Mott-Hubbard criticality in paramagnetic CMR pyrochlores

L. Craco\(^1\), C. I. Ventura\(^2\), A. N. Yaresko\(^3\), and E. Müller-Hartmann\(^1\)

\(^1\)Institut für Theoretische Physik, Universität zu Köln, Zülpicher Straße 77, 50937 Köln, Germany
\(^2\)Centro Atómico Bariloche, 8400 - Bariloche, Argentina and
\(^3\)Max-Planck-Institut für Physik Komplexer Systeme, Nöthnitzer Straße 38, 01187 Dresden, Germany

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We present a correlated \textit{ab initio} description of the paramagnetic phase of Tl\(_2\)Mn\(_2\)O\(_7\), employing a combined local density approximation (LDA) with multiorbital dynamical mean field theory (DMFT) treatment. We show that the insulating state observed in this colossal magnetoresistance (CMR) pyrochlore is determined by strong Mn intra- and inter-orbital local electron-electron interactions. Hybridization effects are reinforced by the correlation-induced spectral weight transfer. Our result coincides with optical conductivity measurements, whose low energy features are remarkably accounted for by our theory. Based on this agreement, we study the disorder-driven insulator-metal transition of doped compounds, showing the proximity of Tl\(_2\)Mn\(_2\)O\(_7\) to quantum phase transitions, in agreement with recent measurements.

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Among the manganese oxides exhibiting colossal magnetoresistance (CMR)\(^1\), the family of pyrochlores represented by Tl\(_2\)Mn\(_2\)O\(_7\), and the related compounds prepared by substitution of its different components\(^2\),\(^3\),\(^4\) stands out. Though presenting similar coupling between magnetic and transport properties as the CMR perovskite manganites like La\(_{1-x}\)A\(_x\)MnO\(_3\) (A= Ca,Sr,Ba), in the last nine years experiments have established many differences of their electronic properties\(^2\), lattice behavior\(^2\),\(^3\),\(^4\), spin dynamics\(^8\), etc. In particular, transport and magnetism in CMR pyrochlores seem to be primarily related to different electronic orbitals\(^2\),\(^3\) coupled by hybridization. Mechanisms like double exchange, involving the transfer of electrons between neighbor Mn\(^{3+}\) – Mn\(^{4+}\) ions which favours ferromagnetic alignment of the Mn core spins\(^5\), and effects like Jahn-Teller distortions\(^10\) were early discarded for pyrochlore compounds. A series of alternative theoretical proposals were put forward and explored in connection with the experimental results\(^11\),\(^12\),\(^13\),\(^14\). The first microscopic model studied for Tl\(_2\)Mn\(_2\)O\(_7\) was the intermediate valence model (IVM)\(^11\), proposed to explore the suggestion\(^2\) of the presence of a small effective internal doping of the type \(T\)\(_2\)\(^{3+}\)\(_2\)\(^{2+}\)\(_2\)\(^{5+}\)\(_2\)O\(_7\) (\(x\sim 0.005\)).

The presence of spin-dependent hybridization gaps (or pseudogaps), and the predicted temperature and magnetic field dependent changes of the electronic structure allowed description of the observed magnetotransport\(^11\). In particular, the predicted evolution towards a gapped paramagnetic state above \(T_c\) explained the drastic reduction of the number of carriers at \(T_c\) in Hall data\(^2\),\(^4\). Recently, thermopower and optical conductivity were qualitatively described using the IVM\(^14\). Majumdar and Littlewood\(^12\) explored the scenario of spin fluctuations around \(T_c\) in the presence of very low carrier densities, first suggested in Refs.\(^1\),\(^2\). Considering Hund and superexchange couplings\(^12\), they explained CMR in terms of spin polarons. Later, a generic effective model for Tl\(_2\)Mn\(_2\)O\(_7\)\(^15\) was introduced to explore and compare various proposals\(^2\),\(^4\),\(^12\),\(^13\),\(^14\),\(^10\). Interestingly, its electronic structure was shown\(^13\) to exhibit similar features to the IVM model\(^11\), for appropriate parameters, and the experimental spin dynamics\(^8\) is described\(^17\) if ferromagnetic superexchange is assumed\(^10\).

