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Colossal magnetoresistance manganites: a laboratory for electron–phonon physics

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It is argued that the 'colossal' magnetoresistance rare earth manganites present an unusual opportunity for condensed matter physics because they are metals in which the electron–lattice interaction is both unusually strong and tunable; i.e. variable over a wide range by variation of chemical composition, strain, magnetic field and temperature. The variability will allow systematic and controlled study of properties of a high density of electrons strongly coupled to phonons.

Keywords: magnetoresistance; double exchange; polaron; transition metal oxide; Jahn–Teller effect; charge ordering

1. Introduction

The 'colossal' magnetoresistance (CMR) rare earth manganese perovskites have been of recent interest for their spectacular magnetoresistive properties (von Helmholt *et al*. 1993; Jin *et al*. 1994), which could be of technological importance. It will be argued here that they are of very substantial basic physics interest for quite a different reason: in them the *electron–lattice coupling* is both unusually strong and easily tunable. The materials therefore offer the opportunity to investigate in detail the physics of a *metallic density* of electrons strongly coupled to phonons. In what follows, the physics underlying the strong coupling and the tunability will be outlined, the strength of the electron–phonon and electron–electron coupling will be estimated, a few physical consequences will be discussed, and some open issues will be mentioned. The estimate of the electron–phonon coupling corrects errors arising from inconsistent normalization conventions in my previous work (Millis 1996; Millis *et al*. 1998*a*).

The CMR materials crystallize in variants of the 'ABO_3' perovskite structure. The prototype compound is $La_{1-x}Ca_xMnO_3$ in which the A-site is randomly La or Ca and the B-site is Mn. Variant compounds with the same crystal structure exist in which different rare earths are substituted for La or different divalent alkali ions for Ca. A wider class of variants, the so-called Ruddlestone–Popper series of layered materials, has also been grown (Kimura *et al*. 1996; Mitchell *et al*. 1997). All materials share the basic feature of a network of Mn ions six-fold coordinated by oxygen. The electrically active sites are the Mn d-orbitals; in $La_{1-x}Ca_xMnO_3$ the number of d-electrons is $4 - x$. The d-electrons are subject to a variety of interactions, of which the most important are a crystal field of approximately cubic symmetry which splits the five-fold degenerate d-levels into a lower-lying t_{2g} symmetry triplet and two higher lying states, which form an e_g symmetry doublet if the crystal field has cubic symmetry, and a strong on-site Hund coupling which requires that all d-electrons on a given Mn

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ion have the same spin. The combination of these two interactions means that of the $4-x$ electrons on a given Mn ion, three go into the t_{2g} levels and make up a $S_c = 3/2$ core spin, which turns out to be electrically inert in the compounds of interest, while the remaining $1-x$ electron goes into a linear combination of the e_g levels and is free to move from Mn ion to Mn ion, subject to the constraint that an e_g electron on site i must have its spin parallel to the core spin on that site. The Hund coupling is, of course, not infinite, so three possible higher energy configurations are allowed: flipping the e_g electron relative to the t_{2g} spin, putting the t_{2g} electrons in a non-maximal spin state, and putting the extra $1-x$ electron into the t_{2g} levels instead of into the e_g levels. Recent optical data (Quijada *et al.* 1998) suggest that the e_g antiparallel configuration is about 3 eV higher than the e_g parallel configuration; the energies of the other two configurations have not been measured but are expected to be higher; thus for most purposes the Hund energy may be taken to be infinite.

