Optical and magneto-optical response of half-metallic manganites

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Abstract. Motivated by the recent optical and magneto-optical measurements on half-metallic ferromagnetic three-dimensional manganites, we combine a tight-binding fit of the one-particle bandstructure with the dynamical mean-field theory, which treats the dynamical orbital correlations and the combination of Jahn–Teller and doping-induced disorder on the same footing. We show how all of the above effects are necessary to obtain good semiquantitative agreement with experimental features. As applications, we show how modest external magnetic fields drive drastic changes in the (B_{1g}) electronic Raman scattering lineshape, optical and magneto-optical spectra, demonstrating the colossal magnetoconductivity reported earlier. Good semiquantitative agreement with published experimental work is found, providing strong evidence for dynamical multi-orbital electronic correlations even in the well-doped half-metallic ferromagnetic state in CMR manganites.
1. Introduction

In view of its potential applications, the phenomenon of colossal magnetoresistance (CMR) has attracted renewed attention in the past few years. The sensitivity of transport, optical, and responses to small magnetic fields promises to open up new, attractive applications in new devices [1]. Theoretically, a fascinating aspect of CMR materials is the intimate connection between orbital/lattice/spin correlations and the charge dynamics as a function of hole doping ($x$ in $A_{1-x}B_xMnO_3$ in cubic perovskite manganites). A wide plethora of experiments [1] manifest this remarkable connection in very clear ways. Given that the CMR effect results upon doping the correlated orbital and spin ordered insulator (G-type orbital order (OO), A-type AF spin order), a consistent description of the CMR demands a unified treatment of real bandstructure features along with strong local, multi-orbital correlations and disorder on an equal footing. This is very complicated even for early transition metal oxides [2], and numerically very expensive for such systems.

The importance of strong orbital correlations along with Jahn–Teller (JT) distortions and doping-induced chemical disorder in conjunction with double-exchange (DE) have by now been demonstrated to be essential ingredients of a consistent theory for CMR [3]. To simplify matters without losing realistic features, we choose the tight-binding (TB) fit to model the actual bandstructure, keeping the electronically active states intact, an attractive option in the present complicated situation. This is a strategy that has been used with success for the case of cuprates [4].

In this work, we use this strategy to study the field-dependent optical, Raman and magnetooptical response (FDMOR) of the well-doped ($x = 0.3$) perovskite manganites. Our main motivation comes from recent studies [5] reporting large changes in optical conductivity and infrared (IR) light transmission near the Curie temperature in modest external magnetic fields. For a well-doped ($La_{0.67}Ca_{0.33}MnO_3$) ferromagnetic sample, a 1000-fold decrease in light transmission on crossing $T_{FM}^c = 270\,\text{K}$ is found. Similar large changes are found in a magnetic field. In addition, the authors of [5] also studied the linear transverse Kerr effect (TKE) as a function of $T$ and found interesting correlation of the TKE with the magnetization. We also compute the electronic Raman scattering lineshape, pointing out its possible relevance to an investigation of the role of orbital correlations in the CMR materials. These findings are of
potential interest for the use of doped manganites for optoelectronic devices controlled by magnetic or thermal fields [5].

We concentrate on the well-doped, half-metallic ferromagnetic phase of the CMR manganites in what follows, and show explicitly how these fascinating observations can be semiquantitatively understood within a proper theoretical framework. The idea is to combine the TB-fit of the actual one-electron (LAPW) bandstructure with dynamical mean-field theory (DMFT) to treat the dynamical effects of local, multi-orbital correlations along with additional strong scattering due to combined JT and doping-induced chemical disorder in a self-consistent way. We show how all the above effects are indeed crucial to obtain a consistent picture of the optical and magneto-optical response and explicitly demonstrate the large sensitivity of these quantities to modest external fields.

2. Experimental review

In this section, we briefly review the key experiments carried out on the CMR manganites. We focus on the well-doped FM state found in the CMR region, around \( x = 0.3 \) in La\(_{0.7}X_{0.3}\)MnO\(_3\) with \( X = \text{Ca}, \text{Sr} \), in order to pinpoint the ingredients necessary for a consistent theoretical modelling of this state. Obviously, we require that such an endeavour be consistent with the known proximity of the FM phase to orbital-ordered (OO)/magnetically ordered (AF/F) phases in the global \( T_c \) versus \( x \) phase diagram. See, for example, [1] and references therein.

Undoped LaMnO\(_3\) is a (G-type) OO/AF (A-type) ordered, correlated insulator with a large gap of \( O(2 \text{ eV}) \) to charge excitations. It is important to notice that given an LDA bandwidth of \( O(4.30 \text{ eV}) \) for \( e_g \) orbitals, the estimated value of the JT distortion (0.5–0.7 eV) is insufficient to open up such a large gap (even introducing staggered AF-OO by hand), and is a persuasive argument for inclusion of strong electronic correlations. A good theoretical estimate gives \( U = 7.0 \text{ eV}, J_H = 0.7 \text{ eV}, U' \simeq (U - 2J_H) = 5.6 \text{ eV} \) along with \( t_{dd\sigma} = 0.41 \text{ eV} \) and \( \Delta_{ct} = 5.5 \text{ eV} \). Of course, the JT distortion lifts the \( e_g \) degeneracy at the outset, and, given AF-OO, is a relevant quantity (it acts like an effective ‘magnetic’ field in the \( e_g \) sector. This gives the intersite superexchange \( J \simeq 23 \text{ meV} \), giving reasonable values for \( T_N \) [6].

