Metal insulator transition in TlSr$_2$CoO$_5$ from orbital degeneracy and spin disproportionation

D. Foerster, CPTMB, Université de Bordeaux I
33405 Talence, France

R. Hayn, Institut für Festkörper- und Werkstofforschung (IFW)
01171 Dresden, Germany

T. Pruschke and M. Zöllf, Institut für Theoretische Physik, Universität Regensburg
93040 Regensburg, Germany

H. Rosner, Department of Physics, University of California
95616 Davis, California, USA

To describe the metal insulator transition in the new oxide TlSr$_2$CoO$_5$ we investigate the electronic structure of its high temperature tetragonal phase by local density band structure (LDA) and model Hartree-Fock calculations. Within LDA we find a homogeneous metallic and ferromagnetic ground state, but when including the strong Coulomb interaction in the 3$d$ shell more explicitly within the Hartree-Fock approximation, we find an insulating state of lower energy that exhibits both spin and orbital order. The instability of the metallic state towards the insulating one is driven by orbital degeneracy and a near degeneracy in energy of the states of intermediate ($s=1$) and high ($s=2$) spin. We also interpret our results in terms of a simple model.

PACS numbers: 71.30.+h, 71.20.-b, 75.50.-y

Introduction

Six years ago, the observation of colossal magneto resistance in doped manganites has lead to renewed interest in transition metal oxides, see [1] for a review. These materials often exhibit complex phases with coexisting magnetic and orbital order and with Jahn-Teller like distortions. The origin of this complexity is the subtle interplay between different types of local Coulomb interactions within their 3$d$ electronic orbitals.

The Co$^{3+}$ analogue TlSr$_2$CoO$_5$ of non superconducting TlSr$_2$CuO$_5$ is a recent addition to this class of materials. It is of perovskite structure with a first order transition at $\approx 310$ K from a tetragonal and metallic phase with ferromagnetic Curie-like susceptibility at high temperature to an orthorhombic and insulating phase with two inequivalent kinds of Co ions at low temperature [3]. Below $T \approx 150$ K antiferromagnetic long range order sets in. Special interest in this new oxide is due to its quasi two dimensional (2D) character and, from the point of view of applications, it may be useful that the metal insulator transition in it occurs at room temperature.

In this paper we explain the 310 K metal insulator transition of TlSr$_2$CoO$_5$ in terms of an instability of its high temperature electronic structure. We show that the homogeneous ground state can lower its energy by breaking orbital degeneracy and by acquiring simultaneously both orbital and spin order.

Method of analysis

(i) Band structure calculation

We start with a density functional band structure calculation in the high-temperature phase using the local density approximation (LDA) for the exchange and correlation potential, see [4] for a review. Above the transition temperature of 310 K, the crystal structure is tetragonal with P4/mmm space group (see Fig. 1). As input parameters of the calculation, we used experimentally determined lattice parameters of $a = 0.375$ nm, $c = 0.877$ nm and relative strontium and apex oxygen (01) positions (that are not fixed by the space group) of $z = 0.2903$ and $z = 0.2330$, respectively [3]. We employed a recently developed full-potential nonorthogonal local-orbital (FPLO) minimum basis scheme [5] that imposes no shape restriction on the potential. The calculation was scalar-relativistic, with the spatial extent of the basis orbitals controlled by a confining potential of $(r/r_0)^4$ that was optimized with respect to the total energy. The thallium $\{5s, 5p, 5d, 6s, 6p\}$, strontium $\{4s, 4p, 5s, 5p, 5d\}$, cobalt $\{3s, 3p, 4s, 4p, 3d\}$ and oxygen $\{2s, 2p, 3d\}$ orbitals were treated as valence orbitals, while the lower lying orbitals were treated as core states. The inclusion of Tl $\{5s, 5p, 5d\}$, Sr $\{4s, 4p\}$ and Co $\{3s, 3p\}$ states in the valence states was necessary to account for
non-negligible core-core overlaps. The O 3d states were taken into account to increase the completeness of the basis set. The results of this LDA calculation will be discussed in detail further below.

(ii) Tight-binding Hartree-Fock calculation

To take into account the strong Coulomb interactions in the Co d shell more accurately we could have used the LDA + U approach described in detail in \[8\]. Instead, and in order to gain a more direct insight into the mechanism of the metal insulator transition at work, we included the Coulomb interactions in a minimal tight binding Hamiltonian of all cobalt 3d and oxygen 2p orbitals in the CoO$_2$ plane and used the results of the previously described LDA calculation to determine the hopping parameters of this model (see \[7\] for similar work). According to Koster-Slater type symmetry considerations \[8\], the overlap between d- and p-orbitals may be parametrized in terms of two parameters which we denote as $t_{eg}$ and $t_{t_{2g}}$, respectively. Due to the perovskite structure, there is no direct Co-Co hopping and we assume absence of direct O-O hopping. With these approximations, the transfer matrix elements for the planar Co-O bond in $x$-direction are as follows

$$
\begin{pmatrix}
    p_x^d & p_y^d & p_z^d \\
    d_x & t_{dp}(\vec{x}) & 0 \\
    d_y & 0 & 0 \\
    d_z & 0 & 0 \\
    d_{x^2-y^2} & 0 & 0 \\
\end{pmatrix}
$$

