Lattice effects in magnetoresistive manganese perovskites

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The discovery of spectacularly large magnetoresistive responses in a class of metallic manganese oxides has raised hopes that these compounds might be of practical utility. But regardless of whether this promise is realized, these materials provide an ideal system in which to elucidate the properties of metals in which electron–lattice interactions play a key role.

Transition-metal oxides have long been the subject of study, because they exhibit a wide range of exotic and still imperfectly understood structural, magnetic and electronic behaviour. This behaviour cannot be explained within the context of the usual one-electron band theory that accounts well for the properties of most other solids, indicating the importance of strong electron–electron and electron–lattice correlations. The properties of these materials continue to surprise; for example, 1986 saw the discovery of high-temperature superconductivity in materials based on copper oxide.

More recently, attention has become focused on a certain class of manganese oxides, the manganite perovskites. Although these materials have been studied for many years[1], the current burst of activity was stimulated by reports by Helmholt *et al.*[2] and Jin *et al.*[3] of spectacularly large—"colossal" as Jin *et al.*[3] put it—magneto-resistance in this family of compounds. Magnetoresistance, the variation of electrical resistance with magnetic field, is crucial to several areas of technology, such as magnetic data storage, and much of the impetus for the present interest in the manganites stems from the possible utility of their magnetoresistive properties. Whether the manganite perovskites currently under consideration will prove technologically useful is still far from clear. But the observation of colossal magnetoresistance has stimulated a considerable amount of work aimed mainly at understanding and improving their mag-netoresistive properties, and at examining other related classes of transition-metal oxides (such as spinels, pyrochlores and mag-netites) which display similar behaviour and may have more technologically convenient properties.

But here I will argue that the manganites are also important for basic condensed-matter physics for quite a different reason. In these materials, the interaction between the electrons and lattice vibra-tions (phonons) is unusually strong, leading to a wide range of striking physical phenomena and, most crucially, can be 'tuned' over a wide range by variation of chemical composition, tempera-ture and magnetic field. These materials therefore provide an unprecedented opportunity to study the poorly understood physics of systems in which a high density of electrons is strongly coupled to phonons and, in particular, to elucidate the interplay between local structural deformations and global properties. This interplay is becoming the focus of attention in many contexts, including conducting polymers[4] and ferroelectrics[5] (for a summary of other recent work on local structures, see ref. 6).

Basic phenomenology

The 'colossal magnetoresistance' (CMR) manganites are com-pounds based on the ABO_3 perovskite structure shown in Fig. 1a. The most widely studied family has the chemical formula $Re_{1-x}A_xMnO_3$ (where Re is a rare earth such as La or Nd, and A is a divalent alkali such as Sr or Ca), but there is also growing interest in the 'Ruddlestone–Popper' series of layered materials $Re_{n+1}Mn_nO_{3n+1}$. The important electrons are the Mn d electrons, of which there are $4 - x$ in $Re_{1-x}A_xMnO_3$. The atomic physics of manganese is such that all of the electrons on a given Mn ion in these compounds must have parallel spin, so each Mn ion has a magnetic moment.