Hole-doping this charge transfer insulator leads to a transition to a different kind of OO/FO insulator. That this state is not very easy to characterize is evidenced, for example, by the fact that an external magnetic field stabilizes the OO, in contrast to expectations from simple double exchange (even with JT coupling), where \( H_{cd} \) would increase the carrier hopping, weakening the OO state [7]. It should be emphasized that doping creates (Mn\(^{4+}\)) JT-inactive vacancies in the AF-OO matrix of pure LaMnO\(_3\), distorting neighbouring MnO\(_6\) octahedra, and leading to formation of orbital (JT) polarons, which can still produce more complicated OO patterns, as evidently observed [8]. In the strong coupling picture, the size of this polaron is expected to be \( O(2 - 3d_{\text{Mn-Mn}}) \), about 10 Å. Another effect of hole doping is to create local impurity potential (this can be large, see [9] for example). Both effects need to be accounted for in practice.

Further increase in \( x \) leads to an insulator–metal (I–M) transition accompanied by loss of this AF-OO. It is in this regime, around \( x = 0.3 \), that the CMR effect is observed, with its spectacular responses to various external perturbations (\( H_{ext} \), laser radiation [10], strain [11], etc).

(i) Volume thermal expansion, small-angle neutron scattering (SANS) and magnetic susceptibility studies show compelling evidence of localized magnetic clusters of size 12 Å above \( T_c \) [12]. It is plausible that at doping level of \( x = 0.3 \), the orbital (JT) polarons form...
an orbitally disordered network, and it is interesting that their size is very close to that of
the FM clusters above $T_c$. It is remarkable that the anomalous volume change exactly tracks
the magnetic SANS intensity, also in $H_{\text{ext}}$, and that these changes correlate with the CMR
in a way that forces one to conclude that the CMR effect is driven by the $T$-dependence of
these short-range magnetic/orbital/JT clusters and their modification by applied magnetic
fields.

(ii) Photoemission measurements [13] reveal characteristic strong correlation signatures.
Firstly, large $T$-induced spectral weight transfers, from high to low energy over a scale
of 3.0 eV, are clearly seen upon decreasing $T$. In the FM regime at low-$T$, clear signatures
of quasicoherent response is seen (given the amount of JT + doping induced disorder, it
should be no surprise that the quasicoherent peak seems to be washed out, although some
semblance of a Fermi edge can still be seen). Furthermore, the fact that $I_{\text{PE}}(\omega) \simeq |\omega|^\alpha$
with $\alpha = 0.7–1$ seen in the region $-0.5 \text{ eV} \leq \omega \leq -0.05 \text{ eV}$ for the PI phase at $x = 0.4$ is
a strong evidence for the relevance of static disorder effects in a correlated environment.

(iii) Optical conductivity studies reinforce these conclusions [14]. Firstly, measurements done
on properly cleaned samples do show that a quarter of the optical weight at low $T$ resides
in the quasicoherent Drude part, the remainder being distributed among an incoherent mid-
IR hump and high-energy continuum. The effective carrier mass estimated from optics is
$m^*/m_b \simeq 3–4$, close to that extracted from the low-$T$ specific heat, suggesting that charge
ordering correlations are not relevant deep in the FM phase. Finally, the integrated optical
weight scales with the magnetization as $\int_0^\infty \sigma_{xx}(\omega, M) \simeq (1 + M^2)$, characteristic of a DE
scenario (large $J_H$, which also means even larger $U', U$, even in the FM state).

(iv) Hall effect measurements reveal a large Fermi surface [15], consistent with up-to-date
electronic structure calculations. However, taken with (ii) + (iii) above, it is clear that
these bandstructure calculations need to be extended to treat dynamical effects of strong
correlations.

(v) Finally, recent transverse Kerr effect (TKE) measurements [5] show distinct features that
are consistent with (i)–(iii) above.

3. Effective Hamiltonian

In a completely ab initio formulation for realistic correlated systems, one proceeds as follows:

(i) The one-electron density-of states (DOS) in the actual crystal structure is computed from
the state-of-the-art bandstructure calculations. For the CMR problem, an extensive amount
of work has already been done along these lines. A particularly clear and illuminating
calculation is the LAPW work of Pickett and Singh [16].

(ii) Using constrained LDA, the parameters $U, U'$ (defined below) are computed within a
procedure where dynamical screening (due to itinerance) causes an appreciable reduction
of these parameters from their free atomic values. This is still an approximation, because,
in the real correlated system, the processes leading to dynamical screening (resulting from
highly correlated, rather than free carriers) are themselves modified in unknown ways by
correlation effects. This constitutes an unsolved theoretical problem at present. In general, its
is accepted that this may lead to up to 20% uncertainty in the estimation of these quantities. The atomic Hund’s rule coupling, $J_H$, is, however, not modified by such effects.