The superscript $\vec{x}$ for the $p$-orbitals indicates that they belong to the oxygen at $\frac{1}{2}a\vec{e}_x$, and the corresponding matrix for the Co-O bond in $y$-direction is obtained by formally interchanging $x \leftrightarrow y$ in the above table. The results of the band structure calculation determine also the Co d shell crystal-field parameters $\epsilon_i$, $i = \{xy, yz, zz, z^2, x^2-y^2\}$ and the on site energy $\epsilon_p$ of the oxygen $p$ orbitals (we neglect the splitting of the oxygen $p$ states due to tetragonal distortion). Tetragonal symmetry at the Co site leaves $\epsilon_{yz} = \epsilon_{zx}$ degenerate. The sum of on-site energies and of hopping amplitudes in the $x$- and $y$-directions defines the noninteracting part of a tight-binding model

$$
H = H_{tb} + H_{Coulomb}
$$

$$
H_{tb} = \sum_{i,j,R,R',s} t_{ij}(\vec{R} - \vec{R}') a^\dagger_{i,s}(\vec{R}) a_{j,s}(\vec{R}')
$$

where the orbital indices $i,j$ range from 1 to 11 ($1 \ldots 5$ are the Co 3d orbitals) and $s$ denotes the spin component. To complete the model, we add the local Coulomb energy at the Co sites as expressed in tight-binding orbitals

$$
H_{Coulomb} = \frac{1}{2} \sum_{i,j,k,l,s,s'} V_{ijkl} a^\dagger_{i,s} a_{j,s} a_{k,s'} a_{l,s'} \text{ with } V_{ijkl} = \langle ij | \frac{e^2}{| \vec{r} - \vec{r}' |} | kl \rangle
$$

To express the $V_{ijkl}$ coefficients we use the rotational symmetry of the Coulomb matrix $\tilde{V}_{ijkl}$ in terms of spherical harmonics $Y_{km}$ \[11\]

$$
\tilde{V}_{m_1m_2n_1n_2} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \int dr_1 dr_2 \frac{r_1^k}{r_2^{k+1}} R_{\ell_1}^2(r_1) R_{\ell_2}^2(r_2) \int d\Omega_1 Y_{2m_1}^* Y_{2n_1} Y_{km} \int d\Omega_2 Y_{2m_2}^* Y_{2n_2} Y_{km}^*
$$

$$
= 25 \sum_{k=0,2,4} (-1)^{m_1+n_2} F(k) \begin{pmatrix} 2 & 2 & k \\ 0 & 0 & 0 \\ -m_1 & 2 & m \end{pmatrix} \begin{pmatrix} 2 & 2 & k \\ 0 & 0 & 0 \\ -n_2 & 2 & m \end{pmatrix}
$$

$$
F^{(0)} = A + \frac{7}{5} C, \quad F^{(2)} = 49 B + 7 C, \quad F^{(4)} = \frac{441}{35} C
$$

and transform $\tilde{V}$ to $V$ in standard cubic orbitals given by

$$
\begin{pmatrix}
    d_{xy} \\
    d_{yz} \\
    d_{zx} \\
    d_{xz} \\
    d_{x^2-y^2}
\end{pmatrix} = \begin{pmatrix}
    \sqrt{2} & 0 & 0 & 0 & i \\
    0 & \sqrt{2} & 0 & 0 & 0 \\
    0 & 0 & \sqrt{2} & 0 & 0 \\
    0 & 0 & 0 & 1 & 0 \\
    \frac{1}{\sqrt{2}} & 0 & 0 & 0 & \frac{-1}{\sqrt{2}}
\end{pmatrix} \begin{pmatrix}
    Y_{2_{-2}} \\
    Y_{2_{-1}} \\
    Y_{2_{0}} \\
    Y_{2_{1}} \\
    Y_{2_{2}}
\end{pmatrix}
$$
In [1], \( R_d(r) \) is the radial part of the 3d wave function, \( \{ A, B, C \} \) are Racah parameters and we used formula C.16, p. 1057 of [11]. Please note that expression (3) is rotationally invariant and that all Coulomb interactions were included. Although we used the full expression for \( V_{ijkl} \) in our calculation, the Racah parameter \( B \) is rather small and when it is taken to be zero we find a much simpler expression (in the cubic basis)

\[
(V_{ijkl})_{B=0} = C(\delta_{ij} \delta_{kl} + \delta_{il} \delta_{jk}) + (A + C) \delta_{ik} \delta_{jl} \tag{6}
\]