The main physical consequence of the Hund and crystal-field couplings is 'double-exchange', a term introduced by Zener (1952) to denote the connection between magnetic correlations and hopping. The point is that the very large Hund coupling means that the amplitude for an electron to hop from one Mn site to another depends on the relative orientation of the core spins on the two sites, because the electron must get itself from being parallel with the core spin on its initial site to being parallel to the core spin on its final site. The hopping is therefore modulated by a spin overlap factor which is maximal when the spins are parallel and minimal when they are antiparallel. The consequences of double exchange have been studied in detail by many authors (e.g. Anderson & Hasegawa 1955; de Gennes 1960; Kubo & Ohata 1972; Furukawa 1994; Millis *et al.* 1995; Mueller-Hartmann & DaGotto 1996; Li *et al.* 1997). This work has established that if double-exchange is the only important interaction then in the fully polarized ferromagnetic state the kinetic energy is maximal and the carriers are not scattered, while if the core spins become completely uncorrelated (because, for example, the temperature is raised to well above the Curie point), the kinetic energy decreases to about 2/3 of its maximal value. The kinetic energy is therefore tunable by temperature and magnetic field, both of which tend to align the spins. In addition, it is tunable by chemical composition (especially by variation of the 'A-site' ion in the 'ABO_3 structure), for reasons of crystal chemistry explained elsewhere (Hwang *et al.* 1995). The physics of double-exchange, although fascinating in its own right and still not completely understood (Mueller-Hartmann & DaGotto 1996), is insufficient to account for the physics of the CMR materials. Most notably, although double-exchange implies that spin disorder leads to a modest scattering rate for the electrons, the resulting resistivity is much too small to account for the observed very large resistivities at $T > T_C$ (Millis *et al.* 1995, 1996*a*, *b*; Li *et al.* 1997). Additional interactions must be invoked, most notably the electron–phonon one.

Several authors have argued that electron–electron interactions are also important (Varma 1996; Nagaosa *et al.* 1998). In estimating the strength of these interactions, a little care is called for. Intuition from atomic physics, along with photemission evidence (Saitoh *et al.* 1996) suggests that the Mn d-electrons are subject to an intrinsically strong Coulomb repulsion, perhaps of order 10 eV. However, although we refer to them as d-electrons, the objects of interest for the low energy (less than 4 eV, say) physics are hybridized combinations of Mn d- and O p-electrons, as noted by Saitoh *et al.* (1996). The effective interaction relevant for these states may be much less than the atomic 10 eV. I argue here that optical data show that the electron–electron interaction is relatively weak and the electron–phonon interaction is relatively strong. This conclusion is in agreement with band theory calculations (Soloviev *et al.* 1996*a*, *b*), which indicate that the properties of $LaMnO_3$ are well described by the local spin density approximation, and that remaining discrepancies may be resolved by adding a modest 'U' involving mainly t_{2g} electrons.

$LaMnO_3$ has a mean density of one e_g electron per site, is an insulator with an optical gap of slightly larger than 1 eV (Arima & Tokura 1995) and has a large-amplitude lattice distortion away from the ideal perovskite structure (Ellemaans *et al.* 1971). The fundamental low energy optical process involves moving an Mn d-electron from one site to another. In simple terms, if the initial state has four d-electrons (three t_{2g} and one e_g) per site then the final state has one site with three d-electrons and one with five. The energy of this final state is given roughly by the sum of the effective e_g–e_g Coulomb interaction and any lattice distortion energy. Qualitatively, the final state energy is not large and is more or less determined by the lattice distortion, leaving rather little room for the Coulomb interaction.

To see this more quantitatively, first consider the lattice distortion occurring in $LaMnO_3$. In the ideal perovskite structure, each Mn has six near-neighbour oxygen ions; all Mn–O bonds are of equal length and all bond angles are 90°. In the measured structure all bond angles are still very near 90° but the bond lengths are unequal. For the O ions displaced in the $\pm x$ direction, the measured lengths (Ellemaans *et al.* 1971) are $u_x = 1.91$ Å; for the y and z directions, $u_y = 2.17$ Å and $u_z = 1.97$ Å. (This distortion actually alternates throughout the crystal in a $(\pi, \pi, 0)$ pattern, but this will not be important for the subsequent analysis.) The distortions imply a mean Mn–O bond length of $\bar{u} = 2.017$ Å with an even parity biaxial (Jahn–Teller) distortion superposed.

