Electronic and magnetic properties of perovskite selenite and tellurite compounds: CoSeO$_3$, NiSeO$_3$, CoTeO$_3$ and NiTeO$_3$

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Selenium and tellurium are among the few elements that form ABO$_3$ perovskite structures with a four valent ion in the A site. This leads to highly distorted structures and unusual magnetic behavior. Here we investigate the Co and Ni selenite and tellurite compounds, CoSeO$_3$, CoTeO$_3$, NiSeO$_3$ and NiTeO$_3$ using first principles calculations. We find an interplay of crystal field and Jahn-Teller distortions that underpin the electronic and magnetic properties. While all compounds are predicted to show an insulating G-type antiferromagnetic ground state, there is a considerable difference in the anisotropy of the exchange interactions between the Ni and Co compounds. This is related to the Jahn-Teller distortion. Finally, we observe that these four compounds show characteristics generally associated with Mott insulators, even when described at the level of standard density functional theory. These are then dense bulk band or Slater, Mott-type insulators.

I. INTRODUCTION

Perovskite oxides constitute an exceptionally broad class of compounds, and exhibit many diverse properties and useful functionalities.[1] This includes high temperature superconductors,[2] widely used ferroelectric and piezoelectric materials,[3] colossal magnetoresistive compounds,[4] ionic conductors,[5] and many other important materials. The structure type is characterized by an ABO$_3$ stoichiometry, based on corner linked BO$_6$ octahedra arranged on a simple cubic lattice, often distorted. These distortions are key to the chemical flexibility of the perovskite structure. For example, A-site ions that are too small for the site can be accommodated by coordinated tilting of the corner linked BO$_6$ octahedra, thus allowing small ions to be inserted, and at the same time providing a chemical tuning mechanism for modulating the bond angles and properties that depend on them. The chemical and structural tunability of this structure type also leads to fascinating physics including quantum critical phenomena, Mott and other metal insulator transitions, and magnetoelectric materials. The manganites in particular, but other materials as well, have also highlighted the importance of coupling between structure and electronic properties in perovskites.[6,7,8,9]

In this regard, investigation of compounds with unusual perovskite chemistry or structure is useful in understanding the range of possible behaviors.

Here we investigate the cobalt and nickel containing selenite and tellurite compounds, CoSeO$_3$, CoTeO$_3$, NiSeO$_3$ and NiTeO$_3$. These compounds, although known since the 1970's,[10,11] have been relatively little studied. These are highly unusual perovskites. In particular, they have extremely strong distortions leading to very strong deviation of the metal-O-metal bond angles from the ideal value of 180° and they have exclusively divalent cations at the perovskite B-site, while normally only partial occupancy of divalent B-site ions, counter-balanced by higher valence ions on other B-sites can occur in perovskites. This is as rationalized by the Pauling rules,[12] in which the corner sharing perovskite structure is stabilized by repulsion between highly charged B-site ions. Here, the unusual structures are presumably stabilized by covalent interactions between O and the Se or Te, leading to a chemistry intermediate between, on the one hand normal ionic perovskite crystals, in this case stabilized by strong off-centering and lone pair activity of the very small Se$^{4+}$ and Te$^{4+}$ ions, and on the other hand salts based on complex anions,[13] specifically, (SeO$_3$)$_2^-$ or (TeO$_3$)$_2^{-}$. It is known that CoSeO$_3$, CoTeO$_3$, NiSeO$_3$ and NiTeO$_3$ all have magnetic ground states. While transport data and spectroscopy have not been reported, based on their reported colors[14] they are probably insulating. Unlike MnSe$_3$, insulating behavior in these compounds is not an obvious result from electron counting. The corresponding Cu compounds show a strong dependence of magnetic order on structure, including a cross-over from antiferromagnetic to ferromagnetic behavior as the bond angle is distorted in the CuTeO$_3$ – CuSeO$_3$ alloy system.[15]

Remarkably, in the present study we find all four of these materials to exhibit a novel type of insulating character, specifically they are predicted to be band insulators at the PBE level both in their ground state and in the disordered paramagnetic state. This is a character-
The calculations presented here were done in the framework of density functional theory (DFT) using the general potential linearized augmented planewave (LAPW) method\cite{10} as implemented in the WIEN2k code\cite{13}. We used the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE)\cite{11} We tested different Brillouin zone samplings and did calculations with different choices of LAPW sphere radii. The main results shown here were obtained with LAPW sphere radii of 1.8 Bohr for Ni, Co, Se and Te, and 1.4 Bohr for O. The LAPW plus local orbital basis sets were used with planewave sector cutoffs, $K_{\text{max}}$, determined by the criterion $R_{\text{min}}K_{\text{max}}=7$, where $R_{\text{min}}$ is the smallest, i.e. the O, sphere radius. This leads to an effective value of 9 for the metal, Se and Te atoms.

