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Orbital ordering and strong correlations in manganites

By M. W. Long

School of Physics, University of Birmingham,
Edgbaston, Birmingham B15 2TT, UK

We investigate the doped perovskite manganites by using some elementary strong-correlation models. We focus mainly on the electronic motion through double-exchange and include the spin and lattice fluctuations solely to lift any residual degeneracy. We consider the low-energy physics of the strong-coupling limit, incorporating the spatial structure of the orbitals carefully. Due to a mismatch between the point-symmetries of the orbitals and the lattice, we find a highly geometrically frustrated Hubbard-like model. When orbital superexchange is dominant, the system finds ordering very difficult, and when the charge-carrier motion is dominant, the styles of orbital order are expected to be fairly complicated. Unless the system exhibits Fermi-liquid behaviour, the strong correlations are suggested to be uncontrollable at present.

Keywords: manganites; orbital ordering; frustration; Hubbard model

1. Introduction

Perovskite manganites have been much studied because of their giant magnetoresistance (Ramirez 1997). In simple terms, due to the presence of strong correlations, the electrons may only move freely between a very restricted subset of the available states: pairs of atoms with spins and orbitals carefully aligned. At high temperature the configurations are disordered and the motion is curtailed, whereas at low temperature the atoms become highly correlated in order to permit this motion. Since the electronic motion is enhanced when all the atoms have parallel spins, there is a major change in resistive properties when the system goes ferromagnetic. Since the resistance is being controlled by this ferromagnetic ordering, there is a large effect when a magnetic field is introduced to interfere with this ordering. This basic physical picture is undoubtedly substantially correct, but there are a few 'details' which need to be considered in order to assess their role, if any.

One clear fact is that structural effects are significant in the region where the system is going ferromagnetic (Billinge *et al*. 1996). Indeed, a sizeable isotope effect is measured at the ferromagnetic phase transition (Zhao *et al*. 1996), a fact not easy to explain using a solely magnetic description. Another related fact is the existence of an orbital degeneracy present on the manganese atom: the systems of interest are $La_{1-x}Sr_xMnO_3$ and variants. The chemistry is closed shell La^{3+}, closed shell Sr^{2+}, closed shell O^{2-} and hence a mixed valance for the manganese atom $Mn^{3+}_{1-x}Mn^{4+}_x$. The Mn^{4+} ion involves three electrons in the three t_{2g} orbitals, strongly aligned and behaving like an effectively closed shell to charge fluctuations. The Mn^{3+} ion involves four electrons, three in the t_{2g} orbitals, also irrelevant to the charge motion, together

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with one remaining electron in the e_g orbitals. Since there are two e_g orbitals, there is a degeneracy associated with which orbital to put the fourth electron in. It is this degeneracy, and how it is lifted which is the issue of interest in the current article. It should be noted that these e_g orbitals are usually highly anisotropic, and hence if only one is ever occupied, one would expect a measurable local structural distortion: a Jahn–Teller distortion (Goodenough 1955). Static distortions are not easily observed in the metallic regime, and the structural anomalies are often explained in terms of dynamic Jahn–Teller distortions.

When modelling the manganites, one needs to dispense with most of the complications and write down an elementary model which captures the physics. This is a significant task, because it is not always clear which physical interaction is the root cause of any particular experimentally observed effect. The magnetism is directly measurable, and so has been fairly cleanly explained (Perring *et al.* 1996; Millis *et al.* 1995), but any orbital ordering is either guessed, or surmised from structural distortions or consistency with the observed magnetic state. The Jahn–Teller effect involves the lifting of the orbital degeneracy, making use of structural distortions to provide an energy gain. In the manganites it is not at all clear that it is a strain energy which dominates. In the doped ferromagnetic region of the phase diagram there is no evidence for static distortions, and further, at the ferromagnetic phase transition, there is clear evidence of a structural component to the transition itself. This raises the possibility that it is the motion dictating the spin physics, through so-called double-exchange, which also dictates the orbital ordering. It is this possibility that we investigate here.

There are a host of different phenomena which we ignore in this investigation and these will now be listed: First, temperature will be ignored. Even though the interesting physical transition is when temperature disorders the system, we will investigate solely zero temperature and try to assess the likely orbital order. Secondly, the spin physics will be ignored. Once again, the crucial physical effect is the interference to the magnetic ordering when a field is imposed close to the transition, but we will be at low temperature when all the spins are aligned and we have a pure ferromagnet. Thirdly, there are clear signatures of structural effects involved in the transition and we will completely ignore all these effects arguing that they slavishly follow the desires of the correlated electronic motion. Fourthly, we ignore the static structural distortions which are known to occur at certain regions of parameter space, on the grounds that they are too difficult to incorporate in the modelling. This is a source of physical errors which we will allude to. Finally, we will ignore almost all of the atomic physics details, like the t_{2g} orbitals, and will restrict attention to the e_g orbitals.