Changing the carrier concentration x produces a variety of phases, which may be characterized by their magnetic, transport and 'charge-ordering' properties. A phase diagram in the doping (x) and temperature (T) plane for one representative material, $La_{1-x}Ca_xMnO_3$, is shown in Fig. 2. At $x = 0$, the material is 'insulating' (that is, it has a resistivity which is very high and grows as the temperature is lowered) at all temperatures. The material is paramagnetic (it has no long-range magnetic order) at high temperature, but below about 140 K it becomes a $(0, 0, \pi)$
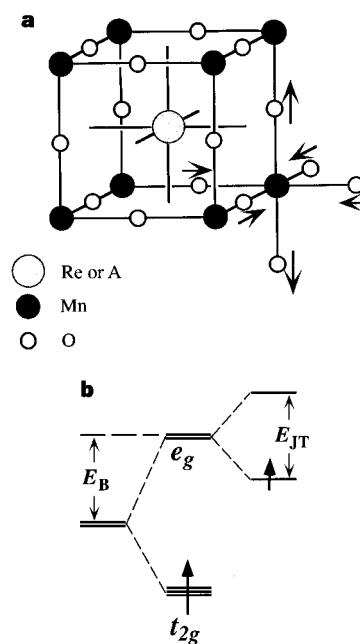
Figure 1 Crystal structure and electronic structure of the manganite perovskite. **a**, The basic perovskite structure, with oxygen motions in one Jahn–Teller distortion indicated by arrows. **b**, Schematic energy levels of the Mn ion. The central portion is for the undistorted lattice; it shows the low-lying t_{2g} levels occupied by three parallel-spin electrons forming a $S_c = 3/2$ core spin (indicated by large arrow), and the higher-lying e_g doublet (two-fold degenerate in the ideal perovskite crystal structure). The right-hand portion of the figure shows that if the e_g level is singly occupied, a Jahn–Teller distortion of the surrounding O_6 octahedron may occur (see **a**), which would split the e_g doublet by an energy E_{JT}. The left-hand portion of the figure shows that if the e_g level is unoccupied, a 'breathing' distortion may occur (see text) which lowers the energy of the unoccupied e_g doublet by an amount E_B relative to its energy in the ideal structure.

antiferromagnet: in a given plane perpendicular to the crystal c-axis the magnetic moments on Mn sites are aligned, but the moment direction alternates from plane to plane. The ground state remains insulating for $x < x_{MI} \approx 0.2$ but the magnetic order changes in a complicated (and still controversial) way, eventually becoming a fully polarized ferromagnet (all spins aligned in the same direction). In the phase diagram of Fig. 2, this sequence of phases is denoted by CAF (for canted antiferromagnet) and FI for ferromagnetic insulator. One sees also that charge order (CO—a periodic pattern of Mn sites in different valence states) develops inside the ferromagnetic insulator phase. At $x = x_{MI}$ the ground state changes from insulating to metallic. This is shown in Fig. 2 as the vertical dotted line separating the FI (ferromagnetic insulator) and FM (ferromagnetic metal) phases. For $x_{MI} < x < 0.5$ the ground state is a ferromagnetic metal. For $x > 0.5$ the ground state again becomes insulating and antiferromagnetic, and is in addition 'charge-ordered'.

As the temperature is raised in the region $x_{MI} < x < 0.5$, there is a ferromagnet–paramagnet transition at a $T_c(x) \approx 200–250$ K. The magnetic phase boundary also separates a low-temperature 'metallic' phase from a high-temperature 'insulating' phase. (Here 'metallic' and 'insulating' have quotation marks because a precise distinction between metal—finite resistivity—and insulator—infinite resistivity—is only possible at zero temperature; here the terms are used in the qualitative sense that the resistivity at $T < T_c(x)$ is relatively low and increases as T is increased, whereas at $T > T_c(x)$ the resistivity is very high and (for most x) *decreases* as T is increased). The magnetoresistance for $T \approx T_c(x)$ can be very

large: some representative data[7] are shown in Fig. 3a. The large magnetoresistance is perhaps not surprising: ferromagnetic transitions are in general very sensitive to applied magnetic fields and in the materials of interest the ferromagnetic transition is also a 'metal'–'insulator' transition, so it is natural to expect the resistivity to depend strongly on magnetic field in the vicinity of this transition. What *is* surprising is the very existence of the metal–insulator transition: it implies there is a mechanism for localizing the carriers at $T > T_c$ and 'turning off' the localization as T is lowered through T_c.