The four compounds studied are all reported to occur in an orthorhombic $Pnma$ (spacegroup 62) structure with four formula units per unit cell. This is a very common perovskite variant. However, they are unusual in the size of the distortions from the ideal cubic structure, which are extremely large in these materials. Our calculations are based on the experimental lattice parameters. The internal atomic coordinates in the unit cells were determined by total energy minimization with a ferromagnetic ordering. We also did calculations for antiferromagnetic orderings. However, the calculated forces remained small independent of the specific ordering pattern, and so we conclude that relaxation based on ferromagnetic ordering is sufficient.

The structure of CoSeO$_3$, which is representative, is depicted in Fig. 1. The calculated structural data is summarized in Supplemental Table S1. As seen, the structures, while perovskite in nature with the characteristic motif of corner sharing $MO_6$ octahedra, are very strongly distorted from the cubic perovskite structure. This is evident also in the reported experimental lattice parameters, which deviate from the pseudo-cubic relationship, $a=\sqrt[3]{2}a^*$, $b=2a^*$, where $a^*$ is the effective cubic lattice parameter. The Co compounds have larger lattice parameters and bond lengths than the corresponding Ni compounds. This simply reflects the larger ionic radius of high spin Co$^{2+}$ compared to high spin Ni$^{2+}$\cite{12}. Within the structure, all four $MO_6$ octahedra are equivalent, and from the perspective of the octahedra and their connectivity, the local structure is characterized by three metal-O bond lengths and two metal-O-metal bond angles, as illustrated in Fig. 1(a), 1(c) and 1(d). Specifically, as illustrated, the three angles are $\angle \text{Co-O1-Co}$, $\angle \text{Co-O2-Co}$ and $\angle \text{Co-O3-Co}$, but $\angle \text{Co-O2-Co}$ and $\angle \text{Co-O3-Co}$ are the same ($\angle \text{O1}$ is the connection to the Co along the $b$-axis, while $\angle \text{O2}$ and $\angle \text{O3}$ are the $O$ that connect in the $ac$-plane directions). These parameters are given in Table I along with an octahedral distortion parameter\cite{20}

$$\Delta_d = \frac{1}{6} \sum_{n=1,6} \left[ \frac{d_n - d^*}{d} \right]^2,$$

where the $d_n$ are the six metal–O distances in an octahedron, and $d$ is the average. This distortion parameter was previously used in the analysis of Jahn-Teller splittings in manganites\cite{20}. As seen, the bond angles characterizing the octahedral rotation are similar for the four compounds, and are slightly lower (corresponding to stronger rotation) for the selenite compounds, consistent with the smaller size of Se$^{4+}$ compared to Te$^{4+}$. The distortion of the octahedra on the other hand is sensitive to the metal atom, and is substantially larger for the Co compounds as compared to the corresponding Ni compounds.

### Table I. Structural parameters of the four compounds, based on the relaxed atomic positions (see text and Fig. 1).

| Compound  | $M-O1$ (Å) | $M-O2$ (Å) | $M-O3$ (Å) | $\theta(M-O1-M)$ | $\theta(M-O2-M)$ | $\Delta_d$ |
|-----------|------------|------------|------------|-----------------|-----------------|----------|
| CoSeO$_3$ | 2.129      | 2.211      | 2.056      | 126.2$^\circ$   | 131.3$^\circ$   | 0.00088  |
| NiSeO$_3$ | 2.110      | 2.146      | 2.058      | 126.1$^\circ$   | 132.0$^\circ$   | 0.00030  |
| CoTeO$_3$ | 2.079      | 2.287      | 2.082      | 129.2$^\circ$   | 133.7$^\circ$   | 0.00205  |
| NiTeO$_3$ | 2.072      | 2.189      | 2.101      | 129.6$^\circ$   | 134.6$^\circ$   | 0.00055  |