The investigation involves only two degrees of freedom per atom, the two possible e_g orbitals, which are only presumed occupiable with electrons whose spins are parallel to the otherwise irrelevant t_{2g} electrons on the atom. We take the spatial nature of these orbitals seriously, representing them carefully as pseudo-spins. The only other input into our modelling is the strong correlations and the consequent occupancy restrictions. Our charge-carriers do not behave as free electrons but are dominated by Coulombic atomic physics, exhibiting intermediate valence between only two permitted charge states.

The competition between direct- and superexchange is quite transparent in perturbation theory; it occurs at fourth order. The initial gambit is an oxygen electron hopping on to a Mn^{3+} ion to form a Mn^{2+} ion. The spin 5/2 state is very strongly

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stabilized by Hund's rules and is probably dominant. The second step is one of two: either the e_g electron on the other Mn^{3+} neighbour replaces the oxygen electron which moved, or a second oxygen electron hops on to the remaining Mn^{3+}, converting it to Mn^{2+} as well. The final two hops then repair the damage. The first process can only occur if the original spins are parallel, whereas the second 'prefers' the original spins to be antiparallel. There is a wide range of antiferromagnetic states found in the experimental phase diagram of $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ (Wollan & Koehler 1955) and we are erroneously presuming that the spin physics is ferromagnetic. The conclusions that we infer are all therefore subject to this unquantified experimental dominance of the omitted antiferromagnetic bonds.

We will generate a type of Hubbard model in describing the orbital degrees of freedom. There are many similarities between our development and that of the standard Hubbard model, but there are two fundamental differences that make the physics quite different. First, the orbitals do not have the same point symmetry as the lattice. This introduces a style of frustration quite reminiscent but not identical to geometric frustration. The difficulties that the system has in finding an appropriate classical order all stem from this source. Secondly, the isotropy of the spins which much simplifies the standard Hubbard model is not present. The overall quantization direction for any magnetic order is irrelevant for the Hubbard model. For our pseudo-spin Hubbard model, the main task is to try to *find* the chosen quantization direction preferred by the system.

In § 2 we develop the model, in § 3 we investigate the Mott insulating limit, demonstrating a surprising failure to order, and in § 4 we look at the metallic regime in the very low doping limit. This final problem is seen to be very difficult as we exhibit by analysing simpler but equally subtle analogue models. In § 5 we conclude, showing that we have not improved the understanding of the manganites to any great degree.

2. An effective Hubbard-like model

We are modelling the e_g orbitals, and our first task is to represent them in a useful way. We have chosen to use a pseudo-spin representation, where the two orbitals play the equivalent role as the two states of a spin-half. Much of our development corresponds to the previous work of Kugel & Khomskii (1972, 1973), although we arrive at a rather different eventual argument. For the current problem there is no pseudo-spin isotropy, and the interactions are strongly coupled to space. We elect to use the choice,

$$\begin{aligned} u^\dagger|0\rangle &\equiv [5/8\pi]^{1/2}(\hat{x}^2\omega^2+\hat{y}^2\omega+\hat{z}^2)\psi(r) \\ &= [5/8\pi]^{1/2}(\sin^2\theta(\cos^2\phi\omega^2+\sin^2\phi\omega)+\cos^2\theta)\psi(r), \\ d^\dagger|0\rangle &\equiv [5/8\pi]^{1/2}(\hat{x}^2\omega+\hat{y}^2\omega^2+\hat{z}^2)\psi(r) \\ &= [5/8\pi]^{1/2}(\sin^2\theta(\cos^2\phi\omega+\sin^2\phi\omega^2)+\cos^2\theta)\psi(r), \end{aligned}$$

where $\omega=\exp(2\pi\mathrm{i}/3)$ is a non-trivial cube-root of unity, $\psi(r)$ is the radial wavefunction and $|0\rangle$ denotes the Mn^{4+} ion. This choice provides the unique point-group symmetric combinations of the orbitals which map on to each other times phases under the action of the point-group. The associated charge density is symmetric under the point-group.

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Our first task is to represent the double-exchange in this description. We will use a tight-binding description and assume that all the action passes across the oxygen atoms and that the direct manganese interactions are irrelevant. Since the O^{2-} are closed-shell, the initial gambit needs to be an oxygen electron hopping on to a manganese ion. For the double-exchange process, this requires to be on to an 'empty' Mn^{4+} ion. The final step is then for the e_g orbital on the Mn^{3+} ion to replace the electron on the intermediate oxygen atom. The available states on the oxygen atom are s- or p-electrons, and hence *only one* of the two e_g orbitals can be active in this process. For the case of hopping in the z-direction, the

$$\frac{1}{\sqrt{2}}[u^\dagger + d^\dagger]|0\rangle \equiv \left[\frac{15}{8\pi}\right]^{1/2} \frac{1}{\sqrt{6}}(-\hat{x}^2 - \hat{y}^2 + 2\hat{z}^2)\psi(r)$$