Electronic and magnetic structure

In the ideal perovskite structure, each Mn is in a locally cubic environment and the crystal field splits the five d orbitals into a t_{2g} triplet and an e_g doublet. These levels are shown in the central portion of Fig. 1b. The t_{2g} levels seem to lie substantially ($\sim$2–4 eV) below the e_g levels. The on-site Coulomb repulsion is apparently strong enough that (1) no d orbital may be occupied by more than one electron and (2) all electron spins on a given Mn are ferromagnetically aligned by a large Hunds-rule coupling. The resulting physical picture is thus that 3 of the $(4 - x)$ d electrons fill up the t_{2g} levels, forming an electrically inert core spin S_c of magnitude 3/2, while the remaining $(1 - x)$ electron goes into a linear combination of e_g orbitals and may move through the crystal subject to the constraint that when it is on site i its spin must be parallel to S_c^i. This means that the amplitude for a carrier to hop from site i to site j is modulated by the overlap between having its spin parallel to S_c^i and
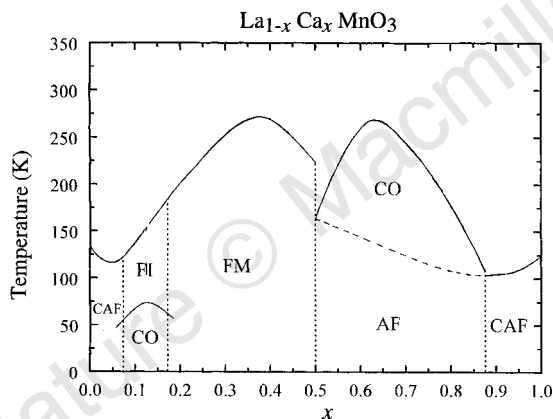
La$_{1-x}$Ca$_x$MnO$_3$

◀ **Figure 2** Phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ showing magnetic and structural phase boundaries (S.-W. Cheong, personal communication). The horizontal axis shows the value of x in the formula. Phases include charge-ordered (CO), antiferromagnet (AF), canted antiferromagnet (CAF), ferromagnetic metal (FM), ferromagnetic insulator (FI). The unlabelled region of the phase diagram has neither magnetic nor charge order.
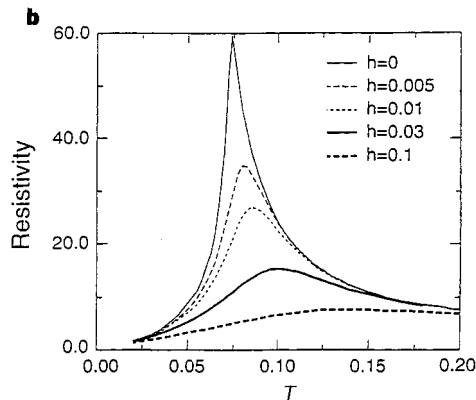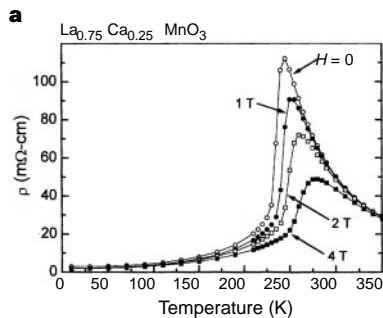

Figure 3 Measured and calculated resistivity of La$_{0.75}$Ca$_{0.25}$MnO$_3$. **a**, Measured resistivity at different magnetic fields: from ref. 7. **b**, Calculated resistivity (arbitrary unites) versus temperature T in different magnetic fields h, from ref. 16. $h = 0.01$

corresponds to a field of 6 T. $T = 0.1$ corresponds to a temperature of 1/40 of the bandwidth used in the calculation.

having its spin parallel to $\mathbf{S}_c^j$ so ferromagnetic order maximizes the hopping and antiferromagnetic order minimizes it. This connection between magnetic correlations and transport is called "double-exchange"[8] and has been extensively studied[9,10].

Double-exchange provides a mechanism for the resistivity to change on passing through the paramagnetic–ferromagnetic transition: in the high-temperature phase the spins are disordered and scatter electrons, while in the low-temperature phase the spins are ordered, and do not scatter electrons. The difficulty is that even maximal spin disorder does not scatter electrons very much[9]. The spin scattering increases the resistivity somewhat, but (as has been shown most convincingly in recent numerical work[11]) it localizes only a negligible fraction of the carriers in the band. Additional physical processes must therefore be invoked to explain the observed insulating behaviour. I will argue here that the crucial additional process is electron–lattice coupling.

