

CHARGE DISPROPORTIONATION AND MAGNETIC ORDERING IN CaFeO_3

Transition metal oxides adopting the perovskite crystal structure (or one of its relatives) have occupied a place in the scientific limelight for nearly fifty years now. Beginning with the discovery of ferroelectricity in BaTiO_3 , following World War II, the dielectric properties of perovskites have been extensively studied over this entire period. Today perovskite dielectrics, due to their widespread usage in telecommunication, are still extensively studied. The discovery of superconductivity first in doped BaBiO_3 , and later in the cuprates, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, triggered an unprecedented avalanche of scientific activity in the late 1980's and early 1990's. More recently, phenomena such as colossal magnetoresistance (CMR), charge, orbital and spin ordering, and phase separation in the manganate perovskites, $(\text{Ln}_{1-x}\text{A}_x)\text{MnO}_3$ (Ln = lanthanide ion, A = alkaline earth ion), have captured the imagination of the condensed matter scientific community.

Ultimately the electronic and magnetic properties of a material depend upon the behavior of the outermost or valence electrons. In a first row transition metal oxide the valence electrons are shared, though not equally, between the 3d orbitals of the transition metal ion and the 2p orbitals of oxygen. In compounds with the perovskite structure the oxygen atoms are arranged in an octahedral geometry about the transitional metal ion; each oxygen is then shared by two transition metal ions to form a three dimensional network of corner sharing MO_6 octahedra. The octahedral coordination removes the energetic degeneracy of the 3d orbitals, forming the familiar triply degenerate t_{2g} and doubly degenerate e_g set of orbitals. The e_g orbitals point directly at the oxygen ligands to form a strongly antibonding σ^* bond. In contrast, the t_{2g} orbitals have a smaller overlap with the oxygen 2p orbitals, which leads to a weakly antibonding π^* band. If this covalent bonding interaction between the transition metal and oxygen is weak, the valence electrons are localized and a magnetic insulator is typically observed. If we increase the strength of the interaction sufficiently, either by increasing the electronegativity of the transition metal ion or the spatial overlap of the metal 3d and oxygen 2p orbitals, partial delocalization of the valence electrons can occur. Frequently, this leads to metallic conductivity. In a number of transition metal oxides the metal-oxygen interaction strength is such that delocalized

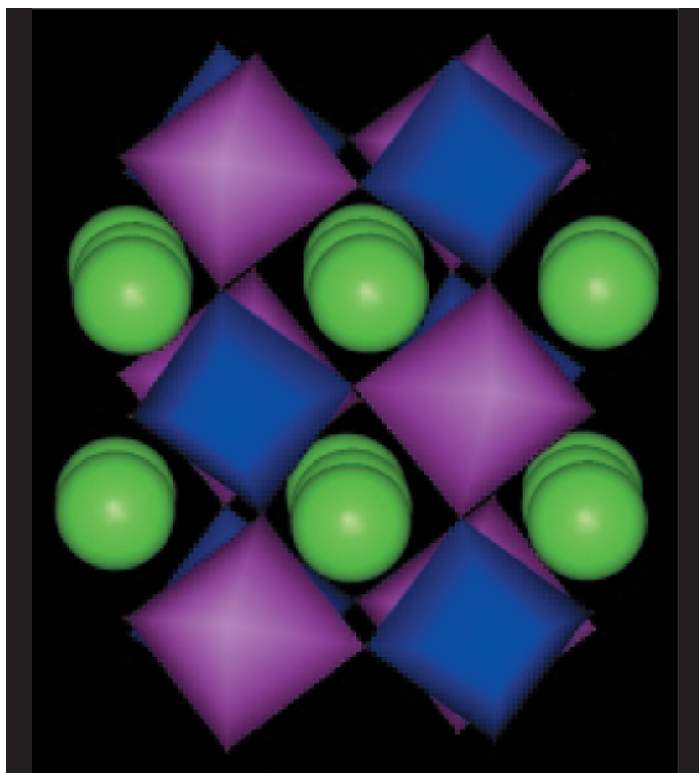


FIGURE 1. The low temperature structure of CaFeO_3 . The green spheres depict the calcium ions. The other shaded objects represent iron centered octahedra, where an oxygen atom can be found at each vertex and an iron atom at the center of each octahedron. The purple and blue objects represent Fe^{3+} centered and Fe^{2+} centered octahedra respectively.

electrons and metallic conductivity are seen at higher temperatures but give way to a magnetically ordered, insulating ground state upon cooling.