Tl\(_2\)Mn\(_2\)O\(_7\) is cubic at room temperature, with an \(Fd\bar{3}m\) arrangement of corner-sharing Mn-O6 octahedra\(^2\),\(^4\). Its large magnetoresistance accompanies a ferromagnetic metal to paramagnetic insulator transition, with \(T_c\) around 130 K\(^2\),\(^4\),\(^12\). The magnetization below \(T_c\) is believed to be determined by ferromagnetic superexchange coupling in the Mn\(^{4+}\) sublattice\(^4\),\(^10\). Hall data indicate a very small electron-like carrier density\(^2\)\((\sim 0.001-0.005 e/\text{f.u.})\), connected with the presence of extended Ti\(_{6s}\) orbitals hybridizing with O-2p and Mn-\(t_{2g}\) states near the Fermi level\(^13\),\(^14\),\(^19\). Upon Bi-substitution on the Ti site, magnetoresistance increases drastically and transport above \(T_c\) is strongly modified\(^13\). Notably, CMR is achieved at room temperatures, indicating the possibility of technological applications of Tl\(_2-x\)Bi\(_x\)Mn\(_2\)O\(_7\) and related compounds.

The electronic band structure of Tl\(_2\)Mn\(_2\)O\(_7\) has been calculated in local density approximation (LDA) by various groups\(^12\),\(^13\),\(^14\). They obtained similar results for the ferromagnetic metallic ground state, characterizing it as a half-metal with minority-spin free-electron-like carriers. However, no attention has been payed to the paramagnetic (PM) phase. In this work, we are presenting the first \textit{ab initio} study of the paramagnetic phase of Tl\(_2\)Mn\(_2\)O\(_7\). We found that LDA calculations predict a metallic paramagnetic state, in contrast to recent optical conductivity\(^20\) and photoemission\(^21\) experiments clarifying its insulating nature. By including multiorbital correlations through a combination of LDA with dynamical field theory (DMFT), we characterize the paramagnetic phase as a Mott-Hubbard insulator, with a
correlation-induced gap. We calculated optical conductivity contributions, and discuss our results in the context of recent experiments \[19, 20\] and effective model calculations \[11\]. Finally, we focus on the insulator-metal transition induced by chemical substitution.

LDA band structure calculations were performed for the experimental crystal structure of Tl\(_2\)Mn\(_2\)O\(_7\) \[14\] using the LMTO method \[22\] in the atomic sphere approximation. The overlap of atomic spheres was decreased by adding two sets of empty spheres in 8\(\alpha\) and 32\(\epsilon\) Wyckoff positions of the \(Fd\bar{3}m\) space group. Our ferromagnetic phase results (not shown) agree with previous ones \[10, 15\], while the electronic structure obtained for the paramagnetic phase is shown in Fig.\(\text{I}\). The differentiated hybridization between Tl and Mn with the two kinds of O atoms present is evident. Clearly, a metallic paramagnetic state is predicted by LDA, in contradiction with the insulating behavior recently established experimentally \[20, 21\].

Let us briefly outline the scheme of electronic structure calculation used. To include the real band structure and reliably treat the effect of correlations in the PM phase, as well as study metal-insulator transitions, we adopted the combined LDA+DMFT approach, which is becoming widely recognized as suitable for the realistic description of transition metal oxides. Previous similar applications of the technique include, e.g., the study of the insulator-metal transition in V\(_2\)O\(_3\) and the ferromagnetic metallic state of CrO\(_2\) \[23\]. The multi-orbital many-body Hamiltonian considered for the LDA+DMFT study of Tl\(_2\)Mn\(_2\)O\(_7\) is:

\[
H = \sum_{kao\beta \sigma} (e_{koa} + e_\alpha^0 \delta_{\alpha\beta}) c_{kao\sigma}^\dagger c_{kao\sigma} + U \sum_{ia} n_{ia\uparrow} n_{ia\downarrow} + U' \sum_{i\alpha \neq \beta} n_{ia\alpha} n_{ia\beta} - J_H \sum_{i\alpha \neq \beta} S_{ia\alpha} S_{ia\beta},
\] (1)

where \(\alpha, \beta\) denote the three \(t_{2g}\) orbitals. Due to the pyrochlore crystal field, the \(t_{2g}\) sub-shell is split into an \(a_1g\) singlet and an \(e_g\) doublet. The size of the splitting \(\Delta = \delta_{e_g} - \delta_{a_1g}\) (\(\delta_\alpha\) being the center of gravity (c.g.) of the \(\alpha\) band) within LDA is: \(\Delta_{\text{LDA}} = 0.037\) eV. To avoid double-counting of interactions included already in the LDA in average, \(e_\alpha^0\) reads:

\[
e_\alpha^0 = e_\alpha - U(n_{a\alpha} - \frac{1}{2}) + \frac{J_H}{2} \sigma(n_{a\alpha} - 1),
\]

with \(e_\alpha\) being the on-site energies of the \(t_{2g}\) orbitals. The first term in Eq. (1) describes the Hund’s rule coupling: being \(J_H\) poorly screened, we take it of the order of its atomic value in \(\text{Mn}^{4+}\), \(J_H = 1\) eV. Rotational invariance fixes:

\[
U' = U - 2J_H.
\]