### III. Electronic Structure

As mentioned, the structure relaxation was done using an assumed ferromagnetic ordering and the standard PBE GGA density functional. Ferromagnetic so-
Solutions were found for all four compounds (note that as discussed below there are lower energy antiferromagnetic orderings). The calculated electronic densities of states are shown along with projections in Fig. 2 and Fig. 3. Remarkably all the compounds are insulating with this ferromagnetic ordering. This is similar to what was found previously for MnSeO₃, which has the d⁵ ion Mn²⁺, forming a high spin antiferromagnetic insulating ground state.²¹,²² The spin magnetizations are 3 μB per formula unit for CoSeO₃ and CoTeO₃ and 2 μB per formula unit for the Ni compounds, NiSeO₃ and NiTeO₃.

The electronic structure of the four compounds in the valence energy range consists of occupied O 2p derived bands from ~7 eV to ~-1 eV, with respect to the energy zero, which is set to the highest occupied state. The chalcogen s states are below the window shown. The transition metal states show strong exchange splittings, as seen. Additionally, there is a strong spin dependent hybridization between the O 2p states and the transition metal d states. The spin dependence is seen in the differences in shape of the majority and minority d character in Figs. 2 and 3. It arises from the fact that the majority d states overlap the top of the O 2p bands, while the minority d states are mainly above the 2p bands. However, while the minority spin shows weaker hybridization than the majority, the hybridization is substantial in both spin channels. This is evident from the sizable crystal field splitting of the minority spin d states, which amounts to ~2 eV for both the Co and Ni compounds (note that in transition metal oxides crystal field splitting is due metal-ligand hybridization). The nominally unoccupied p states of Se and Te occur above the transition metal bands starting at ~3 eV for the Ni compounds and ~2 eV for the Co compounds. These are formally the antibonding combinations of O 2p and Se/Te p states from the (SeO₃)²⁻ and (TeO₃)²⁻ complex anions within a view of the crystal structure as a salt.

The insulating nature of the Ni compounds can be understood in a standard crystal field scheme. In an octahedral environment the 3d states are crystal field split into a lower lying t₂g manifold with three states per spin and a higher e_g manifold with two states per spin. The eight 3d electrons of Ni²⁺ suffice to fill the majority spin t₂g level plus the minority spin t₂g level. This then can lead to insulating behavior provided that the band widths are narrow enough to leave clean gaps between the minority spin t₂g and e_g crystal field levels. This is evidently the case in ferromagnetic NiSeO₃ and NiTeO₃ as can be seen from Fig. 2. It should be noted, however, that this is unusual, since ferromagnetic ordering is particularly favorable for hopping and therefore is the ordering that typically has the largest band widths in oxides. For example, as pointed out by Slater,²³ it is possible to have insulating gaps in antiferromagnetic systems due to band structure effects. This includes the prototypical Mott insulator, NiO.²⁴ However, the insulating character of NiO in this band structure point of view depends crucially on the particular magnetic order. In contrast, in the present...
case the bands are exceptionally narrow leading to narrow crystal field split levels. Thus the crystal field splitting is not washed out, even with ferromagnetic order. This is a consequence of the highly distorted perovskite structure that includes very strongly bent metal-O-metal bonds.

More remarkably, we find that both CoSeO$_3$ and CoTeO$_3$ have insulating gaps with ferromagnetic order. Co$^{2+}$ has one less electron than Ni$^{2+}$. This means that there are only two minority spin electrons. As a result, there is one hole in the $t_{2g}$ crystal field level. Such partial filling of the $t_{2g}$ level should normally lead to a metallic state especially with ferromagnetic order. However, in the Co compounds, unlike the corresponding Ni compounds, we find a clean gap in the minority spin $t_{2g}$ levels at 2/3 filling. This is a Jahn-Teller splitting that results from the lowering of local symmetry due to the distortion of the CoO$_6$ octahedra. This corresponds to the more distorted octahedra that we find in the relaxed structures of the Co compounds, characterized by the parameter, $\Delta_d$ (Table I).