The driving force for the lattice distortion is the Jahn–Teller effect: in the ideal perovskite structure the two e_g orbitals are degenerate; an even parity distortion of the MnO_6 octahedron lowers the energy of one orbital and raises the energy of the other, producing an energy gain if the e_g orbital is preferentially occupied. Conversely, a preferential occupancy of one orbital will induce a lattice distortion. This physics may be expressed as an electron–lattice interaction. The magnitude of the interaction constant depends on the manner in which the atomic displacements are to be defined. Consider an MnO_6 octahedron. Choose the Mn position to be the origin of coordinates and let + and − subscripts denote O ions in the + and − directions. Define $v^x = (u^x_+ - u^x_-)$ (and similarly for y and z). Then, if the spring constant of an Mn–O bond is K, the harmonic energy of distortion for an octahedron is

$$E_{\text{harm}} = \frac{1}{2} K \sum_{a=x,y,z} (v^a)^2. \tag{1.1}$$

K may be estimated from the observed phonon spectrum. The highest-lying mode is at $\omega \approx 0.09$ eV and presumably corresponds to an oxygen vibrating between two Mn. Writing $\omega^2 = 2K/M_{\text{oxy}}$ yields $K \approx 15$ eV Å^{-2}.

Equation (1.1) implies that the conventionally defined 'bulk modulus' is $B = Ka^2/3 \approx 81$ eV, while the Jahn–Teller shear modulus is $C^* = Ka^2/2 \approx 122$ eV, with the Mn–Mn distance $a \approx 4$ Å. Then define $v_3 = (\sqrt{3}/2)(2v^z - (v^x + v^y))$, $v_1 = (v^x - v^y)$ and $\boldsymbol{Q} = (v_1, 0, v_3)/a$. These definitions are chosen so that the energy of a volume-preserving strain is

$$E_{\mathrm{JT}} = \tfrac{1}{2}C^{*}\boldsymbol{Q}^{2}. \tag{1.2}$$

Finally, choose the $|z^2 - r^2\rangle$, $|x^2 - y^2\rangle$ basis for the electrons, and define $\boldsymbol{\tau} = (\tau_1, 0, \tau_3)$, with $\tau_{1,3}$ two of the usual Pauli matrices. Then we define the electron–phonon Jahn–Teller coupling Hamiltonian H_{JT} and coupling constant g via

$$H_{\mathrm{JT}} = (g/a)d_a^{\dagger}\boldsymbol{\tau}_{ab}d_b \cdot \boldsymbol{Q}. \tag{1.3}$$

This equation expresses the fact that a Jahn–Teller distortion of magnitude Q splits the energies of the appropriate linear combination of d-orbitals by an amount $\Delta = 2gQ$, while a difference in orbital occupancy Δn exerts a force on the oxygen displacements Q given by $g\Delta n$. From equations (1.2), (1.3) one finds that

$$Q = g\Delta n/C^{*}. \tag{1.4}$$

In $\mathrm{LaMnO_3}$ the displacements $\boldsymbol{v}$ are $v_x = 0.214$, $v_y = -0.306$ $v_z = -0.096$, implying $Q = 0.13$ and thus $g\Delta n \approx 16$ eV. Turning the argument around then implies that *the observed lattice distortion implies a d-level splitting* $\Delta = (g\Delta n)^2/C^{*} \approx 2.1(\Delta n)^2$ eV. Note that this estimate is independent of the value of the Coulomb interaction. This interaction will, of course, increase the value of Δn and the energy splitting Δ, but will not affect the coupling parameters we have deduced.

Now the optical data exhibit a gap of about 1.5 eV and an absorbtion peak at about 2.5 eV (Arima & Tokura 1995). It is reasonable to identify the peak energy as the d-level splitting; it is also reasonable to assume Δn is a little less than unity. One sees, then, that there is rather little room for the Coulomb interaction, which may thus be safely neglected.