Electron–lattice coupling

There are two sorts of electron–lattice coupling. One, called 'tolerance factor', involves the effect of the static crystal structure on electron hopping. In $Re_{1-x}A_xMnO_3$, different choices for Re and A have different atomic sizes and therefore produce different internal stresses acting on the Mn–O–Mn bonds. If the bond is compressed, it reacts by buckling, and the effective Mn–Mn hopping is a very sensitive function of this buckling, decreasing rapidly as the buckling increases. The change in average hopping amplitude as a function of average Re/A size has been studied in detail[12].

The other electron–lattice coupling is the conventional dynamical electron–phonon coupling, which links instantaneous deviations of atoms from their ideal crystallographic positions to the instantaneous deviations of electron configuration from the average values. There are three important modes: a 'breathing' distortion of the O_6 octahedron around a given Mn which couples to changes in the e_g charge density, and two linearly independent even-parity uniaxial volume-preserving distortions (Jahn–Teller modes) which couple to preferential occupancy of one e_g orbital over the other. One such distortion, indicated by arrows on Fig. 1a, involves a stretching of the Mn–O bonds along z and compression in the x–y plane and is favoured by occupancy of the '$3z^2 - r^2 > e_g$' orbital. The corresponding change in the energy levels is shown in Fig. 1b.

A strong electron–phonon coupling may localize carriers, because the presence of an electron in a given Mn orbital causes a local lattice distortion which produces a potential minimum: this

minimum tends to trap the electron in that orbital. If the coupling is strong enough, these tendencies lead to the formation of a 'self-trapped' state called a polaron. However, according to the Pauli principle, two electrons can only occupy the same orbital if they have opposite spin; in the manganites this is prevented by the strong Hunds coupling, so 'bipolarons' do not occur. I note also that the usual polaron problem involves a single electron coupled to a deformable medium. The novelty of the manganites is the occurrence of self-trapping at a high density of electrons.

Self-trapping competes with the delocalizing tendency of electron hybridization. The competition is parametrized by a dimensionless quantity λ which is the ratio of the energy E_{latt} gained from the electron–phonon coupling in the absence of hybridization to the 'bare' electron kinetic energy t_{eff}; thus $\lambda \approx E_{latt}/t_{eff}$. In the manganites, the nature of the double-exchange and the tolerance factor means that t_{eff} and therefore λ may be changed over a wide range by varying magnetic field and temperature, which change spin correlations, and also by changing Re and A, which change the tolerance factor and carrier concentration. Several recent theoretical papers[13–16] have shown that the change in λ may be large enough to affect dramatically the behaviour of the materials, causing, for example, the high-temperature 'insulating' behaviour of $La_{0.75}Ca_{0.25}MnO_3$. The argument is that in the high-temperature state t_{eff} is sufficiently small that λ is so large that the electron–phonon interaction localizes the electrons; as T is decreased through $T_c(x)$, the growing ferromagnetic order increases t_{eff} and thus decreases λ sufficiently that metallic behaviour occurs. One calculation[15] (based on these ideas) of the field and temperature dependence of the resistivity is shown in Fig. 3b; the qualitative agreement with the data suggests the calculation contains the correct physics.

Evidence for strong electron–lattice coupling

Jahn–Teller effects are known to be strong in at least some members of the family. For example, $LaMnO_3$ is an insulator with one e_g electron per Mn. In this compound the Jahn–Teller coupling causes an 'antiferrodistortive' deviation from the basic perovskite structure, in which some Mn–O bond lengths decrease and others increase, in a '$(\pi, \pi, 0)$' pattern which alternates from Mn-site to Mn-site throughout the crystal[17]. Because the changes in bond length are long-range ordered and coherent throughout the crystal, they may be determined via conventional Bragg diffraction experiments: and have been found to be large: ~0.2 Å or 10% of the mean Mn–O distance, implying a very strong Jahn–Teller coupling in $LaMnO_3$. As x is increased from 0, the structural transition temperature and the size of the coherent, long-range structural distortion both decrease rapidly[17]. However, the theoretical models discussed above[15,16] predicted that strong local distortions would persist over a wide range of doping, in the $T > T_c$ 'insulating' phase.