We emphasize that here we performed standard GGA calculations and obtain these insulating states. This differs from calculations done with additional terms, such as in DFT+U methods, where an interaction that increases the separation of occupied and unoccupied $d$ levels is applied. Furthermore, we use the relaxed atomic positions obtained with standard GGA calculations, and still obtain a sufficient Jahn-Teller distortion to open a clean gap in the minority spin $t_{2g}$ levels of the Co compounds, even for the ferromagnetic ordering. This is particularly remarkable considering that the orbital involved is Co $d$ - O $p$ π antibonding $t_{2g}$, which generally may be expected to be much less Jahn-Teller active than the $\sigma$ antibonding $e_g$ orbitals.

### IV. MAGNETISM

We now discuss the magnetic properties. Experiment shows all four compounds to be antiferromagnetic based on temperature dependent susceptibility measurements. However, the particular magnetic order has not been established. The primitive unit cell contains four transition element atoms. Within one unit cell it is therefore possible to consider four collinear magnetic orders, denoted F, G, A and C, and corresponding to ferromagnetic order, nearest neighbor antiferromagnetic order, ferromagnetic layers stacked antiferromagnetically along the crystallographic $b$-axis, and nearest neighbor antiferromagnetic layers, stacked ferromagnetically along $b$ to yield ferromagnetic chains along $b$, respectively. We calculated the total energy and electronic structures for all these orders, for each compound. These energies are given relative to the ferromagnetic order in Table II. The last row is the ratio of the experimental $k_B T_N$ to the energy difference between the F and G orders. This energy difference is a measure of the average superexchange strength in a nearest neighbor model.

| Order | #AF | CoSeO$_3$ | CoTeO$_3$ | NiSeO$_3$ | NiTeO$_3$ |
|-------|-----|-----------|-----------|-----------|-----------|
| F     | 0   | 0         | 0         | 0         | 0         |
| A     | 2   | -0.0013   | -0.0064   | -0.0226   | -0.0240   |
| C     | 4   | -0.0263   | -0.0300   | -0.0516   | -0.0615   |
| G     | 6   | -0.0275   | -0.0337   | -0.0735   | -0.0821   |
| ratio |     | 0.15      | 0.20      | 0.11      | 0.13      |

In all cases the G-type order had the lowest energy, and all antiferromagnetic orders had lower energy than the ferromagnetic order. Within a nearest neighbor superexchange scheme, this shows that all the bonds of a metal atom to its six nearest neighbor metal atoms have antiferromagnetic coupling.

In all cases and for all orders studied we find insulating gaps. Furthermore, in all cases, the fundamental band gap increased in going from the ferromagnetic to the antiferromagnetic ground state. Band gaps for the different orders are presented in the Supplemental Table S2. The Se compounds have larger band gaps than the corresponding Te compounds. Also the band gap increase with change of the order to antiferromagnetic is much stronger for the Ni compounds. In these Ni compounds the gap is between the occupied minority spin $t_{2g}$ or majority $e_g$ (for ferromagnetic) manifolds and the unoccupied minority $e_g$ manifold and the increase amounts to $\sim$0.5 eV. In the Co compounds, the gap is between the lower and upper Jahn-Teller split $t_{2g}$ sub-manifolds, and the increase amounts to less than 0.1 eV. This reflects the superexchange mechanism, which involves the $e_g$ levels as discussed below. We note that the above places the magnetism in these compounds in the local moment (as opposed to the itinerant) limit.

As mentioned, all the compounds are antiferromagnetic, with a G-type ground state. Experimentally, the Neel temperatures, $T_N$, show considerable variation among these materials. The reported values are 49 K, 78 K, 98 K and 125 K, for CoSeO$_3$, CoTeO$_3$, NiSeO$_3$ and NiTeO$_3$, respectively. It is of interest to develop understanding of these differences.

We begin with the structure. Subramanian and coworkers emphasized the importance of the metal-O-metal bond angles controlled by $A$-site size in explaining the cross-over from antiferromagnetism to ferromagnetism in the Cu(Se,Te)O$_3$ alloy system. The Goodenough-Kanamori rules imply that the strongest antiferromagnetic tendency of these materials should be for straight bonds. In the present case, the perovskite framework is extremely distorted, with bond angles very far from the ideal 180°, and so the validity of extrapolating...
from the properties of mildly distorted perovskites may be questioned. However, the experimental $T_N$ are indeed higher for the Te compounds than for the corresponding Se compounds. It is expected that the bonds will be straighter for Te than Se due to the larger size of Te. This is in fact the case based on our calculated structure data (Table I). Fig. 1 shows the correlation between the two different bond angles and the experimental $T_N$ for the Co and Ni compounds. This illustrates the trend, which is as expected from the Goodenough-Kanamori rules. Furthermore, while the $T_N$ for the Ni compounds is consistently higher than for the Co compounds, this is not a consequence of different bond angles, e.g. from the smaller ionic radius of Ni, since in fact the bond angles are similar. It is also of interest to observe that the effect on the absolute $T_N$ of comparable changes in bond angle are similar between the Co and Ni compounds.