Usually, one denotes the diagonal elements as \( U = V_{iii} = A + 3C \) and the Coulomb repulsion between different \( (i \neq j) \) orbitals \( V_{ijkl} = A + C \) is smaller. However, in our context, it is more convenient to express the Coulomb energy in terms of the total electronic charge \( N = \sum_i n_i \) and total electronic spin \( s^\text{tot} = \sum_i s_i \) per site:

\[
(H_{\text{Coulomb}})_{B=0} = C \sum_{ij} P_i^j P_j - C \sum_i s_i \cdot s_j + \frac{2A + C}{4} \sum_{ij} n_i n_j
\]

\[
\approx J_H \left[ D - (s^\text{tot})^2 \right] + u \frac{N^2}{2}
\]

with \( n_i = a_i^\dagger a_i + a_i^\dagger a_i \), \( P_i = a_i^\dagger a_i \) and \( D = \sum_i P_i^j P_i \),

with \( u = A + C/2 \), \( J_H = C \) and where \( \tilde{\cdot} \) indicates that terms that merely renormalize the chemical potential were ignored. In the last line we retained only the diagonal contribution of the pair hopping terms.

Treating the Coulomb interaction in an unrestricted HF approximation [13] that allows for all spin and charge conserving correlations gives the following renormalization of the on-site Hamilton matrix

\[
\Delta t_{ij} = \sum_{l,m} V_{ilmj} \sum_{s'} n_{lm}^{s'} - \sum_{l,m} V_{ilmj} n_{lm}^s
\]

where \( i,j \) denote the orbital indices of Co 3d and the density matrix

\[
n_{lm}^s = \frac{1}{N_k} \sum_{k,\alpha} \psi_m^{\alpha\bar{\alpha}}(\bar{k}) \psi_m^{\alpha} (\bar{k})
\]

is calculated from the normalized wave functions \( \psi_m^{\alpha\bar{\alpha}}(\bar{k}) \) with band index \( \alpha \) and momentum \( \bar{k} \) \( (N_k \text{ corresponds to the number of } k \text{ points}) \). The total energy is given by

\[
E = < H_{tb} > + < H_{\text{Coulomb}} >
\]

where

\[
< H_{tb} > = \frac{1}{N_k} \sum_{k,\alpha,s} \sum_{l,m} \psi_i^{\alpha\bar{\alpha}}(\bar{k}) t_{lm}(\bar{k}) \psi_m^{\alpha} (\bar{k})
\]

is the mean (unrenormalized) kinetic energy, and

\[
< H_{\text{Coulomb}} > = \frac{1}{2} \sum_{m_1,m_2,m_3,m_4,s,s'} V_{m_1m_2m_3m_4} n_{m_4m_2} n_{m_3m_1} - \frac{1}{2} \sum_{m_1,m_2,m_3,m_4,s} V_{m_1m_2m_3m_4} n_{m_4m_1} n_{m_3m_2}
\]

is the interaction energy.

**Results**

(i) Full-potential local-orbital method

We performed two band structure calculations, one spin symmetric (see Fig. 2) and the other one allowing for spin polarization (Fig. 3). Both solutions are metallic but the magnetic one is energetically preferred by 0.54 eV per formula unit. The density of states (DOS) shows a high degree of covalency such that part of the magnetic moment
(calculated with all the overlap contributions) sits on oxygen \(m_O = 0.2 \mu_B\) giving a total moment \(m = 2.1 \mu_B\) \((m_{Co} = 1.9 \mu_B)\). The corresponding occupation numbers are \(n_{Co} = 7.2\) and \(n_O = 5.1\).

The band structure of the nonmagnetic solution together with the DOS for an easier identification of the structures is shown in Fig. 4; the size of the dots included in the band structure in Fig. 4 symbolizes the relative cobalt 3d-weight in the band. Evidently, the five bands crossing the Fermi level have predominantly Co 3d character. They hybridize quite strongly with 2p bands of the in-plane O(2) located at about 4 to 6 eV binding energy. The 2p bands of the other oxygens O(1) and O(3) are nonbonding and located in between Co-3d and O(2)-2p. The Co-3d bands have only a small dispersion in z-direction (with the exception of Co 3d_{x^2-z^2}) confirming the 2D character of the compound under consideration. To determine the energetic order of the 3d orbitals we used the bands at the \(\Gamma\) point plus their predominant orbital character [4] and found, in increasing order: \(d_{xy}, d_{xz/yz}, d_{z^2}, d_{x^2-y^2}\). Due to tetragonal symmetry, there is exact degeneracy between the \(d_{zx}\) and the \(d_{yz}\) orbital in the LDA calculation.