(iii) Using the parameters $U$, $U'$ and $J_H$, a full multi-orbital DMFT calculation is performed using the LDA DOS as input into the DMFT scheme [2]. Various methods have been developed to ‘solve’ the multi-orbital impurity model of DMFT. These are denoted by LDA + DMFT($X$), where $X = $ IPT, QMC. Other techniques like numerical renormalization group (NRG) are more (numerically) exact, but have not been amenable to application for real systems due to their technical complexity and prohibitive numerical cost. Quantum Monte Carlo (QMC) is almost (numerically) exact, but suffers from the minus-sign problem for fermionic models (for cases of interest in TMO-based materials, this means that such calculations cannot access temperatures below $T \simeq 400$ K, precluding detailed analyses of precisely the region where interesting physics occurs. Furthermore, extraction of the dynamical self-energy is clearly problematic within QMC. Finally, the iterated perturbation theory (IPT) has also been used in this context: in contrast to QMC, it is not numerically exact, but has been shown to reproduce spectral functions in very good quantitative agreement with exact diagonalization (ED) studies for the one- and two-orbital Hubbard models. The details of the phase diagram computed using IPT are in qualitative agreement with NRG and DMRG [17], although there are quantitative differences between the two. In view of this, a judicious choice of $X$, suitable for the aspects of a given problem under consideration, is called for.

(iv) An additional complication in real TMO-based systems of interest comes from intrinsic (‘melted’ JT) and/or extrinsic (doping related chemical) disorder in the strongly correlated situation. In contrast to weakly disordered cases, perturbative calculations incorporating disorder effects are inadequate. This is because in the limit where the coherent bandwidth is strongly renormalized downwards by dynamical correlations, one is effectively in the strong disorder regime, requiring truly a non-perturbative analysis via the coherent-potential approximation (CPA) [18] which needs to be self-consistently combined with LDA + DMFT($X$).

(v) Solution of the full LDA + (DMFT($X$) + CPA) [19] equations yields the partial DOS for each orbital, and spin (for magnetically ordered states). In $d = \infty$, this is sufficient to compute the optical conductivity, a program which is however quite non-trivial and has been carried out only for the 3d$^1$ system La$_{1-x}$Sr$_x$TiO$_3$ [20]. Calculation of the magneto-optic response for transition-metal oxides is much harder within LDA + DMFT, and has not been attempted to date.

The procedure (i)–(v) constitutes an ambitious theoretical program, and to date has been implemented only for early transition-metal oxides like [21] as well as for elemental ferromagnets Fe and Ni [22] in addition to certain f-electron systems like Ce and Pu [23]. In all these cases, good semiquantitative agreement with certain key experimental results has been demonstrated. For oxides of the late-TM series, however, this is a truly formidable enterprise, since the O 2p bands cannot be projected out (via downfolding the full LDA spectrum) in this case. Additional features such as the charge transfer energy, p–d hybridization, coulomb repulsion on O as well as the Madelung energy ($U_{pd}$) need to be included consistently along with the 3d states. We are still quite far from being able to accomplish such a complex task.

In addition, consideration of symmetry-breaking in the orbital/spin sector leads to further technical complexities, and is a completely open problem even for the early TMO systems.
As remarked in the introduction, we choose a simpler way out of this complicated situation by performing a detailed tight-binding fit to the actual LAPW bandstructure without losing any of the essential aspects of the problem under study. Such a choice leads to various advantages: these will become clear in due course.

We start by noticing that in the LAPW [16] calculation, the majority $e_g$ bands, providing the conduction states, split from the $t_{2g}$ bands, but overlap with the O p bands. However, the two $e_g$ bands are clearly identified along the symmetry directions, making a mapping to an effective two-band model possible. Constructing Mn-centred Wannier functions with strong O-p $\sigma$ character, only the $dd\sigma = t_\sigma$ and $dd\delta = t_\pi$ overlaps are nonzero. Using Slater–Koster tables for the cubic perovskite structure, the $e_g$ bands are $\epsilon_k^\pm = \epsilon_k \pm D_k$, where $\epsilon_k = (t_\sigma - t_\delta)(c_x + c_y + c_z)$ (note that $t_\sigma \neq t_\delta$),

$$D_k = -(t_\sigma - t_\delta)\sqrt{c_x^2 + c_y^2 + c_z^2 - c_xc_y - c_xc_z - c_yc_z}$$

and $c_\alpha \equiv \cos(k_\alpha a)$. The half $e_g$ bandwidth is $D = 3(t_\sigma + t_\delta)$. To fix the parameters above, notice that the dispersion along $\Gamma - X$ equals $4t_\delta$. Since the overlap of the majority $e_g$ bands with the O 2p bands is omitted in the two-band fit, one uses the average value of the $\Gamma - X$ dispersion, giving $4t_\delta = -0.12$ or $t_\delta = -0.03$ eV. From $D = 2.15$ eV, one has $t_\sigma = -0.69$ eV. The Fermi level is set to zero by choosing the parameter $\epsilon = 0.81$ eV, completing the simple TB fit to the actual LAPW bandstructure. The corresponding total DOS is shown in figure 1; it clearly differs from the model DOS used in model treatments, and describes the doubly degenerate $e_g$ bandstructure in the cubic perovskite geometry. It also reproduces most of the features of the LAPW bandstructure for the relevant $e_g$ bands to a very good accuracy [16, 24], almost coinciding with the full LAPW results in the region $-2.0 \leq \omega \leq 2.0$ eV. Since the Mn $t_{2g}$ orbitals can be considered strongly localized to a very good accuracy, this TB fit to the actual LAPW results is indeed a quantitatively accurate representation of the one-particle DOS of the cubic manganites. Explicit comparison

Figure 1. TB fit DOS to the actual LAPW bandstructure.
of the TB-fit DOS (figure 1) with the LAPW DOS [16] in the region $-2.0 \leq \omega \leq 2.0$ eV shows the extremely good quality of the TB-fitting procedure.