Turning to the energies, it is notable that the energy difference between the ferromagnetic and G-type antiferromagnetic ground state follows the same order as the experimental values of $T_N$, i.e. $\text{CoSeO}_3 < \text{CoTeO}_3 < \text{NiSeO}_3 < \text{NiTeO}_3$. However, there is not a simple proportionality, which might be expected in an isotropic nearest neighbor Heisenberg model. Instead, the Co compounds show higher $T_N$ than would be expected from scaling down the Ni compound values according to the F - G-type energy difference. This is seen in the ratios given in the last line of Table I.

This suggests a difference between the compounds, which is somewhat surprising due to the fact that the basic features of the electronic structure, especially as regards the $e_g$ orbitals are similar between the Co and Ni compounds. The $e_g$ states are formally the $\sigma$ antibonding $d - O \ p$ combinations. Therefore with fully occupied majority $e_g$ orbitals and unoccupied minority $e_g$ orbitals, as in the present compounds, the strongest superexchange channel in perovskites involves the coupling of the $e_g$ states, which as mentioned are similar between the four compounds.

One possible explanation could be in the chemical differences between Ni and Co, for example different amounts of hybridization, and different correlation strengths. One measure of the strength of hybridization that is readily available is the crystal field splitting. We focus on the minority spin in the ferromagnetic case, where the $t_{2g}$ and $e_g$ levels are separated from each other and from the $O \ 2p$ bands. We obtain the center of the corresponding peaks in the density of states by integration of the first energy moment and thereby obtain the average minority spin crystal field splitting. In the Co compounds we include both sub-peaks of the $t_{2g}$ bands in the calculation of the average $t_{2g}$ energy. The obtained crystal field splittings are 1.72 eV, 1.69 eV, 2.00 eV and 1.97 eV, for $\text{CoSeO}_3$, $\text{CoTeO}_3$, $\text{NiSeO}_3$ and $\text{NiTeO}_3$. Thus the Ni compounds have larger crystal field splittings, indicating stronger hybridization. This may be the simple result of the fact that the Ni $d$ states are closer in energy to the $O \ 2p$ bands as seen in the projected densities of states (Figs. 2 and 3). In any case, it is consistent with stronger superexchange, since superexchange depends on metal - ligand hybridization. This is as found in the present results. This type of superexchange due to $e_g - e_g$ interactions with occupied $t_{2g}$ orbitals increases the band gap for the antiferromagnetic state, since antiferromagnetism both narrows the bands and shifts the $e_g$ level to higher energy. In the case of the Co compounds, the gap is between sub-manifolds of $t_{2g}$ states. In this case band narrowing can increase the gap, but an up-shift of the $e_g$ level will not directly affect the gap, explaining the smaller band gap increases upon antiferromagnetic ordering in the Co compounds.

This is related to the possible explanation that strong correlations are present with different values of $U$ that could be included in PBE+$U$ calculations with $U$ fit experiment. However, while $U$ generally can be used to reduce exchange couplings and fit $T_N$, and typically some $U$ improves agreement with experiment in most transition metal oxides, it would be desirable to have a more first principles explanation if possible. Also, the apparently stronger hybridization in the Ni compound as indicated by the crystal field, does not support a view that the Ni compound should have a larger $U$, since in general hybridization provides screening, which reduces the effective $U$. In any case, these results suggest that there may be a difference in the magnetic behavior also at the PBE level.