The density of states of the ferromagnetic solution (Fig. 3) indicates a finite value for the majority spin part. From this we conclude that TlSr\(_2\)CoO\(_5\) is not a half-metal and that it may conduct electric current even in the spin disordered phase. An orbital analysis (that is not documented here) shows that for majority spin only \(3d_{x^2-y^2}\) is partly occupied, while all the remaining majority bands \((3d_{xy}, 3d_{xz/yz}, 3d_{z^2})\) are completely below the Fermi level. For minority spin, \(3d_{xy}, 3d_{xz/yz}\) and \(3d_{z^2}\) are partly filled, whereas \(3d_{x^2-y^2}\) is nearly empty. It is difficult to interpret such an itinerant ferromagnet in an ionic picture. But its magnetic moment \(m = 2s\mu_B > 2\mu_B\) indicates a state between intermediate \((s = 1)\) and high spin \((s = 2)\).

(ii) Tight-binding Hartree-Fock calculation

We used the nonmagnetic LDA solution of Fig. 4 to fix the parameters of the Hartree-Fock model (the magnetic solution contains the same information, except that the spin up and spin down bands are shifted against each other). By comparing the five relevant bands of the FPLO result (Fig. 4) with the nonmagnetic HF solution we estimated the crystal field parameters to be \((\text{in ev}): \varepsilon_{xy} = -1.0, \varepsilon_{xz/yz} = -0.5, \varepsilon_z = -0.2, \varepsilon_{x^2-y^2} = 0.5\). The bandwidth determines the transfer terms \(t_{xz} = 1.9\) and \(t_{d_{yz}} = 1.4\). The Racah parameters \(B\) and \(C\) are fixed to their ionic values for trivalent Co as determined by infrared spectroscopy \((B = 0.06, C = 0.46)\) [4], whereas \(A = 2\) was chosen as a typical value for Co. The choice of \(\epsilon_p\) depends on \(A\) due to the mean field shift of the 3d level and we used \(\epsilon_p = 11\) such that the position of the oxygen levels (visible as the lower part in Fig. 6) coincides with the O(2)-2p position in LDA. In fact, the position of the oxygen bands does not change very much for different Hartree-Fock solutions. The tight-binding bands resulting from these parameters are shown in Fig. 5 and agree reasonably well with the nonmagnetic LDA band structure of Fig. 4.

Concerning the values of the crystal field parameters, we note that due to tetragonal symmetry, there is exact degeneracy between the \(d_{zx}\) and \(d_{yz}\) orbitals in the LDA calculation. However, the values \(\varepsilon_{xy} = -1.0, \varepsilon_{xz/yz} = -0.5\) seem to violate "standard lore" [4], according to which the elongation of the octahedra in the \(z\) direction should shift \(d_{xy}\) to higher energies compared to \(d_{xy/yz}\). One should note, however, that the \(\varepsilon_i\) are approximately the energies at the \(\Gamma\) point whereas the "standard lore" is valid in the ionic picture and would correspond, in our case, to the center of gravity of the different bands. Due to the larger bandwidth of the "two dimensional" \(d_{xy}\) band in comparison with the "one dimensional" \(d_{xz/yz}\) bands the corresponding centers of gravity nearly coincide in Figs. 4 and 5. For the electronic structure of the metallic, ferromagnetic high temperature phase of TlSr\(_2\)CoO\(_5\) it is crucial that all three bands \(\{d_{xy}, d_{xz/yz}\}\) cross the Fermi level which is due to their widths being larger than their crystal field splittings, see Fig. 4. It remains an open question, however, how the difference in dimensionality and width among the \(\{d_{xy}, d_{xz/yz}\}\) bands affects the screening of the Coulomb interaction. This question was considered in detail [11] in the context of Sr\(_2\)RuO\(_4\), another layered perovskite.

We now discuss the magnetic solutions of the HF approach. The homogeneous ferromagnetic one (see Table 1) is metallic and 650 meV lower in energy than the nonmagnetic solution. The good agreement with the energy gain in LDA (540 meV) and similar occupation numbers in LDA and HF indicate that our parameter assignment is satisfactory. Allowing for different occupations of \(d_{zx}\) and \(d_{yz}\) in a chess board like pattern, we find a metastable state with orbital order that decays into a ground state with both orbital and spin order and which contains Co sites with two different configurations, \(m_B = 3.11 \mu_B\) (close to high spin) and \(m_A = 2.01 \mu_B\) (intermediate spin). The energy gain due to the combined orbital and spin order is 67 meV. The origin of the instability of the homogeneous ferromagnetic state is the orbital degeneracy of \(d_{zx}\) and \(d_{yz}\) and the near degeneracy of intermediate and high spin configurations. This instability occurs in a rather large parameter region near the values which were derived for TlSr\(_2\)CoO\(_5\). However, due to the large dimensionality of the parameter space of our HF model [2], we did not perform a systematic study. In Fig. 6 we give the spectral density of the ferromagnetic and of the two chess board like ordered states. As we can see, any kind of order leads to a decrease of spectral density at the Fermi level, but only the orbital- and spin-ordered
solution is insulating. That is also visible in the HF band structure (Fig. 7).