The one-electron part of the Hamiltonian is

$$H_0 = \sum_{k \alpha} \epsilon_{k \alpha} c_{k \alpha}^\dagger c_{k \alpha},$$

(2)

where $\alpha = a, b$ label the orbital indices for the doubly degenerate $e_g$ sector for the case of the cubic manganites. The spin index is dropped since one of the spin species is projected out of the problem in the double-exchange limit [25]. $J_H \to \infty$ implies that the intra-orbital $U \to \infty$ as well. Additionally, the $e_g$ orbital degeneracy will be immediately lifted at the outset by the co-operative JT effect entailing a moderate coupling of $e_g$ holes to symmetry-allowed lattice distortions. In this situation, the interaction part of the Hamiltonian containing multi-orbital Coulomb interactions and the JT coupling is given by [26]–[28]

$$H_{int} = U_{ab} \sum_i n_{ia} n_{ib} - g \sum_i (Q_{ij} \tau_i^z + Q_{ij} \tau_i^x) + \frac{k}{2} \sum_i (Q_{ij}^2 + Q_{ij}^3).$$

(3)

Since we focus only on the well-doped FM-metallic state ($0.2 \leq x \leq 0.45$) in La$_{1-x}$Sr(Ca)$_x$MnO$_3$, the cooperative JT distortion is short-ranged (disordered), and follows the random distribution of the doped holes. We model this disorder by a binary distribution $P(Q_i) = (1-x)\delta(Q_i \pm Q) + x\delta(Q_i)$.

Furthermore, the $J_H \to \infty$ limit introduces a DE projection factor [29] into the hopping, which depends on the nearest-neighbour core-spin correlation function $t \to t_{ij} = t[1 + \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle/2S^2]^{1/2}$ [29], and is temperature- and magnetic-field-dependent. The one-particle part is now written as

$$H_0 = \sum_{(ij)\sigma\sigma'} t_{ij}^{\sigma\sigma'} (M) (c_{i\sigma}^\dagger c_{j\sigma'} + \text{h.c.}).$$

(4)

The total Hamiltonian of the system in the FM phase is thus $H = H_0 + H_{int}$. To simplify matters further, we make a local rotation in the two-dimensional $Q_2$–$Q_3$ space, so that the local quantization axis is parallel to $z$. Using a local unitary transformation $U_j^T [\mathbf{Q}_i, \tau_i] U_j = Q_i \tau_i^z$ along with $a_{i\alpha} = U_i c_{i\alpha}$, the Hamiltonian is

$$H = - \sum_{(ij)\sigma\sigma'} t_{ij}^{\sigma\sigma'} (M) U_j^T U_i (a_{i\alpha}^\dagger a_{j\sigma} + \text{h.c.}) + U_{ab} \sum_i n_{i\uparrow} n_{i\downarrow} - g \sum_{i\sigma} Q_i \sigma n_{i\sigma}$$

(5)

relabelling $a_{i\uparrow} = a_i$ and $a_{i\downarrow} = b_i$. With this, we have simplified the two-band model in the DE limit to a Hubbard-like model with a disordered ‘magnetic field’ acting in the orbital $e_g$ sector whose source is the disordered JT distortions which exist in the well-doped FM state.

A plausible parameter range for the problem at hand is $U_{ab} > D(M) = 2zt(M)$ and $gQ \equiv v \leq U_{ab}$, requiring one to treat the dynamical effects of strong local correlations and repeated scattering produced by moderately strong, local JT-disorder on the same footing. This is achieved by using the dynamical mean-field theory (DMFT) as an approximation to our three-dimensional problem.
4. LDA(TB) + DMFT solution

In the $d = \infty$ case, the full lattice problem is mapped onto a single site problem, with the ‘impurity’ embedded self-consistently in a dynamical bath ($\Delta(\omega)$). In the multiband case, and without symmetry breaking (orbital ordering in our case), the Green function and the purely local self-energy are functions of frequency only: $G_{\alpha\alpha'}(\omega) = G(\omega)\delta_{\alpha\alpha'}$ and $\Sigma_{\alpha\alpha'}(\omega) = \Sigma_\alpha(\omega)\delta_{\alpha\alpha'}$. So the DMFT self-consistency condition becomes

$$G_{\alpha\alpha'}(\omega, M) = \frac{1}{N} \sum_k \frac{1}{(\omega - \Sigma(\omega))\delta_{\alpha\alpha'} - (H_{0}^{TB}(k, M))_{\alpha\alpha'}}. \quad (6)$$