To summarize, a simple analysis of the structural and optical properties of $\mathrm{LaMnO_3}$ leads to the conclusion that in this compound (and therefore by extension in the doped compounds) an electron–phonon interaction coming from a Jahn–Teller coupling of distortions of the $\mathrm{MnO_6}$ octahedra to the e_g level splitting is very strong and is indeed the dominant interaction. The consequences of this interaction (and especially its interplay with the tunable kinetic energy) have been studied theoretically in various approximations (Millis *et al.* 1996*a*, *b*; Millis 1996; Röder *et al.* 1996) and the theoretical predictions have been at least qualitatively confirmed by experiments, most notably optical conductivity measurements (Kaplan *et al.* 1996; Quijada *et al.* 1998) and determinations of the temperature dependence of local lattice distortions (Billinge *et al.* 1996; Booth *et al.* 1998). A notable weakness of the theoretical calculations to date has been the neglect of 'intersite' effects. All of the calculations so far have been performed using one or another sort of local approximation which neglects intersite correlations (e.g. those coming from the fact that each O ion is shared between two Mn). These intersite correlations are obviously crucial in producing the 'charge order' observed in manganites with $x > 0.5$ and are probably important also for dopings in the 'CMR' regime. In particular, despite substantial optical evidence for a large carrier mass enhancement at low frequencies, specific heat data indicate only a small enhancement over band values. This can only be explained if the electron self-energy has a strong momentum dependence, which is inconsistent with the local approximations so far employed.

The strong coupling to Jahn–Teller phonons suggests that the materials may be anomalously sensitive to applied strain, such as would occur if a film is grown on a poorly lattice-matched substrate.

Preliminary indications (Millis *et al.* 1998*a*, *b*) are that these effects are large, raising the interesting possibility of tuning the physics with strain.

One crucial open question concerns the physics of layered 'Ruddlestone–Popper' materials. These tend to be much less conductive than the cubic materials at similar dopings, but also display 'colossal' magnetoresistance. I suggest that their more insulating behaviour is due in part to the fact that the crystal structure implies a substantial Jahn–Teller distortion is already frozen in (as in films with a large strain). But the similar phenomoenology to the cubic materials suggests a more dynamical phonon is also at work. Identifying this phonon (or ruling out its existence) is a very important issue.

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References

Anderson, P. W. & Hasegawa, H. 1955 *Phys. Rev.* **100**, 675.

Arima, T. & Tokura, Y. 1995 *J. Phys. Soc. Jpn* **64**, 2488.

Billinge, S. J. L., DiFrancesco, R. G., Kwei, G. H., Neumeier, J. J. & Thompson, J. D. 1996 *Phys. Rev. Lett.* **77**, 715.

Booth, C. H., Bridges, F., Kwei, G. H., Lawrence, J. M., Carnelina, A. T. & Neumaier, J. J. 1998 *Phys. Rev. Lett.* **80**, 853.

de Gennes, P. G. 1960 *Phys. Rev.* **118**, 141.

Ellemaans, J. B. A. A., van Laar, B., van der Veer, K. J. R. & Loopstra, B. O. 1971 *J. Sol. St. Chem.* **3**, 238–242.

Furukawa, N. 1994 *J. Phys. Soc. Jpn* **63**, 3214.

Hwang, H. Y., Cheong, S.-W., Raedelli, P. G., Marezio, M. & Batlogg, B. 1995 *Phys. Rev. Lett.* **75**, 914–917.

Jin, S., Tiefel, T. H., McCormack, M., Fastnacht, R. A., Ramesh, R. & Chen, L. H. 1994 *Science* **264**, 413–415.

Kaplan, S. G., Quijada, M., Drew, H. D., Tanner, D. B., Xiong, G. C., Ramesh, R., Kwon, C. & Venkatesan, T. 1996 *Phys. Rev. Lett.* **77**, 2081.

Kimura, T., Tomioka, Y., Kuwahara, H., Asamitsu, A., Tamura, M. & Tokura, Y. 1996 *Science* **274**, 1698.

Kubo, K. & Ohata, A. 1972 *J. Phys. Soc. Jpn* **33**, 21–32.

Li, Q., Zang, J., Bishop, A. R. & Soukoulis, C. M. 1997 *Phys. Rev.* B **56**, 4541–4544.

Millis, A. J. 1996 *Phys. Rev.* B **53**, 8434.

Millis, A. J., Littlewood, P. B. & Shraiman, B. I. 1995 *Phys. Rev. Lett.* **75**, 5144.

Millis, A. J., Shraiman, B. I. & Mueller, R. 1996*a* *Phys. Rev. Lett.* **77**(1), 175–178.