The chess board like superstructure found here does not correspond to the orthorhombic low-temperature phase seen experimentally with a 2:1 ratio of high spin and intermediate spin states [3]. We also investigated this experimental superstructure of the CoO$_2$ plane within the model Hartree-Fock approach but found no solution with lower energy than those with chess board order. The lattice degrees of freedom may have to be included into the model to obtain the correct pattern, because the nearest neighbor Co-O distance for high spin is probably larger than the corresponding distance for intermediate spin (as can be concluded from the analogy to the famous Invar alloys Fe$_2$Ni$_{1-x}$ [7]). The present investigation of the electron system alone can only indicate the instability of the high temperature phase but it is not able to predict the correct low-temperature crystal structure.

**Interpretation of results**

We now interpret the results of our LDA and HF calculations in terms of a simplified model. As a first step, we recall that there is only $d \leftrightarrow p$ hopping and neither direct $d \leftrightarrow d$ nor $p \leftrightarrow p$ hopping. This and the fact that only cobalt $d$ states are at the Fermi level allows us to extract an effective $d \leftrightarrow d$ hopping by eliminating the oxygen orbitals in standard fashion [18]

$$t_{dd}^{\text{eff}}(\vec{a}) = \varepsilon_{d\vec{d}d'} + \frac{t_{dp}(\vec{a})t_{dp}(-\vec{a})}{\Delta \varepsilon} = \varepsilon_{d\vec{d}d'} - \frac{t_{dp}(\vec{a})t_{dp}(-\vec{a})}{\Delta \varepsilon}$$

where $\vec{d} \epsilon \{\vec{x}, \vec{y}, -\vec{x}, -\vec{y}\}$ denotes the direction of hopping and $\Delta \varepsilon$ is the offset between the Co and oxygen bands. Actually, due to the high degree of $d \leftrightarrow p$ hybridization the second order expression (3) is certainly not sufficient to provide correct numbers for $t_{dd}^{\text{eff}}$ but nonetheless it should give the correct matrix structure. Just like the original hopping the effective $t_{dd}^{\text{eff}}$ is also anisotropic and orbitally dependent, with $d_{xz}$ and $d_{yz}$ electrons hopping in the $x$ respectively $y$ direction and forming one dimensional bands. Using the Coulomb energy of Eq. (7) this provides us with a simplified model that involves only $d$ orbitals:

$$H = \sum_{d,s,\vec{R}} \varepsilon_{d\vec{d}s}(\vec{R}) a_{d,s}(\vec{R}) + \sum_{d,d',s,\vec{R},\vec{R}'} t_{dd}^{\text{eff}}(\vec{R} - \vec{R}') a_{d,s}^\dagger(\vec{R}) a_{d',s}(\vec{R}') + \sum_{\vec{R}} j_H \left[ D_{\vec{R}} - \left( \varepsilon_{tot,\vec{R}} \right)^2 \right] + \frac{u}{2} N_R^2$$

where $j_H$ and $u$ are renormalized values of $J_H$ and $\tilde{U}$ due to the elimination of the oxygen orbitals. But the precise amount of renormalization is difficult to calculate and beyond the scope of the present discussion.

The above five band model must be simplified further to extract the relevant degrees of freedom. We first note that the crystal field parameters derived in the previous section are such that in the ionic case ($t_{dd}^{\text{eff}} = 0$) the three configurations of Fig. 8 are lowest in energy. We further highlight the orbitals closest to the Fermi level and which we believe to be itinerant by bold arrows. This suggests a minimal model with three itinerant electron species, namely $d_{xz-y^2}$ and the two degenerate minority spin bands $d_{xz}$ and $d_{yz}$. This physical picture is also supported by the ferromagnetic HF solution where only $d_{x^2-y^2}^\dagger$ is partly occupied among all the majority spin bands and the occupation of $d_{xz}^\dagger$ and $d_{yz}^\dagger$ in Table I is indeed small (the occupation of $d_{xy}^\dagger$, however, deviates quite strongly from unity). The low energy sector responsible of the metal insulator and spin transition should be the competition between

$$s = 1: \quad xy \uparrow \downarrow, \quad zx \uparrow \downarrow, \quad yz \uparrow \downarrow, \quad 3z^2 - r^2 \uparrow \text{ or } x \leftrightarrow y$$

$$s = 2: \quad xy \uparrow \downarrow, \quad zx \uparrow \downarrow, \quad yz \uparrow \downarrow, \quad 3z^2 - r^2 \uparrow, x^2 - y^2 \uparrow$$