The dynamical self-energies $\Sigma_\alpha(\omega)$ are computed within the extended multi-orbital iterated-perturbation theory (MO-IPT) which generalizes the IPT for the one orbital case to the multi-orbital situation, for any temperature [19] and band-filling [21]. Explicitly,

$$\Sigma_\alpha(\omega) = \sum_{\gamma} A_{\alpha\gamma} \Sigma_{\alpha\gamma}^{(2)}(\omega) \frac{1}{1 - \sum_{\gamma} B_{\alpha\gamma} \Sigma_{\alpha\gamma}^{(2)}(\omega)}, \quad (7)$$

where, for example,

$$\Sigma_{\alpha\gamma}^{(2)}(\omega) = \frac{U_{\alpha\gamma}^2}{\beta^2} \sum_{n,m} G^0_n(i\omega_n) G^0_{\gamma}(i\omega_m) G^0_{\gamma}(i\omega_m + i\omega - i\omega) \quad (8)$$

and

$$G^0_\alpha(\omega) = \frac{1}{\omega + \mu_\alpha - \Delta_\alpha(\omega)}. \quad (9)$$

The multi-orbital dynamical bath $\Delta_\alpha(\omega)$ in (9) is determined using the DMFT self-consistent condition which requires that the local impurity Green function to be equal to the local Green function of the lattice (6). In (7), $A_{\alpha\gamma} = (n_\alpha(1-2n_\alpha) + D_{\alpha\gamma}[n]/n_\alpha^0(1-n_\alpha^0))$ and $B_{\alpha\gamma} = ((1-2n_\alpha)U_{\alpha\gamma} + \epsilon_\alpha - \mu_\alpha)/2U_{\alpha\gamma}^2 n_\alpha^0(1-n_\alpha^0)$. Here, $n_\alpha$ and $n_\alpha^0$ are particle numbers determined from $G_\alpha$ and $G^0_\alpha$, respectively, and $D_{\alpha\gamma}[n] = \langle n_\alpha n_\gamma \rangle$ is calculated using $\langle n_\alpha n_\gamma \rangle = \langle n_\alpha \rangle \langle n_\gamma \rangle - (1/U_{\alpha\gamma}) \int_{-\infty}^{\infty} f(\omega) \text{Im}[\Sigma_\alpha(\omega)G_\alpha(\omega)] d\omega$. The last identity follows directly from the equations of motion for $G_\alpha(\omega)$.

Finally, repeated scattering effects of the local JT (disordered) distortion by a proper combination of the IPT with the coherent-potential approximation (CPA), which solves the static disorder problem exactly in $d = \infty$ [18]. In this procedure, the IPT self-energy is fed into the CPA local potential, which now becomes $V_i = v_i - \Sigma_{\text{int}}(\omega) - \Sigma_{\text{CPA}}(\omega)$. The IPT local propagator is then used along with this in the disorder-averaged $T$-matrix (CPA) equation (but with $\Sigma(\omega) = \Sigma_{\text{int}}(\omega) + \Sigma_{\text{CPA}}(\omega)$): the local GF used in the CPA equation is

$$G(\omega, M) = \frac{1}{N} \sum_{k,\pm} \frac{1}{\omega - \Sigma_{\text{int}}(\omega, M) - \Sigma_{\text{CPA}}(\omega, M) - \epsilon_k}. \quad (10)$$

Solution of the CPA equation $\langle T_{ii}^\alpha(\Sigma(\omega)) \rangle = 0$, gives the total self-energy corrected simultaneously for scattering caused by interactions (IPT) and disorder (CPA). This is fed
back into the IPT scheme that calculates a new self-energy, \( \Sigma_{\text{new}}^{\text{int}}(\omega) \) and a new local GF, \( G_{\text{new}}^{\text{int}}(\omega) \). These are fed back into the modified CPA equations, and the procedure is iterated to self-consistency. The interacting DOS is then obtained from the usual equation

\[
\rho(\omega, M) = -\frac{1}{\pi} \text{Im} G(\omega, M).
\]

We present our results below. We concentrate on a non-half-filled band at low-temperature regime. At ‘half-filling’, the true state is a Neel-ordered orbital antiferromagnet with additional correlated distortions coming from the JT coupling. To study the well-doped FM regime with ‘melted’ orbital order, we consider only the para-orbital state. This should be a good approximation at \( x = 0.3 \), the regime considered here.

5. Results and discussion

In figures 2 and 3, we show our results for the local spectral function (DOS) for \( U_{ab} = 2D \). For \( v = 0 \), figure 2 shows features associated with the development of a correlated Fermi liquid metal due to collective screening of ‘orbital’ moments, in analogy with what happens in the usual \( d = \infty \) Hubbard model. However, we observe a rich structure of the DOS directly related to the use of the TB e\( _{g} \)-bandstructure (see figure 1) instead of idealized model input bandstructure used in model Hamiltonian treatments.

The effect of moderate local JT disorder is modelled by a binary disorder distribution

\[
P(Q_i) = x\delta(Q_i) + (1 - x)\delta(Q_i - Q),
\]

where \( x \) is the concentration of the Mn\( ^{4+} \) sites upon doping. This is justified because hole doping creates locally JT-inactive Mn\( ^{4+} \) sites, which are randomly distributed in the host lattice of JT active Mn\( ^{3+} \) ions. To make close contact with experiment, we choose \( x = 0.3 \). In figure 3 we show our results for the two values of \( t_{ij} \), i.e., for \( t_{ij} = D \) and \( t_{ij} = \sqrt{2}D \) corresponding to external field \( H_{\text{ext}} = h_{\text{sat}} \) and for \( v = U_{ab}/2 \).
In particular, beyond a critical $v = v_c$, the spectrum is completely incoherent, due to strong (resonant) scattering off the disordered JT potentials. The DOS is characterized by a pseudogap feature at low energy, invalidating the coherent Fermi liquid quasiparticle description, and resulting in an anomalous spectroscopic and optical response.