We solve Eq. (1) in \(d = \infty\) using multi-orbital iterated perturbation theory (MO-IPT) \[24\]. Assuming no symmetry breaking in the spin/orbital sector, we have \(G_{\alpha\beta\sigma\sigma'}(\omega) = \delta_{\alpha\beta} \delta_{\sigma\sigma'} G_{\alpha\sigma}(\omega)\) and \(\Sigma_{\alpha\beta\sigma\sigma'}(\omega) = \delta_{\alpha\beta} \delta_{\sigma\sigma'} \Sigma_{\alpha\sigma}(\omega)\). The DMFT solution involves (i) replacing the lattice model by a self-consistently embedded multi-orbital, asymmetric Anderson impurity model, and, (ii) a selfconsistency condition requiring the local impurity Green’s function (GF) to be equal to the local GF for the lattice. The calculation follows the philosophy of the one-orbital IPT, with the Green functions and self-energies being matrices in the orbital indices. The equations for the multi-orbital case are the same as used before \[23\]. They are solved selfconsistently with the LDA density of states as input, until convergence is achieved.

We now present our LDA+DMFT results. In Fig.\(\text{I}\) we plot the \(t_{2g}\) density of states of the Mn-ions. Using \(U = 7\) eV and \(U' = 5\) eV as intra- and interorbital corre-

![FIG. 1: (Color online) LDA band structure for paramagnetic Tl\(_2\)Mn\(_2\)O\(_7\). O\(_1\) (O\(_2\)) denotes Oxygen ions nearest to Mn (Tl).](image-url)
lution values, we obtain a clear Mott-Hubbard insulating state with an energy gap at the Fermi level. Compared to the LDA results of Fig. 2, optical response has been transferred to the Hubbard satellites close to maxima of the Tl and O bands, therefore reinforcing hybridization effects. Thus, one may envisage an overall gapped (insulating) state resulting from rehybridization, in a scenario with common features to those predicted by the effective IVM for paramagnetic Tl$_2$Mn$_2$O$_7$ [11]. Recent photoemission experiments at room temperature [21] confirmed the insulating nature of the paramagnetic phase. Finding a higher weight for O-2p to Mn-3d bands, out of the scope of the present work.

We have employed our LDA+DMFT result for $U = 7$ eV to evaluate the $t_{2g}$ contribution to the optical conductivity in the paramagnetic phase. Here, we consider only the $t_{2g}$ intraband optical transitions: due to orthogonality of these orbitals, one would expect negligible contributions from interband transitions [22]. Within the $t_{2g}$-subshell the contributions to optical conductivity are calculated from:

$$\sigma(\omega) \propto \sum_{\alpha k} \int d\omega' A_{\alpha k}(\omega') A_{\alpha k}(\omega' + \omega) \left( \frac{f(\omega') - f(\omega + \omega')}{\omega} \right)$$

where $f(\omega)$ is the Fermi function and $A_{\alpha k}(\omega)$ = $\frac{1}{\pi} \text{Im}[\omega - \Sigma_{\alpha}(\omega) - \epsilon_{\alpha k}]^{-1}$ is the spectral density.

In Fig. 3 we show the calculated optical conductivity together with the experimental data at room temperature [20]. Apart from phonon related peaks (not included in our theory), a remarkable agreement is found at low energies (below 0.8 eV). The absence of optical response observed at very low energies evidences the insulating nature of the paramagnetic phase. For higher energies, a quantitative description of experiments would require to include the effect of inter-band charge-transfer excitations, from O-2p to Mn-3d bands, out of the scope of the present work.

Motivated by the remarkable agreement between our theory and the optical spectra, we now address the effect of disorder induced by chemical substitution [8]. The problem is treated within the LDA+DMFT(IPT+CPA) [26] approach, which treats disorder exactly in high-dimensions and has been used to describe the doping-driven insulator-metal transition in LaTiO$_3$. However, differently from Ref. [20] here we consider only the effect of substitutional disorder: without the introduction of extra holes or electrons in the system. [Notice that in a binary-alloy distribution for disorder (CPA), a fraction $x$ of the sites have an additional local potential $v$ for an electron (or hole) hopping onto that site.] By this, we aim to account for a host of experimental realizations in the limit of small impurity con-
centrations. Having in mind the possibility of technological applications upon Bi-substitution, in our calculation we use a disorder potential $v = 2.5$ eV, corresponding to the energy difference between the Ti-6$s$ band and the Bi-6$p$ band. Fig. 4 shows that introduction of a small amount of impurities metallizes the system, in agreement with. Due to the pyrochlore structure, the Mott-Hubbard insulating state seems to be very unstable, allowing for first-order insulator-metal transitions upon small perturbations. According to our results, disorder or chemical pressure may drive $\text{Tl}_2\text{Mn}_2\text{O}_7$ into a bad metal fixed point, similar to that obtained for $U = 6$ eV (Fig. 2).