In other words, $xy \uparrow \downarrow$ is only a spectator orbital while $\{zx \uparrow, \ yz \uparrow, \ 3z^2 - r^2 \uparrow\}$ provide a total spin of 3/2 and the exact degeneracy between $d_{zx}$ and $d_{yz}$ is kept as one of the driving mechanisms of the transition. The spin transition is then due to the competition between a down spin electron $zx \downarrow$ or $yz \downarrow$ and an up spin electron $x^2 - y^2 \uparrow$. Combining the spins of $\{zx \uparrow, \ yz \uparrow, \ 3z^2 - r^2 \uparrow\}$ into an effective spin 3/2 degree of freedom, we can represent this competition as follows:
\[ \{S^+_\uparrow, zx \downarrow\} \text{ or } \{S^+_\uparrow, yz \downarrow\} \Leftrightarrow \{S^+_\uparrow, x^2-y^2 \uparrow\} \] (12)

where we used Hund’s coupling to exclude misaligned spins. To describe these qualitative ideas more precisely, we propose the following model:

\[
H = \varepsilon \sum_{\mathbf{R},s} a^\dagger_{3,s}(\mathbf{R}) a_{3,s}(\mathbf{R}) - \sum_{\mathbf{R},\mathbf{R}',s,i=1}^{3} t_{ii}^{eff} (\mathbf{R} - \mathbf{R}') a^\dagger_{i,s}(\mathbf{R}) a_{i,s}(\mathbf{R}') - 2J_H \sum_{\mathbf{R}} \mathbf{S}_{\mathbf{R}} \cdot \mathbf{S}_{\mathbf{R}} \] (13)

where the orbitals are numbered as \{1, 2, 3\} \leftrightarrow \{zx, yz, x^2-y^2\} and \(t_{ii}^{eff}\) is an anisotropic and orbitally dependent hopping matrix. Model (13) is formulated in an extended phase space in comparison to (10) since \(|S^+_\uparrow, zx \uparrow\) and \(|S^+_\uparrow, yz \uparrow\) do not exist in the 5 band model. But those unphysical states are at a high energy due to Hund’s coupling \(j_H\). The origin of the antiferromagnetic exchange coupling \(j\) should be the virtual superexchange of the singly occupied states that were excluded from our model and the coupling \(\mathbf{S}_{\mathbf{R}} \cdot \mathbf{S}_{\mathbf{R}}\) makes sure that the spins of electrons in the orbitals \(i=1,2\) are antiparallel to the spin 3/2 vector and vice versa for \(i=3\). A detailed estimate of the model parameters in (13) is beyond the scope of the present paper, but it is clear that we have to consider the range of parameters \(u \gg j_H \gg \varepsilon, t, j\). The condition \(j_H \gg t\) suppresses virtual hopping processes for antiparallel nearest neighbor spins \(\mathbf{S}_{\mathbf{R}}\), whereas they remain possible for parallel spins. In the limit of \(j_H \gg \varepsilon, t\) the fermions are spin polarized, double occupation of the same orbital is automatically excluded by Fermi statistics and we therefore dropped the local double occupation D-term in equation (13). The above model still admits high energy processes (involving energy costs of \(u\) and \(j_H\)) that must be integrated out to obtain a true low energy model.

To argue for the minimal model (13) we compare some of the possible two site clusters in second order perturbation theory (Fig. 9) (for simplicity we use identical transfer amplitudes \(t\) and restrict ourselves to leading terms). We see that for a ferromagnetic spin arrangement there is a competition between an orbitally ordered state \(s=1\) (realized for \(\varepsilon > t^2/u\)) and a mixed orbital and spin ordered state (\(\varepsilon < t^2/u\)) which is also realized in the model HF approach. Next, we see from the mixed spin cluster in the figure that hopping processes are influenced by the relative spin orientation. In this cluster, there is a competition between ferromagnetic order favored by a gain in delocalization energy \(\sim \frac{t^2}{u} \frac{\varepsilon}{u}\) and antiferromagnetic order favored by a gain in magnetic energy \(\sim j\). The ferromagnetic delocalization energy is expected to dominate \(j\) and therefore neighboring high spin and intermediate spin states should order ferromagnetically (see 3) and it is easy to see that neighboring high spin states (\(s=2\)) have an antiferromagnetic exchange in our simplified model (13).