5.1. Optical response

The optical conductivity is computed from the Kubo formula. Because our two-orbital model resembles a disordered Hubbard-like model, we are able to compute both the intra-band and inter-band contributions to the optical conductivity without drastic modifications in the usual procedure. In $d = \infty$, the vertex part does not enter the Bethe–Salpeter equation for the conductivity [30] so that

$$\sigma_{xx}(\omega, M) = \sigma_0 \sum_\sigma \int \rho_0(\epsilon) d\epsilon \int d\omega' D^2(M) A_{M\sigma}(\epsilon, \omega') A_{M\sigma}(\epsilon, \omega + \omega') \frac{f(\omega') - f(\omega' + \omega)}{\omega}. \quad (11)$$

The calculated $\sigma_{xx}(\omega)$ in $d = \infty$ clearly shows the magnetic-field-induced spectral weight transfer in the ‘bad metal’ state above $T_{c}^{FM}$ for $x = 0.3$. In figure 4, we show $\sigma_{xx}(\omega, M)$ with the above parameters for two values of $t_{ij}$, which correspond to $H_{ext} = 0 (D(M) = D)$ and $H_{ext} = h_{sat} (D(M) = \sqrt{2}D)$, as explained above. With $H_{ext} = 0$ and $v = U_{ab}/2$, the Drude-like part in $\sigma_{xx}(\omega)$ at $T > T_{c}^{FM}$ is strongly suppressed. This suppression is caused by the combined effects of the decrease of $D(M)$ at high-$T$, the $T$-dependent reduction of the spectral weight (due to the $T$-dependence of the quasicoherent collective Kondo peak in our Hubbard-like model in $d = \infty$) and strong scattering off disordered (local) JT distortions, which by itself would tend to open up a dip feature in the DOS. With $H_{ext} = h_{sat}$, we see a strong enhancement of the optical
Figure 4. Optical conductivity for $U_{ab} = 2D$ and two values of the JT disorder and the external magnetic field as shown.

spectral weight in the low- and mid-infrared part of the spectrum. This is understood in terms of the physics of the $d = \infty$ Hubbard-like model, where $U_{ab}/D(M)$ controls the distribution of spectral weight; for large $U_{ab}/D(M)$, most of the weight is concentrated in the high-energy part, and a small fraction comprises the coherent part (in the para-orbital metallic state), in agreement with the fact that the resistivity magnitude places the material in the ‘bad metal’ class. With increasing $D(M)$, high-energy spectral weight is transferred over energies on the scale of $U_{ab}$ to the quasicoherent part. This transfer scales with the form of $D(M)$ as $D^2(M) = D^2(1 + M^2)/2$, completely consistent with experiment, as mentioned earlier in the paper.

What is interesting is that at low energies, the fractional increase $\Delta \sigma_{xx}(\omega, M)/\sigma_{xx}(\omega, 0)$ is a few hundred per cent! (see figure 5). We call this colossal optical magnetoconductivity (COM). Amazingly, exactly such a phenomenon has been observed by Gan’shina et al [5] for $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. In practice, $H_{\text{ext}}$ is a few tesla, and, along with the fully spin-polarized nature of the ferromagnetic metallic state, this phenomenon makes for interesting field-dependent optical applications. We emphasize the crucial role of dynamical orbital correlations and JT effects here: the $T$ and $M$-dependent transfer of spectral weight has no analogy in a non-interacting system.

A similar calculation of $\sigma_{xx}(\omega)$ by Millis et al [26] for the case $U_{ab} = 0$ gives a completely incoherent optical response, in contradiction with experiment, and approaches based on the pure DE model in the cubic geometry of the perovskites overestimate the quasicoherent part vis-à-vis experiment, and completely miss the mid-IR features [31].