LaMnO_3 , SrFeO_3 and CaFeO_3 are isoelectronic; they each have an electronic configuration of $t_{2g}^3 e_g^1$. According to the Jahn-Teller theorem, the presence of a single localized electron in the doubly degenerate e_g set of orbitals is not a stable situation. LaMnO_3 responds to this instability by undergoing a cooperative Jahn-Teller distortion of the MnO_6 octahedra, producing two long and four short Mn-O bonds, thereby, removing the degeneracy of the e_g orbitals. SrFeO_3 takes a different approach, by delocalizing its e_g electrons to form a σ^* band. The contrasting behavior of these two materials can be understood in terms of the strength of the metal-oxygen

interaction. Contrasting LaMnO_3 to SrFeO_3 , the oxidation state of the transition metal increases from +3 to +4, which leads to an increase in the metal-oxygen interaction strength, increasing the width of the σ^* band and stabilizing a metallic ground state. Since they both contain Fe^{4+} , one might expect that CaFeO_3 and SrFeO_3 would behave very much alike. However, Ca^{2+} is smaller than Sr^{2+} , which causes a tilting of the FeO_6 octahedra to satisfy the valence requirements of calcium. This seemingly subtle distortion has several important consequences. The Fe-O-Fe bond is distorted away from the linear geometry observed in SrFeO_3 (the Fe-O-Fe angle is 158° in CaFeO_3). This reduces the spatial overlap of the Fe e_g and O 2p orbitals, and the width of the σ^* band decreases. The reduction in bandwidth triggers an electron localization that occurs just below room temperature (290 K). Once electron localization occurs, a cooperative Jahn-Teller distortion to the LaMnO_3 crystal structure is expected.

However, CaFeO_3 refuses to conform with expectations. Instead CaFeO_3 undergoes a charge disproportionation (CD), $2\text{Fe}^{4+} (t_{2g}^3 e_g^1) \rightarrow \text{Fe}^{3+} (t_{2g}^3 e_g^2) + \text{Fe}^{5+} (t_{2g}^3 e_g^0)$. Evidence for a CD in CaFeO_3 was first proposed over 20 years ago, based on Mössbauer studies [1]. However, crystallographic confirmation of this rare phenomenon has proven elusive. Through the combined use of synchrotron x-ray (X7a-NSLS) and neutron powder diffraction (BT-1 at NCNR), we have elucidated the crystal structure of CaFeO_3 in its CD state for the first time. The resulting structure (Fig. 1) clearly shows the presence of two chemically and crystallographically distinct Fe sites. The average Fe-O bond length about the “ Fe^{5+} ” site is 1.872(6) Å, while the same distance about the “ Fe^{3+} ” site is 1.974(6) Å. The ordered arrangement of $\text{Fe}^{3+}/\text{Fe}^{5+}$ is such that each Fe^{3+} is surrounded by six Fe^{5+} ions, and vice versa (NaCl or G-type ordering), optimizing the Coulomb stabilization of the CD state. Alternately, the CD process can be viewed as the condensation of a breathing phonon mode.

In addition to electronic properties, there has long been both technological and fundamental scientific interest in the magnetic properties and interactions in perovskites containing transition metal ions. Goodenough’s study of the various antiferromagnetic struc-

tures observed in the $(\text{La}_{1-x}\text{Ca}_x)\text{MnO}_3$ system was vital in the development of the Goodenough-Kanamori rules of superexchange [2]. These rules correctly predict an A-type antiferromagnetic structure for LaMnO_3 . Using the same rules, we would expect CaFeO_3 to have a simple ferromagnetic ground state. Perhaps not surprisingly, our investigation showed that again CaFeO_3 defies expectations. Low temperature neutron powder diffraction data reveals instead an incommensurate antiferromagnetic ground state ($T_N \approx 120$ K). Analysis of the data shows the magnetic structure to be either a screw spiral or a sinusoidal amplitude-modulated structure. In either case, it would appear that a long range AFM interaction (probably between next-neighbors) is present in addition to the nearest neighbor FM superexchange interaction.

REFERENCES

- [1] M. Takano, N. Nakanishi, Y. Takeda, S. Naka and T. Takada, *Mater. Res. Bull.* **12**, 923 (1977).
- [2] J. B. Goodenough, *Magnetism and the Chemical Bond*, Interscience, New York (1963).