

PECULIARITIES OF TIGHT BINDING
REPRESENTATIONS OF $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$
QUADRUPLE PEROVSKITES *

M.D. JOHANNES AND W.E. PICKETT

Department of Physics, University of California Davis, Davis CA 95616

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Quadruple perovskites with the *bcc* $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ crystal structure are becoming interesting for unusual magnetic, electronic, dielectric, and structural properties. It is shown here that the magnetic Cu d_{xy} states have unusual interrelationships (in terms of a tight binding representation) that have important implications for magnetic coupling.

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1. Introduction

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) is the prototype of “quadrupled perovskite” structure class, which includes the ferrimagnetic semiconductor $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ as well as some ruthenate metals. CCTO has been the subject of recent interest due to its extremely high, nearly temperature-independent, dielectric constant ($\epsilon \sim 10^4$) in the kHz frequency range. This compound has three-dimensional AFM ordering, and our preliminary study indicates that very long range interactions are present. Here we present some of the details of how the arrangement of the magnetic d_{xy} orbital of Cu^{2+} ions implies the necessity of long range magnetic coupling involving long range electronic hopping processes. Symmetry arguments prohibit interactions between both nearest and next-nearest Cu–Cu neighbors and therefore the simple Néel ordering must have its origins elsewhere.

2. Structure and the Cu d_{xy} orbital

The structure of CCTO is best described as a simple perovskite structure which has been quadrupled $(\text{CaTiO}_4)_4$, followed by a replacement of

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three out of four Ca ions with Cu. The O ions which normally occupy the center of the faces then shift (remaining in-plane) to form a square-planar environment with the Cu ion. This shift has the effect of tilting the TiO_6 octahedra such that one triangular face of each lies along a (111) axis.

In this environment, the Cu ions are d^9 , leaving a single hole in the d_{xy} orbital, which is co-planar with the Cu and O ions. The d_{xy} orbital belonging to each of the three Cu ions in the unit cell is in a different plane, so that the Cu ions form three bcc sublattices containing CuO_4 plaquettes at right angles to one another.

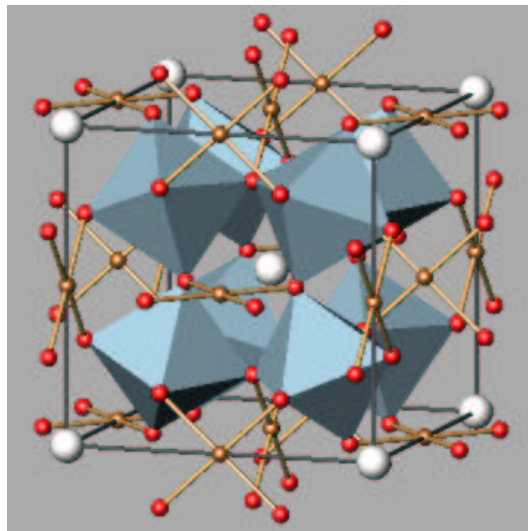


Fig. 1. The quadrupled perovskite structure. TiO_6 octahedra are tilted such that CuO_4 squares (crosses) in this figure are formed.

The tight binding (TB) representation of the band structure of conventional cubic ABO_3 perovskites, where B is a transition metal atom, was studied in detail by Wolfram and Ellialtioglu [4] who noted for example the flat bands that result if the ddd type hopping amplitudes [5] can be neglected, as they often can. Here we note peculiarities of the TB representation of the magnetic states of CCTO that result from the type of magnetic orbitals (d_{xy} in their local coordinate system) and their arrangement on the 1/4-depleted bcc lattice.

2.1. Implications for magnetic ordering

An accurate bandstructure was fit to a tight-binding model. The hopping amplitudes obtained from the TB fit were then used to obtain spin-spin coupling (superexchange) parameters, using $J = \frac{4t^2}{U}$.

The 1st and 2nd neighbors of any given Cu ion are located in the (100) and (110) directions respectively. Since these neighbors are both also located on a different sublattices, their d_{xy} orbitals are orthogonal and therefore the hopping parameter between them is zero. Magnetic ordering in this model must therefore come from interactions between more distant spins. The 3rd neighbor orbitals are not orthogonal, but they are located on the same sublattice. So although this interaction would successfully order each sublattice with a simple Néel ordering, there is no mechanism by which the sublattices can order with respect to one another. The 4th neighbor interactions suffer the same problem: overlap between orbitals is non-zero, but again connect only spins on the same sublattice. Not until the 5th neighbor is there an interaction between spins that is both non-zero and allows hopping between different sublattices. The need to extend the model all the way to 5th neighbors is clear when fitting the bandstructure; until this interaction is added, there are improper degeneracies in the TB model along some directions in k -space. Although the 5th neighbor interaction correctly removes these degeneracies and essentially describes the magnetic ordering correctly, a good fit to the bandstructure actually requires that Cu-Cu interactions up to 7th neighbor be included. Table I shows the hopping parameters which result from fitting to the bandstructure.

TABLE I

t_{3rd}		-53.0 meV	t_{6th}		-7 meV
t_{4th}	π (Ca)	-51.0 meV	t_{7th}	σ	-1.4 meV
$t_{4th'}$	π (no Ca)	16.3 meV	$t_{7th'}$	δ (Ca)	2.7 meV
$t_{4th''}$	δ	20.1 meV	$t_{7th''}$	δ (no Ca)	-9.5 meV
t_{5th}		5.6 meV			

The different designations for neighbors at the same distance (*e.g.* the three distinct 4th neighbors) refer to either a different chemical environment or to a different orientation of orbitals with respect to one another (and therefore a different overlap).

When the TB hopping parameters are applied to the Heisenberg model, $J_{ij}(= \frac{4t_{ij}^2}{U})$ will always be positive, and therefore favor anti-alignment of the two spins which it connects. This means that the 4th neighbor interaction is frustrated since 4th neighbors share a common 3rd neighbor with which they are already anti-aligned. This frustration is moderated by the fact that there are eight 3rd neighbors and only two 4th neighbors with hopping parameters which are on the order of the 3rd neighbor parameter. Table II summarizes the number of neighbors of each kind and the resulting energy produced within the Heisenberg model. The AFM ordering which is experimentally observed is favored (over FM ordering) in this model by 23 meV/Cu.

TABLE II

Type of hopping		z_{nn}	$\frac{4t^2}{U} * z_{nn}$ (FM)	$\frac{4t^2}{U} * z_{nn}$ (AFM)
t _{3rd}		8	22.47 meV	-22.47 meV
t _{4th}	π (Ca)	2	5.2 meV	5.2 meV
t _{4th'}	π (no Ca)	2	0.53 meV	0.53 meV
t _{4th''}	δ	2	0.81 meV	0.81 meV
t _{5th}		8	0.25 meV	-0.25 meV
t _{6th}		12	0.00 meV	0.00 meV
t _{7th}	σ	4	0.01 meV	-0.01 meV
t _{7th'}	δ (Ca)	4	0.03 meV	-0.03 meV
t _{7th''}	δ (no Ca)	4	0.36 meV	-0.36 meV
TOTAL			29.66 meV	-16.58 meV

This model can adequately explain the magnetic order of CCTO but surprisingly, this order depends on interactions between 5th neighbors which are separated by more than a lattice constant. The TB fit suggests that even further interactions (out to 7th neighbor) are present and non-negligible.

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