In our picture, the extreme sensitivity of the ac response to a field of a few teslas arises via the change in the hopping, $t'_{ij}(M)$, which transfers optical spectral weight over large energy scales of $O(D)$. The observation of Simpson et al [15] also has a natural interpretation in terms of Hubbard model like physics in the orbital sector, as shown above. In figure 5, we also show how the COM is reduced by static JT disorder, demonstrating that the COM is related to the increased field-induced itinerance of the $e_g$ holes via $t'_{ij}(M)$.
From equation (11) we compute the electronic Raman scattering intensity in the B₁₇g channel using the Shastry–Shraiman relation, \( I_{\text{B}_{1g}}(\omega) = \omega \sigma'_{xx}(\omega) \) [32]. We emphasize that it is the B₁₇g channel intensity which reflects underlying electronic structure changes in the FM phase in manganites. This is because the TB fit we use results from the strong Mn(e₇g)–O(2p) hybridization in the actual LAPW bandstructure, and also because the Mn–t₂g states are electronically well isolated in the bandstructure result (they constitute the Mn ‘core spin’ in our modelling). This relation is rigorous in \( d = \infty \), i.e., as long as the vertex corrections entering the Bethe–Salpeter equation for \( \sigma_{xx}(\omega) \) vanish identically. In figure 6, we show \( I_{\text{B}_{1g}}(\omega) \equiv I_{xx}(\omega) \) for two values of the ‘JT disorder’ as a function of \( H_{\text{ext}} \). Concentrating on the case of \( v = 0 \), it is clear that the field-induced transfer of high-energy spectral weight to lower energy is also manifested in this case. In particular, the \( h_{\text{ext}} = 0 \) curve has a visible quasicoherent feature at low \( T \), consistent with a carrier self-energy of the form \( \text{Im} \Sigma(\omega) \simeq \Gamma_0 + \alpha \omega^2 \). An external field \( H_{\text{ext}} = h_{\text{sat}} \) suppresses thermal spin fluctuations at finite \( T \) even above \( T_{\text{FM}} \), resulting in increased carrier mobility via \( t_{\text{sat}}(M) \) and resulting in a noticeable transfer of optical spectral weight from high energy to the quasicoherent low-energy region. The relatively sharp low-energy peak is identified as the ‘coherent’ part of the (combined intra- and interorbital) multi-orbital particle–hole response in the correlated (orbital) FL metal. The carrier scattering rate extracted from experiment (\( \text{Im} \Sigma(\omega) \) in our theoretical modelling) varies like \( \Gamma_{\text{B}_{1g}}(\omega) = \Gamma_0 + \alpha \omega^2 \) for low-\( T \) (which has the same effect as \( H_{\text{ext}} \) in our calculation), completely consistent with our findings.

5.2. Magneto-optical response

Knowledge of magneto-optical spectra in the visible and near-UV range (normal absorption) provides information about the detailed electronic structure and its dependence on chemical composition, as well as on the sample magnetization. In particular, the changes in electronic structure accompanying the evolution of the magnetization are reflected in the MO spectra. In
the CMR manganites, these changes are controlled by the ratio of Mn$^{3+}$:Mn$^{4+}$ ions upon hole doping $x$. So the MO spectra, which are proportional to magnetization as well as to probabilities of electronic transitions, reflect the underlying electronic structure of the CMR manganites in detail.

Gan’shina et al [5] have carried out a detailed study of the linear transverse Kerr effect (TKE), namely, the Kerr ellipticity and Kerr rotation in La$_{0.7}$(Sr, Ca)$_{0.3}$MnO$_3$ as a function of $T$ and $H_{ext}$. The TKE is basically a measure of the intensity variation of the light reflected by a magnetized sample with $H_{ext}$ parallel to the sample surface and normal to the plane of incident light. The variation of the intensity of reflected light for a p-wave due to magnetization in a FM sample can be expressed in terms of the real and imaginary parts of the dielectric tensor $\epsilon_{\alpha\beta}(\omega)$. In the linear magnetic field approximation, the diagonal parts describe optical response and the off-diagonal elements are related to the MO response. Gan’shina et al found that the $T$-dependence of the relative change in intensity of the reflected light, $\delta(T)$, revealed clear signatures of the transition to the FM state, and its dependence on isotope (O$^{16}$ or O$^{18}$) substitution. Changes upon sample annealing and in external magnetic field were also clearly reflected in $\delta(T)$. In particular, Gan’shina et al also found a hysteresis in the TKE measured at the same $T = 100$ K upon heating/cooling the sample. In the FM state, the MO spectra are characteristically determined by the electronic transitions in the MnO$_6$ octahedra. In particular, signatures of:

(i) an allowed electric dipole transition in the (MnO$_6$) complex at energy $\hbar\omega = 3.5$ eV and
(ii) spin resolved d–d transitions in Mn$^{3+}$ ions ($\hbar\omega = 2.5$ eV) and Mn$^{4+}$ ions ($\hbar\omega = 2.6, 3.1$ eV), yielding a deep minimum in the TKE spectra around 3.0 eV, are clearly observed in the experiment. The detailed TKE lineshapes thus reflect the details of the intra-atomic (intra- and inter-orbital transitions in the JT-split e$_g$ sector in the half-metallic situation) as well as interatomic electronic transitions in the MnO$_6$ complex; in particular, they are dictated

Figure 6. Electronic Raman scattering intensity $I_{xx} \equiv I_{Br}$ for the same parameters as in figure 4.
by strong transfer of dynamical spectral weight upon changes in $x, T$ and $H_{ext}$, which is characteristic of electronic structure changes, as seen in a host of other responses in CMR materials. From our analysis of the one-particle and optical response above, we anticipate that the combined action of dynamical effects of strong multi-orbital electronic correlations, in concert with strong Hund’s rule coupling, quasistatic JT (short-ranged) and static, doping-induced disorder will determine the details of the TKE as a function of $T$ and $H_{ext}$ in the well-doped half-metallic regime. We will see below that this anticipation is indeed borne out very well in the calculated results on the basis of our LDA(TB) + DMFT modelling.

