the following year by Zaanen, Sawatzky, and Allen (ZSA) [23].

JBG got involved with this material after Mott and before ZSA. In particular, he and coworkers studied what happens to the magnetism when one partially substitutes Li for Ni in $Li_xNi_{1-x}O$ [24]; with $x = 0.5$, one obtains the equivalent of $LiNiO_2$. The Li definitely has a valence of +1, and if one assumes that the O remains as -2, then one expects to have a mixture of +2 and +3 valences on Ni, corresponding to $3d^8$ and $3d^7$ states. JBG observed that, for $x > 0.3$, the doping induced a shift to a rhombohedral crystal structure with ferrimagnetic behavior.

It was not until 1989 that it became possible to properly test the character of the mixed-valence states. X-ray absorption spectroscopy at the O K edge demonstrated that the valence change induced by the Li^{1+} is largely accommodated by reducing the density of O $2p$ electrons [25], consistent with ZSA. (A doped hole on O still has a strong antiferromagnetic coupling to a Ni2+ neighbor, resulting in a net low-spin $S = 1/2$ moment.) There should be a single valence in $LiNiO_2$, Theoretical calculations of the distribution of the between Ni $3d$ and O $2p$ states in $LiNiO_2$ remain challenging [26], and the results suggest a mixture Ni d^7 and Ni d^8L, where L indicates a hole on the ligand O.

Given his experience with $LiNiO_2$ and the mixed-valence metal-ion behavior associated with Li doping, it should not be a shock that, not long after moving to Oxford University, he turned to $LiCoO_2$ as a potential cathode material for a Li-ion battery [27]. In pulling Li out of the $LiMO_2$, one needs a shift from M^{3+} toward M^{4+}. This is challenging for $M =$ Ni, but JGB had already considered such states for Co in the case of another magnetic system, $La_{1-x}Sr_xCoO_3$ [28].

An analog compound, Na_xCoO_2, was studied more recently for different purposes. It was found, at low temperature, to have a large thermopower (a prerequisite for thermoelectric cooling) associated with spin entropy [29]. Various magnetic and charge-ordered phases, as well as Na ordering, have been observed as a function of Na concentration [30]. (As a surprising aside, one can even generate a superconducting phase by adding some H_2O to $Na_{0.35}CoO_2$ [31].) Knowledge of these phases is relevant if one wants to move Na in and out of the lattice in a continuous fashion; the energy differences between different ordered phases would tend to favor certain Na concentrations. In that sense, it is fortunate that the ordered states tend to develop below room temperature.

The analogous phase diagram for Li_xCoO_2 has now been mapped out [32, 33]. Ordering transitions occur below 200 K, so they do not interfere with normal intercalation/deintercalation processes.

Moving to the present, a current fascination makes a parallel with the older nickelate work. Effectively replacing Li^{1+} with Nd^{3+}, Hwang and coworkers [34] have shown that thin films of $Nd_{0.8}Sr_{0.2}NiO_2$ exhibit superconductivity with a transition temperature $T_c \gtrsim 10$ K. A striking complication is that it is not straightforward to get to $NdNiO_2$. In fact, one has to grow $NdNiO_3$, and then remove one O per formula unit by reacting with CaH_2 [34]. So we are back to a deintercalation process, as with batteries. The resulting Ni^{1+} ions in this case are close to d^9, similar to Cu^{2+}; however, it appears that Nd $5d$ states may also play a role. These so-called "infinite-layer" nickelates are the center of continuing research and controversy [35]. It is natural to compare and contrast them with cuprate superconductors, which we will be discuss next.

IV. FROM MOTT INSULATOR TO HIGH-TEMPERATURE SUPERCONDUCTOR

The discovery of superconductivity in a copper-oxide compound came as a great shock to the condensed-matter-physics community. I was starting my career at Brookhaven when the cuprate discovery hit the grapevine. Note that this was before the internet and there was no instantaneous access to new results as there is today. The discovery paper was published in the June 1986 issue of *Zeitschrift für Physik* [11], but that issue did not appear on the library shelf at Brookhaven until several months later. In the mean time, we depended on rumors from colleagues who visited Bell Labs or who attended the fall 1986 Materials Research Society meeting.

As mentioned above, physicists had paid little attention to oxides, so, to get a start, it was necessary to turn to the solid-state-chemistry literature. I still have a xeroxed copy of JBG's 1984 analysis of La_2CuO_4 and La_2NiO_4 [36], which largely relied on his 1973 analysis of these compounds [37]. The introduction of the '84 paper provided a valuable summary of the atomic structures that had been determined by diffraction studies. His earlier paper [37] properly recognized that the single hole per Cu^{2+} in La_2CuO_4 should be in the $d_{x^2-y^2}$ orbital and hybridized with the $2p_\sigma$ orbitals of the 4 O neighbors within each CuO_2 plane; he also noted that the presence of two electrons in the same d orbital would cost a substantial Coulomb energy U, consistent with Mott's idea, as formulated by Hubbard [38]. (Some other details were not quite right, but this was because the early characterizations were generally not on pure La_2CuO_4; I have discussed some of these common confusions and challenges elsewhere [39].)

