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

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Quadruple perovskites with the bcc CaCu$_3$Ti$_4$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

CaCu$_3$Ti$_4$O$_{12}$ (CCTO) is the prototype of “quadrupled perovskite” structure class, which includes the ferrimagnetic semiconductor CaCu$_3$Mn$_4$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 ($\varepsilon \sim 10^6$) 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 (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 TiO₆
octahedra such that one triangular face of each lies along a (111) axis.

In this environment, the Cu ions are d⁶, leaving a single hole in the
dₓᵧ orbital, which is co-planar with the Cu and O ions. The dₓᵧ 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 CuO₄ plaquettes
at right angles to one another.

Fig. 1. The quadrupled perovskite structure. TiO₆ octahedra are tilted such that
CuO₄ squares (crosses) in this figure are formed.

The tight binding (TB) representation of the band structure of conven-
tional cubic ABO₃ 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 dd₀ 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 (dₓᵧ
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{\mu^2}{\alpha}. 
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 Neel 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.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
$\ell_{3rd}$ & $-53.0$ meV \\
\hline
$\ell_{4th}$ & $\pi$(Ca) $-51.0$ meV \\
\hline
$\ell_{4th}$ & $\pi$ (no Ca) $16.3$ meV \\
\hline
$\ell_{4th}$ & $\delta$ $20.1$ meV \\
\hline
$\ell_{5th}$ & $5.6$ meV \\
\hline
\end{tabular}
\caption{Table I}
\end{table}

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, $J_{ij} = \frac{\ell_{ij}}{2m}$ 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.
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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REFERENCES