As mentioned, the local transition metal environment is more strongly distorted in the Co compounds due to the Jahn-Teller effect. This leads to anisotropy in the exchange interactions. This can be seen in the pattern of energy differences in Table I. These energies are plotted in Fig. 5. The results show that the magnetic energy varies nearly linearly with the number of antiferromagnetic bonds in the Ni compounds. In contrast, antiferromagnetic bonds in the $ac$-plane strongly lower the

![Fig. 4. Metal-O-metal bond angles from the relaxed structure and experimental Neel temperature, $T_N$, for the four compounds.](image-url)
FIG. 5. Magnetic energy per formula unit defined as the energy difference from the ferromagnetic state for the F, A, C and G type orders, which have 0, 2, 4 and 6 antiferromagnetic bonds per metal (#AF), respectively. Note the different behavior of the Co and Ni compounds.

energy for the Co compounds. However in the Co compounds the energy differences between the F and A order and between the C and G orders are small. This means that the b-axis interactions are comparatively quite weak. Consequently, while all the compounds have orthorhombic Pnma symmetry, NiSeO$_3$ and NiTeO$_3$ are nearly isotropic from the point of view of their exchange interactions, but CoSeO$_3$ and CoTeO$_3$ are very anisotropic, and are more like layered materials from the point of view of exchange couplings. Based on the obtained energetics, the interactions in-plane are similar between the Ni and Co compounds (note especially the energy differences between A-type and C-type order, which probe this). Thus the Ni and Co compounds have very different anisotropy of the exchange interactions, and so a simple scaling of $T_N$ with the F - G energy difference is not expected between the Co and Ni compounds.

V. SUMMARY, DISCUSSION AND CONCLUSIONS

To summarize the results, we find, using standard density functional calculations at the PBE level, that these compounds are local moment antiferromagnetic insulators. The Ni compounds are insulating because of the narrow bands and sizable crystal field splitting. The Co compounds are also insulating due to a Jahn-Teller distortion of the octahedra. These calculations show near isotropic exchange interactions in the Ni compounds, and a strong anisotropy with weak interactions along the b-axis for the Co compounds. Remarkably, we find that these compounds are predicted to be insulators regardless of the specific magnetic order, even though we did standard PBE calculations.

A key characteristic of Mott insulators that distinguishes them from Slater insulators is the fact that both the ordered magnetic state and the higher temperature paramagnetic state are insulating with similar band gaps. This is a commonly applied experimental test for whether or not a material is a band insulator (i.e. Slater insulator) or a correlation driven Mott insulator. As discussed below, the present compounds mix these two categories as they satisfy the experimental test for a Mott insulator, but can do so for purely band structure reasons.

In local moment systems, such as the compounds discussed here, the phase transition is from an ordered antiferromagnetic state at low $T$ to a high temperature paramagnetic state where the moments persist but are disordered. The spatial homogeneity of the paramagnetic state may then be regarded as due to temporal variations of the moments, that at any given time exist though without long range order. If the temporal variations are not too fast, one may approximate this state by thermodynamic averages over various disordered configurations. This is the so-called disordered local moment picture, which is very successful in describing both local moment materials and even materials such as iron that have some itinerant character.

In the present selenite and tellurite compounds, all configurations have band gaps, with approximately similar values. Therefore, a gap is expected for any disordered configuration and therefore a disordered local moment picture will lead to gaps in the paramagnetic states. This includes the Co compounds where a Jahn-Teller distortion is present.

Thus these compounds present the unusual situation where one has local moment magnetism with insulating character that persists above the ordering temperature without the need for correlations beyond the standard PBE level. Recently, Zunger and co-workers have used a closely related concept to explain properties of transition metal oxides, including monoxides and perovskites. They used special quasi-random structures to model the high temperature state. They did calculations allowing for local heterogeneity consistent with the quasi-random structures. However, in the work it was necessary to either include a correlation effect via a parameter $U$ or to use a density functional such as SCAN that enhances the separation of occupied and unoccupied $d$ levels, similar to a $U$ parameter leading to poor descriptions of itinerant magnets such as iron.

Here we identify four bulk oxides, where the properties are characteristic of a Mott insulator, even at the level of standard PBE calculations, not including any additional correlation terms. This is not to say that the detailed agreement with experiments, when these become available, would not be improved by additional terms, such as $U$. However, our results point out an interesting possibility, realized in these compounds, that suggests further experimental investigations of their detailed properties,
especially band gaps and spectra, as well as spin excitations. These may then be compared with theoretical results and used to constrain models. Spectroscopy in particular will be helpful in determining to what extent the band or Slater Mott-type insulating picture developed above is responsible for the properties of the materials, and conversely how important the Coulomb interactions are in determining the spectra.

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