In general, computation of the TKE requires knowledge of the full ac conductivity tensor. Since the TKE manifests itself (via $\sigma_{xy}$) as the dependence of $\sigma_{xy}$ on the magnetization, it must originate from the spin–orbit interaction. The spin–orbit interaction has two contributions: a relativistic interaction of the spin of the $e_g$ carrier with the local electric field, and the magnetic interaction of the spin of the $e_g$ carrier with the core-spin, $S$. In the JT-distorted case, both will contribute (although their relative weight is difficult to assess without a full first-principles electronic structure calculation). As for our modelling, this is again a single-site (atomic) contribution,

$$ H_{so} = \lambda_{\text{eff}} \sum_i \mathbf{L}_i \cdot (\mathbf{S}_i + \mathbf{s}_i) $$

with $\lambda_{\text{eff}}$ the effective spin–orbit coupling. In terms of the effective Hamiltonian written in the rotated variables, and decoupling the $\mathbf{L} \cdot (\mathbf{S} + \mathbf{s})$ in the mean-field approximation (this should be valid for the half-metallic case we are interested in here), we get

$$ H_{so} = \lambda_{\text{eff}} \langle M \rangle \sum_{i,\sigma} \sigma_{n\sigma}^\prime $$

while calculating $\sigma_{xy}$. Following [33, 34], $\sigma_{xy}(\omega)$ is found from

$$ \sigma_{xy}(\omega, M) = c_{xy} \int_{-\infty}^{\infty} d\epsilon \int_{-\infty}^{\infty} d\omega_1 d\omega_2 A_{M\sigma}(\epsilon, \omega_1) \left[ F(\epsilon, \omega_1; \omega) - F(\epsilon, \omega_2; \omega) \right] $$

$$ + (\omega \rightarrow -\omega) \omega_1 - \omega_2 \] , $$

where $F(\epsilon, \omega_1; \omega) = A_{M\sigma}(\epsilon, \omega_1 - \omega) f(\omega_1 - f(\omega_1 - \omega))$, along with a Kramers–Kronig transform for the real part. The Kerr rotation $\theta_K$ and ellipticity $\epsilon_K$ are given by [35]

$$ \theta_K(\omega) = \frac{4\pi}{\omega} \left[ A \sigma^\prime_{xy}(\omega) - B \sigma^\prime_{xy}(\omega) \right] $$

$$ + \frac{A^2 + B^2}{A^2 + B^2} , $$

$$ \epsilon_K(\omega) = \frac{4\pi}{\omega} \left[ B \sigma^\prime_{xy}(\omega) + A \sigma^\prime_{xy}(\omega) \right] $$

$$ + \frac{A^2 + B^2}{A^2 + B^2} , $$

with $A = (n^3 - 3nk^2 - n)$ and $B = (-k^3 + 3nk^2 - k)$. Here, $(n + ik)^2 = \epsilon_{xx}(\omega) = 1 + (4\pi/\omega)\sigma_{xx}(\omega)$. In the above, $n$ and $k$ are the components of the complex refractive index. Our results for the required quantities, $\sigma_{xx}(\omega)$ and $\sigma_{xy}(\omega)$, which are calculated from the one-electron spectral functions within the LDA(TB) + (DMFT(IPT) + CPA) scheme mentioned before, are shown in figure 7.

In figure 8, we show the calculated Kerr ellipticity and rotation for various values of the static disorder potential. Clearly, given the use of a tight-binding fit to the actual bandstructure, the fit to experiment (see figure 9) is satisfying. In particular, two distinct minima at $\omega_1 = 1.5$ eV and $\omega_2 = 3.0$ eV, along with the overall detailed form of the lineshape, are clearly seen in the calculated result. We thus identify these structures in the TKE spectra to a combination
Figure 7. Diagonal (bottom) and off-diagonal (top) parts of the optical conductivity tensor for $U_{ab} = 2D$ and three values of the JT disorder $v$.

Figure 8. The calculated Kerr ellipticity (top) and rotation (bottom) for the same parameters as in figure 7.

of intra- and interorbital electronic transitions in the JT-split $e_g$ sector in the FM half-metallic state. In view of the fact that we have restricted our TB-fit to $e_g$ bands, we cannot describe the 3.5 eV maximum observed in figure 9; this requires incorporation of the O 2p bands in the TB-fit. Clearly, more work is needed to further improve the agreement: as we discussed in the introduction, this is a truly formidable enterprise even for early TMO systems.
Finally, we are unable to explain the hysteresis in the TKE spectra upon heating/cooling. As pointed out by Gan’shina et al, we believe that short-ranged, ferromagnetic cluster formation needs to be included consistently in our calculation to elucidate this point. We leave it for future work.

6. Summary

In conclusion, we have shown how a combination of essential bandstructure aspects of the cubic perovskite structure with a DMFT treatment of strong orbital correlations in the $e_g$ sector in the DE limit describes the optical and photoemission spectra of the metallic CMR manganites in a semiquantitative way. The good agreement we find is therefore $a$ posteriori evidence for the important roles played by strong multi-orbital correlations, in concert with strong Hund’s rule DE interaction along with short-ranged JT and doping-induced chemical disorder in determining the details of the electronic structure in the FM state of these CMR materials. Our treatment can be extended to include other broken symmetries in the spin and orbital sectors, and should be generally applicable, with suitable modifications, to other half-metallic TM-oxide ferromagnets.

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