There is a similarity between the model we propose here and the Zener double exchange model, [19], except that our model has flipped spins for some of the orbitals to describe the spin transition and we also have a total of 3 species of electrons per site at \(j_H \gg t\). For sufficiently small values of \(u\) there will be, by analogy with the double exchange model, a ferromagnetic and metallic phase because charge transport is possible for parallel spin orientations, while for \(u \rightarrow \infty\) the system is insulating. So we expect a rich phase diagram of this reduced model as a function of its parameters \((\varepsilon, j_H, u, j)\) with phases of mixed magnetic and orbital or spin order and which may be metallic or insulating as a function of its parameters.

**Conclusions**

Using LDA band structure calculations for the high temperature tetragonal phase and a HF approach in a minimal model of the perovskite plane, we found states that are lower in energy than the homogeneous and ferromagnetic state. More specifically we found that the homogeneous state is unstable towards orbital order and spin state disproportionation. We propose this instability to be the driving mechanism of the metal to insulator transition. A dynamical spin disproportionation above the transition temperature would be compatible with Mössbauer data on \(^{57}\)Fe-doped TlSr\(_2\)CoO\(_4\) that suggest the existence of two inequivalent magnetic sites [2]. Based on our calculations, we also proposed a simplified model with only three states per site at \(j_H \gg t\) plus an extra spin of \(S = \frac{3}{2}\) and which we argue to have a rich phase diagram as a function of its model parameters.

**Acknowledgements**

We are indebted to J.-P. Doumerc for many helpful and inspiring discussions on his data, to A. Villesubanne for a comparison with his own band structure results and to D. Khomskii and M. Pouchard for useful criticism. H.
R. acknowledges funding by an individual grant of "Deutscher Akademischer Austauschdienst", T. P. and R.H. both acknowledge support as "Professeur Invité " and D.F. was supported by "Graduiertenkolleg Komplexität in Festkörpern", IFW Dresden and "Groupement de Recherche Oxydes Remarquables". CPTMB is "Equipe Associée au CNRS ERS 2120".

After this paper was completed we were kindly informed by C. Michel of an oxide synthesized at Caen [21] that contains \(\text{CoO}_2\) planes isostructural to the ones considered here.

[1] M. Imada, A. Fujimori, Y. Tokura, Rev. Mod. Phys.; Y. Tokura, N. Nagaosa, Science 288, 462 (2000); see also J.B. Goodenough, Magnetism and the Chemical Bond (Wiley & Sons, New York 1963), pp. 52.
[2] K.I. Kugel and D. I. Khomskii, Sov. Phys. JETP 37, 725 (1974); Sov. Phys. Usp. 25, 231 (1982).
[3] M. Coutanceau, Un Nouvel Oxyde Mixed de Cobalt, Thesis at the Univesity of Bordeaux, 1996; J.-P. Doumerc, J.-C. Grenier, P. Hagenmuller, M. Pouchard and A. Villessuzanne, J. of Solid State Chem. 147, 211 (1999); J.P. Doumerc, J.-C. Grenier, M. Coutanceau, A. Demourges, A. Villessuzanne, P. Dordor, M. Pouchard, VIth European Conference on Solid State Chemistry, Zuerich, 1997.
[4] W. Kohn, Nobel Prize Lecture, Rev. Mod. Phys. 71, 1253 (1999).
[5] K. Koepnik and H. Eschrig, Phys. Rev. B 59, 1743 (1999).
[6] V. I. Anisimov, F. Aryasetiawan, A. I. Lichtenstein, J. Phys. C, 767 (1977).
[7] T. Mizokawa and A. Fujimori, Phys. Rev. B54, 5368 (1996).
[8] A.P. Sutto, Electronic Structures of Material, Oxford University Press, 1993; J.C. Slater and G.F. Koster, Phys. Rev. 94, 1498 (1954). The Slater-Koster tables just express the invariant tensor character of the overlap amplitudes.
[9] S. Sugano, Y. Tanabe, H. Kamimura, Multiplets of Transition Metal Ions In Crystals, Academic Press, N. Y. 1970.
[10] B. H. Brandow, Adv.in Phys. 26, 651 (1977).
[11] A. Messiah, Quantum Mechanics, Vol II, John Wiley, N. Y. 1958.
[12] J. Hubbard, Proc. Roy. Soc. A276, 238 (1963); J. Kanamori, Prog. Theor. Phys. 30, 275 (1963).
[13] N. D. Mermin, Annals of Physics 21, 99 (1963)
[14] H. Rosner, R. Hayn and J. Schuleenburg, Phys. Rev. B 57, 13660 (1998).
[15] C.J. Ballhausen, Introduction to Ligand Field Theory, Mc-Graw-Hill, New York, 1962.
[16] A. Liebsch, A. Liechtenstein, Phys. Rev. Lett. 84, 1591 (2000).
[17] E.F. Wassermann, in Ferromagnetic Materials, edited by K.H.J. Buschow and E.P. Wohlfahrt (North-Holland, Amsterdam 1990), Vol. 5, p. 237.
[18] P. Fulde, Electron Correlations in Molecules and Solids, Springer Series in Solid State Sciences 100, Berlin 1991, p. 289.
[19] C. Zener, Phys. Rev. 82 (1951) 403; P. W. Anderson, and H. Hasegawa, Phys. Rev. 100, 675 (1955).
[20] J.-P. Doumerc, M. Coutanceau, L. Fournes, J.-C. Grenier, M. Pouchard, A. Wattiaux, C. R. Acad. Sci. Paris, t. 2, série II c, 637 (1999).
[21] A.C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, J. Hejtmanek, Phys. Rev. B 62, 166 (2000).
**Figure Captions**