Millis, A. J., Mueller, R. & Shraiman, B. I. 1996*b* *Phys. Rev.* B **54**, 5405–5417.

Millis, A. J., Darling, T. & Migliori, A. 1998*a* *J. Appl. Phys.* **83**, 1588.

Millis, A. J., Goyal, A., Rajeswari, M., Ghosh, K., Shreekala, R., Ramesh, R. & Venkatesan, T. 1998*b* *Appl. Phys. Lett.* (Submitted.)

Mitchell, J. F., Argyriou, D. N., Potter, C. D., Jorgensen, J. D., Hinks, D. G. & Bader, S. D. 1997 Layered CMR manganites: structure, properties, and unconventional magnetism. *Solid State Chemistry of Inorganic Materials. Symposium* (xv+746 pages), pp. 343–348.

Mueller-Hartmann, E. & DaGotto, E. 1996 *Phys. Rev.* B **54**, 6819.

Nagaosa, N., Murakami, S. & Lee, H. C. 1998 *Phys. Rev.* B **57**, 6767.

Quijada, M., Cerne, J., Simpson, J. R., Drew, H. D., Ahn, K. H., Millis, A. J., Xiong, G. C., Ramesh, R., Kwon, C., Rajeswari, M. & Venkatesan, T. 1998 (cond-mat/9803201) *Phys. Rev.* B. (Submitted)

Röder, H., Zang, J. & Bishop, A. R. 1996 *Phys. Rev. Lett.* **76**, 13569.

Saitoh, T., Bocquet, A. E., Mizokawa, T., Namatame, H., Fujimori, A., Abbate, M., Takeda, Y. & Takano, M. 1996 *Phys. Rev.* B **51**, 1342.

Soloviev, I., Hamada, N. & Terakura, K. 1996*a* *Phys. Rev. Lett.* **76**, 4825.

Soloviev, I., Hamada, N. & Terakura, K. 1996*b* *Phys. Rev.* B **53**, 7158.

Varma, C. M. 1996 *Phys. Rev.* B **54**, 7328.

von Helmholt, R. M., Wecker, J., Holzapfel, B., Schultz, L. & Samwer, K. 1993 *Phys. Rev. Lett.* **71**, 2331–2333.

Zener, C. 1952 *Phys. Rev.* **82**, 403.

Discussion

D. Khomskii (*University of Groningen, The Netherlands*). There are in principle two sources of strong electron–lattice interactions: interactions with the Jahn–Teller active phonons and an interaction with the breathing-type mode due to the presence of formally two different valence states, Mn^{3+} and Mn^{4+}. Is it clear which of them is more important? In particular, in the experiment to measure the mean square oxygen displacement mentioned by Dr Millis, what kind of distortion is measured?

A. J. Millis. The data of Booth *et al.* (1998) show clearly that the Mn–O bond length distribution changes. This could be due either to breathing mode or Jahn–Teller distortions of the Mn–O bond. The experiment unfortunately doesn't tell you. I like it because of what it does tell you, that this is a bond length. You're not taking this manganese oxygen bond and buckling it; it really is a change of the Mn–O distance, but as yet they don't have the resolution to know whether Jahn–Teller or the other is dominant, but obviously both are important.

Now, the argument is that at least it has a strong flavour of Jahn–Teller. It's just the crude correspondence between these two, because in this compound there is only Jahn–Teller. Right? But also I should say that one of the things that I just don't understand is if you go back to the lanthanum half–half composition (so, $La_{0.5}$ and $Ca_{0.5}$ manganese oxide). Analysis of the bond lengths observed in the charge-ordered compounds suggests that the Jahn–Teller and breathing distortions have about the same amplitude.

Again, people, most notably S.-W. Cheong and collaborators, have found out where all the oxygens go. That charge-ordered state again has big lattice distortions approximately of this order of magnitude, and you can partition it into Jahn–Teller distortion around the sites which are 4^+, and a breathing about the sites which are 3^+ and they are equal. One of the reasons you see it's equal (and this is the part I never understood) is that the ordered structures stack (if I've understood them well): in one plane you have a chequerboard pattern 4^+–3^+–4^+; you go to the next plane and it's exactly the same pattern. That's their claim.