In contrast, much of the condensed-matter theory community was focused on band structure calculations using density functional theory (DFT); such calculations on La_2CuO_4 predicted that it should be metallic, with a putative Fermi-surface charge-density-wave instability [40, 41]. It took another theorist of Goodenough's generation, one who had cut his teeth on the first experimentally-confirmed antiferromagnet MnO [42], to recognize that La_2CuO_4 should be an antiferromagnetic insulator with spin $S = 1/2$ on each Cu site and superexchange coupling between nearest neighbors determined by U [43]. Antiferromagnetic order was soon confirmed by neutron diffraction [44], and an optical gap of ~ 2 eV was determined by optical spectroscopy [45].

Understanding these materials becomes even more challenging when charge carriers (holes) are doped into the CuO_2 planes [46]. Experiments have shown that the antiferromagnetic correlations survive locally, and seem to accommodate the doped carriers in a spatially-modulated fashion [47]. While there is still considerable controversy, there is a common belief that the superconductivity is a consequence of magnetic correlations [48, 49]. I have my own extreme opinion on this, and have argued that the pairing required for superconductivity occurs within charge stripes that alternate with antiferromagnetic stripes in the planes [50].

One reason for the lack of a widely accepted explanation of the superconductivity in cuprates is the challenge of calculating their electronic properties in a convincing fashion. The DFT approach to calculating electronic structure fails to adequately account for the correlation effects associated with $3d$ orbitals, so a modified version, known as DFT+U was developed [51]. To better describe the interatomic spin and charge correlations, another approach known as dynamical mean-field theory (DMFT) was established [52]. This works very well for short-range correlations, but it remains a challenge to handle correlations that may vary over a substantial distance. Other approaches use a simplified description parameterized in the form of a Hubbard model, typically describing only one orbital per Cu atom. Even this simplified model is challenging to solve. Numerically intensive techniques such as density-matrix renormalization group (DMRG) [53] and quantum Monte Carlo [54] are applied to such models, yielding intriguing-but-not-yet-conclusive results.

In the cuprates, we have been struggling to understand how to deal with a combination of local-moment magnetism and effective mixed-valence states, features of the type originally recognized by Goodenough in spinel [7] and perovskite [9] magnets. It is notable that the first all-electron calculation to yield results both qualitatively and quantitatively consistent with the ordered and disordered phases of the parent insulator La_2CuO_4 was published only a few years ago [55]. To make further progress, some are turning to quantum computing: simulations of the antiferromagnetism and the motion of doped holes within a simple model of a CuO_2 layer have now been performed with a cold-atom quantum simulator [56]. The search for a proper understanding will continue.

V. LESSONS FROM A LONG LIFE

We have seen that John Goodenough's contributions have impacted research on a broad variety of interesting properties of transition-metal oxides. Are there broader lessons that we can take from his career?

One lesson is the creative benefit of research groups involving diverse experience. At MIT Lincoln Laboratory, JBG started off as a theoretical physicist in a group of solid-state chemists and engineers [3]. That combination proved to be quite successful. JBG continued to work closely with experimentalists throughout his career. An efficient connection between theory and experiment is important for rapid progress in materials science. (I also know this from personal experience, as I benefited greatly from regular interactions with the late Vic Emery.)

A related lesson is the effectiveness of working at the boundary between established fields of knowledge. Breakthroughs often result from bringing fresh eyes to a challenging problem.

Finally, we have seen that transition-metal oxides have many lives. A correlated insulator may be turned into a material exhibiting colossal magnetoresistance or high-temperature superconductivity by rather small changes in composition. Such versatility and the potential for unanticipated technologically-important properties is often under appreciated by funding agencies and by the politicians who frequently provide funding constraints with unintended consequences. After two decades of highly productive fundamental research at MIT Lincoln Laboratory, JBG reached a point at which such work was no longer supported. Rather than switching to more applied research, he chose to find a new location where his interests would be appreciated. To do that, he left the US, landing at Oxford University, where he promptly made his key discovery that has enabled Li-ion batteries. A retirement-age requirement eventually brought him back to the US and to the University of Texas. Not all researchers can make such successful transitions. We can only hope that potential future discoveries will not be impeded by unimaginative research support.

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