Fig. 1: Crystal structure of the high temperature tetragonal phase.

Fig. 2: DOS of the nonmagnetic solution.

Fig. 3: DOS of the ferromagnetic state.

Fig. 4: Nonmagnetic LDA band structure. The relative cobalt 3d weight of the bands is symbolized via black dots in the bandstructure. For comparison we also included the DOS (see Fig. 2) at the right hand side of the band structure. The broad line at the Fermi level between X and M is comprised of 3 bands (d_{xy}, d_{zx}, and d_{z2}) which are nearly degenerate.

Fig. 5: Band structure of the nonmagnetic HF solution.

Fig. 6: Comparison of spectral weights for three magnetic HF solutions.

Fig. 7: HF band structure of the orbital- and spin-ordered solution.

Fig. 8: The lowest ionic configurations of Co^{3+} in TlSr_{2}CoO_{5}. Configurations a and b correspond to intermediate spin states and are degenerate (d_{\uparrow}^{1/2}x_{z}, d_{\uparrow}^{1/2}y_{z}) whereas c is a high spin state (d_{\uparrow}^{1/2}x_{z}^{2}−y_{z}^{2}). The bold arrows correspond to itinerant states, the remaining states are localized and are combined into an effective spin 3/2 (middle row). The right row introduces a notation.

Fig. 9: Perturbation theory for configurations of a two site cluster.

**Table I:** Occupation numbers of HF solutions.

| Solution             | Energy/meV | Occupation numbers | Magnetization/µ_{B} |  |
|----------------------|------------|--------------------|---------------------|---|
| Nonmagnetic          | 0          | \(n_{d}\) | 0.84 0.81 0.81 0.76 0.30 | 7.04 |
| Ferromagnetic        | -653       | \(n_{d}^{\uparrow}\) | 1.00 1.00 1.00 0.98 0.63 | 4.61 2.41 |
|          |             | \(n_{d}^{\downarrow}\) | 0.55 0.70 0.70 0.08 0.17 | 2.20 |
| Orbital order        | -674       | \(n_{d}^{1}\) | 1.00 1.00 1.00 0.98 0.67 | 4.65 2.52 |
| (quasistable)        |             | \(n_{d}^{2}\) | 0.69 0.89 0.29 0.09 0.17 | 2.13 |
| Spin and orbital order | -720       | \(n_{d}^{1}\) | 1.00 1.00 1.00 0.99 0.91 | 4.90 3.11 |
|                      |             | \(n_{d}^{2}\) | 0.90 0.90 0.31 0.09 0.18 | 2.38 |
|                      |             | \(n_{d}^{3}\) | 0.37 0.28 0.88 0.09 0.17 | 1.79 |
nonmagnetic TlSr$_2$CoO$_5$

DOS (states eV$^{-1}$ * cell$^{-1}$)

- total
- Co–3d
- O(2)–2p
- O(1)–2p
- O(3)–2p
ferromagnetic TlSr$_2$CoO$_5$

DOS (states * eV$^{-1}$ * cell$^{-1}$)

- total
- Co–3d
- O(2)–2p

energy (eV)
\( \text{TiSr}_2\text{CoO}_5 \)

Energy \( \varepsilon_n(k) \) [eV]

DOS (states \( \text{eV}^{-1} \cdot \text{cell}^{-1} \))

- Total
- Co-3d
- O(2)-2p
- O(1)-2p
- O(3)-2p

\( \Gamma \) \( X \) \( M \) \( \Gamma \) \( Z \) \( R \) \( A \)
nonmagnetic HF band structure
HF spectral density

- orbital and spin order
- orbital order
- ferromagnetic
orbital and spin order – HF band structure
\[ E = \frac{9}{4}J - t^2 / u \]
\[ E = \epsilon + \frac{9}{4}J - 2t^2 / u \]
\[ E = \epsilon - \frac{9}{4}J - 2t^2 / u + 2t^2 J_H / u^2 \]
\[ E = \frac{9}{4}J - t^2 / U + \epsilon \]
\[ E = -\frac{9}{4}J - t^2 / U + \epsilon \]