The only way that can work is the short axis of the Jahn–Teller distortion is exactly the same as short axis made by the breathing distortion. Why it should do that I have no idea, but that seems to be the case. From that it looks like they are just exactly equal in importance (which seems mysterious).

J. R. Cooper (*University of Cambridge, UK*). Could Dr Millis say a little more about the physical origin of the large intercept in the high temperature resistivity?

A. J. Millis. In the calculation one finds an intercept ($\rho(T) = \rho_0 + AT$ with $\rho_0 \neq 0$) when the phonon probability distribution has a double peak structure so that in the $T \rightarrow 0$ limit there is a frozen in lattice distortion. Of course, quantum effects have not been included.

M. Rzchoswki (*University of Wisconsin-Madison, USA*). How similar is the high temperature limit of the theory to activated hopping of small polarons and how similar is the transition to a small to large polaron crossover, a traditional perspective?

A. J. Millis. Qualitatively, but not quantitatively. Forget about all this fancy double-exchange stuff. What you see is that even when parameters in the calculation are such that the behaviour is insulating at low temperature it is very hard to get the resistivity to be activated over a wide range. So the high temperature limit of this theory for these couplings is not activated hopping of small polarons but when the resistivity starts to take off, of course it does ultimately become activated.

In a sense all theories which give you activated behaviour give you the same behaviour, so in a sense this asymptotic divergence is precisely activated hopping, with exactly the energy gap found in the one-electron special function—I have checked!. But the important difference with small polarons in the theory is in fact nicely shown in the spectral function (this graph only shows one half of the spectral function, there is a symmetrical half here), the gap that I am opening here, even in the most resistive case, is small compared to the total bandwidth. Now in the usual small polaron picture, I really just take an electron and I localize it strongly on the lattice site. In a sense that means that the gap is large compared to the underlying bandwidth of my electrons (of course, if I only have one electron, it's down in the bottom of its real band and its Fermi energy is tiny). So a small polaron means the gap is enormous compared to the bandwidth and that is not what we have here. We have gaps which are small, which can also be seen from the optics. So perhaps another way to say it is that in optical conductivity in small polaron theory basically the optical gap and the resistivity gap are the same because you don't have a big band of filled states, you just have a delta function so it has a crude similarity (you do have upturns), but it's not even close if you look at it in detail to small polarons.

Now, consider the small polaron to large polaron transition. Again, what occurs in the model has a similar flavour but it's not exactly the same for this reason: I think there is enough oscillator strength in each of these that is very difficult to make a tenable interpretation just in terms of individual non-overlapping polarons. There is a concept here which I haven't been able to formulate for myself in a satisfactory way. But let me say something which is probably more pretentious than need be. Everything in my calculation is happening in a metallic density of electrons. The concepts that we have are either weakly scattered things or polarons. In this we have some strong flavour of polarons but its not exactly that, so what I'm looking for is the analogy of BCS theory. In superconductivity many of the phenomena have the flavour of a pair of electrons and you only pay attention to Cooper pairs, but we know that the Cooper pairs are strongly interacting and so forth and the real way to describe them is with this BCS wave function. I am looking for, but haven't found, the analogous concept here.

G. A. Gehring (*University of Sheffield, UK*). To what extent have all Dr Millis's calculations been done with classical models for the lattice? Doesn't that mean that the lattice is therefore static and therefore you can't have a real polaron in which the lattice distortions follow the electron around?

A. J. Millis. I would not agree, because there's a perfectly sensible classical limit of the real polaron here. Basically, I guess the right way to say this is that classical doesn't mean static, it just means you can average over everything in an incoherent way and you don't have to worry about the details of time dependence. The way hopping occurs is that an electron sits on a site until, by some thermal fluctuation, the next site becomes a state that is able to accept it, and all that physics is in this calculation. The right way to say it is that I've averaged over the dynamics in a completely incoherent way. A better answer is that if you take this calculation for the very low doping limit, you recover all the canonical classical results for polarons in the high temperature limit.