Recent advances in experimental technique, especially improvements in the measurement of extended X-ray absorption fine structure (EXAFS) and neutron pair distribution functions (PDF), have produced striking evidence for the predicted existence of local lattice distortions. Figure 4 shows the results of EXAFS measurements by Booth et al.[18] of the root-mean-square variation in Mn–O bond length for different members of the $La_{1-x}Ca_xMnO_3$ series. The open symbols at the top of the figure are data for $LaMnO_3$ where, as discussed above, strong long-range distortions occur. The open symbols at the bottom of the figure pertain to $CaMnO_3$, where no distortion at all occurs because the e_g band is empty. At intermediate dopings and high temperatures the variation in the bond-length distribution is of the order of the value found in the long-range ordered material; this indicates that large-amplitude local distortions, of a size comparable to that in the undoped material, exist even though no coherent part is visible in conventional Bragg scattering. As temperature is lowered through T_c, the distortion drops to a value typical of the undistorted
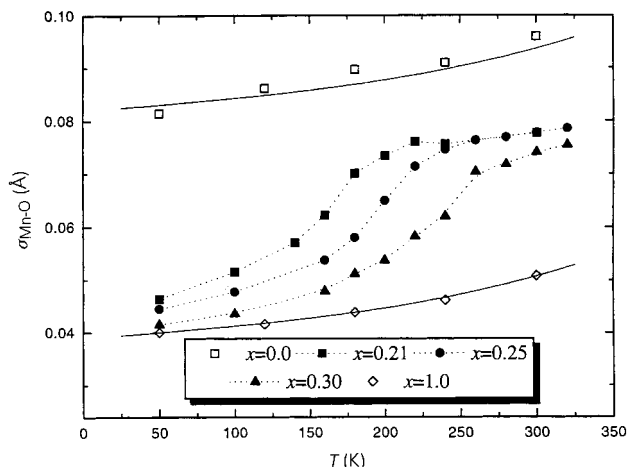
Figure 4 Temperature dependence of variance of Mn–O bond length for $La_{1-x}Ca_xMnO_3$ at various concentrations x, as determined by Booth et al.[18]. In ref. 18 these data are plotted as σ^2 versus T.

Legend in figure: $\square$ $x=0.0$ $\blacksquare$ $x=0.21$ $\bullet$ $x=0.25$ $\blacktriangle$ $x=0.30$ $\diamond$ $x=1.0$

Axis labels: σ_{Mn-O} (Å) versus T (K)

material. Other authors have obtained qualitatively similar results[19,20], although the details of the data and interpretations differ.

Additional experimental results consistent with the importance of an electron–lattice coupling include optical conductivity[21], the large oxygen-isotope effect on the ferromagnetic T_c (ref. 22), the strong pressure dependence of physical properties[23–25], and the ubiquity at $x \geq 0.5$ of 'charge-ordered' phases accompanied by large changes in Mn–O bond lengths[26].

Challenges and opportunities

The manganites are a richly varied and fascinating system. Although a suggestive qualitative agreement between theory and experiment exists, much more needs to be done. Variability of data is a significant issue. For example, the optical data of ref. 21 are qualitatively similar to those reported by other workers[27], but differ substantially in detail. Also, as discussed in refs 15, 16 for instance, the theoretical calculations are oversimplified and a proper treatment including doping dependence, intersite correlations and the Coulomb interaction is urgently needed.

The materials also offer the intriguing possibility of establishing an explicit connection between atomic-scale 'correlated electron' physics and such materials-science questions as the effect of strain on physical properties. The hydrostatic pressure dependence of the ferromagnetic T_c has been measured[25], but if Jahn–Teller effects are important then the effects of volume-preserving uniaxial strain will be much larger. Preliminary work[28] supports this idea, and suggests that a quantitative understanding of strain effects may be possible.

Issues arising in the context of the manganites may be more generally important. One particularly significant theme is the relation between electron correlations, local structure, long-range order and physical properties. In the manganites there is clearly an interesting interplay between these phenomena, and connections have also been suggested for many other materials, including the high-T_c superconductors. Sophisticated techniques for examining local correlations are becoming available, and the manganites seem an ideal system for developing and validating them. This, and the intrinsic interest of the materials, should stimulate research for a long time to come. □

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