To conclude, we have presented the first \textit{ab initio} study of the paramagnetic phase of $\text{Tl}_2\text{Mn}_2\text{O}_7$. Through the inclusion of local multiorbital Coulomb interactions and using a combined LDA+DMFT approach, we describe the insulating nature of this phase. Hybridization effects are reinforced by the spectral weight transfer due to strong correlations. The electronic structure obtained with $U = 7$ eV allows us to provide not only a consistent description of the low-energy optical conductivity data, but also a strong support for our picture of disorder effects induced by chemical substitution. In agreement with chemical doping studies and recent photoemission findings, our results indicate that $\text{Tl}_2\text{Mn}_2\text{O}_7$ is very near to quantum phase instabilities, and illustrate the interplay of strong multi-orbital correlations with disorder and pyrochlore structure effects, thus calling for investigation with higher resolution spectroscopies, including inverse photoemission.

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[1] H. Kuwahara and Y. Tokura, in \textit{Colossal magnetoresistance, charge ordering and related properties of manganese oxides}, ed. by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1998).
[2] Y. Shimakawa, Y. Kubo, and T. Manako, Nature 379, 55(1996).
[3] S. W. Cheong et al., Solid State Commun. 98, 163 (1996).
[4] M. A. Subramanian et al., Science 273, 81 (1996).
[5] A. P. Ramirez and M. A. Subramanian, Science 277, 546 (1997).
[6] J. A. Alonso et al., M. T. Fernández-Díaz, Phys. Rev. Lett. 82, 189 (1999).
[7] Y. Shimakawa et al., Phys. Rev. B 55, 6399 (1997); see also G. H. Kwei et al., Phys. Rev. B 55, R688 (1997).
[8] J. W. Lynn, L. Vasilii-Doloc and M. A. Subramanian, Phys. Rev. Lett. 80, 4582(1998).
[9] C. Zener, Phys. Rev. 82, 403 (1951); P. W. Anderson and H. Hasogawa, Science, 100, 675 (1955); P. G. de Gennes, \textit{ibid.}, 181, 141 (1966).
[10] A. J. Millis, P. B. Littlewood and B. I. Shraiman, Phys. Rev. Lett. 74, 5144 (1995); A. J. Millis, B. I. Shraiman, and R. Mueller, \textit{ibid.} 77, 175 (1996).
[11] C. I. Ventura and B. Alascio, Phys. Rev. B 56, 14533 (1997).
[12] P. Majumdar and P. B. Littlewood, Phys. Rev. Lett. 81, 1314 (1998).
[13] C. I. Ventura and M. A. Gusmão, Phys. Rev. B 65, 14422 (2002).
[14] M. E. Foglio and G. E. Barberis, J. Mag. Mag. Mats. 272-276, 280 (2004); Physica B 354, 35 (2004); Phys. Rev. B accepted preprint (2005).
[15] S. K. Mishra and S. Satpathy, Phys. Rev. B 58, 7585 (1998).
[16] M. D. Núñez-Regueiro and C. Lacroix, Phys. Rev. B 63, 14417 (2001).
[17] C. I. Ventura and M. Acquarone, Phys. Rev. B 70, 184409 (2004).
[18] D. J. Singh, Phys. Rev. B 55, 313 (1997).
[19] Y. Shimakawa et al., Phys. Rev. B 59, 1249 (1999).
[20] H. Okamura et al., Phys. Rev. B 64, 180409 (2001).
[21] J. Sánchez-Benítez et al., Applied Phys. Lett. 84, 4209 (2004).
[22] O. K. Andersen, Phys. Rev. B 12, 3060 (1975).
[23] L. Craco, M. S. Laad and E. Müller Hartmann, Phys. Rev. Lett. 90, 237203 (2003); M. S. Laad, L. Craco and E. Müller Hartmann, Phys. Rev. Lett. 91, 156402 (2003).
[24] K. Held and D. Vollhardt, Eur. Phys. J. B 5, 473 (1998).
[25] E. Pavarini et al., cond-mat/0504034.
[26] L. Craco et al., Phys. Rev. B 70, 195116 (2004).
[27] J. Park et al., Phys. Rev. B 69, 165120 (2004).
[28] P. Velasco et al., J. Mag. Mag. Mats. 242, 725 (2002); P. Velasco et al., Phys. Rev. B 67, 104403 (2003).