can move, whereas the

$$\frac{\mathrm{i}}{\sqrt{2}}[u^\dagger - d^\dagger]|0\rangle \equiv \left[\frac{15}{8\pi}\right]^{1/2} \frac{\mathrm{i}(\omega^2 - \omega)}{\sqrt{6}}(\hat{x}^2 - \hat{y}^2)\psi(r)$$

are immobile. For each of the possible directions of motion, there is a different combination which is mobile and an orthogonal combination which is immobile. Under these assumptions the double-exchange may be rewritten:

$$H_1 = -\tfrac{1}{2}t\sum_{\alpha}\sum_{\langle ii'\rangle_\alpha}[\mathrm{e}^{-\mathrm{i}\phi_\alpha/2}u_i^\dagger + \mathrm{e}^{\mathrm{i}\phi_\alpha/2}d_i^\dagger][\mathrm{e}^{\mathrm{i}\phi_\alpha/2}u_{i'} + \mathrm{e}^{-\mathrm{i}\phi_\alpha/2}d_{i'}],$$

where t is the matrix element, $\alpha = x, y, z$ is a label ranging over the three Cartesian directions of motion, $\langle ii'\rangle_\alpha$ denotes nearest-neighbours in the α direction and $\phi_\alpha = 2\pi/3,\ -2\pi/3,\ 0$ are the three phases picked up in the motion. It is useful to employ spin-half representations in order to interpret this description. The classical state with the pseudo-spin orientated in a direction defined by polar coordinates is

$$|\theta,\phi\rangle \equiv [\cos\tfrac{1}{2}\theta \mathrm{e}^{-\mathrm{i}\phi/2}u^\dagger + \sin\tfrac{1}{2}\theta \mathrm{e}^{\mathrm{i}\phi/2}d^\dagger]|0\rangle \tag{2.1}$$

and so we may reinterpret our Hamiltonian as

$$H_1 = -t\sum_{\alpha}\sum_{\langle ii'\rangle_\alpha}|i,\pi/2,\phi_\alpha\rangle\langle i',\pi/2,\phi_\alpha| \tag{2.2}$$

and the component of pseudo-spin along the orientation of the bond, $(\pi/2, \phi_\alpha)$ in polar coordinates, is the 'piece' that hops. The bonds are extremely directional, and only the component of the pseudo-spin parallel to the direction of the bond can hop on to the electron. The bonds are restricted to the x–y plane, in pseudo-spin space, and are at 120° to each other. It is the fact that the average of the three bonds vanishes which causes all the geometric frustration. The general case of orbital frustration corresponds to

$$\sum_\alpha \mathrm{e}^{\mathrm{i}\phi_\alpha} = 0 \qquad \Rightarrow \qquad \sum_\alpha \mathrm{e}^{2\mathrm{i}\phi_\alpha} = 0$$

for most cases, and we will consider several systems subject to this frustration.

Note that

$$|\langle\theta',\phi'|\theta,\phi\rangle|^2 = \cos^2\tfrac{1}{2}\alpha,$$

where α satisfies

$$\cos\alpha = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi - \phi')$$

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and is the angle between the two classical pseudo-spin directions. The modulus of the hopping matrix element, arising from the action of equation (2.2) above, is proportional to the cosine of *half* the angle between the current spin direction and the orientation of the bond and *not* the classical projection as might naively be guessed.

There is a second *natural* pair of orthonormal orbitals,

$$\frac{u^\dagger + \mathrm{i}d^\dagger}{1+\mathrm{i}}|0\rangle = \left[\frac{15}{8\pi}\right]^{1/2}\left(-\frac{\sqrt{3}+1}{2\sqrt{3}}\hat{x}^2 + \frac{\sqrt{3}-1}{2\sqrt{3}}\hat{y}^2 + \frac{1}{\sqrt{3}}\hat{z}^2\right),$$

$$\frac{u^\dagger - \mathrm{i}d^\dagger}{1-\mathrm{i}}|0\rangle = \left[\frac{15}{8\pi}\right]^{1/2}\left(\frac{\sqrt{3}-1}{2\sqrt{3}}\hat{x}^2 - \frac{\sqrt{3}+1}{2\sqrt{3}}\hat{y}^2 + \frac{1}{\sqrt{3}}\hat{z}^2\right),$$

which are real and have *orthorhombic* symmetry. These orbitals play an important role in the analysis. Similar considerations are encountered in analogous work (Koshibae *et al*. 1997).

The operators $u_i^\dagger$ and $d_i^\dagger$ create electrons and so are subject to Fermi statistics. The only local inclusion permitted with the current degrees of freedom is an atomic physics energy,

$$H_2 = U\sum_i u_i^\dagger u_i d_i^\dagger d_i,$$

which corresponds to the expense of creating Mn^{2+} and Mn^{4+} ions from a pair of Mn^{3+} ions. The insulating nature of the undoped parent compounds leaves us in no doubt that $U \gg t$ and we are dealing with a doped Mott insulator. Obviously, there are additional interactions which are not catered for by this interaction, but this is the only one permitted under our ferromagnetic assumption.

We arrive at the elementary model for the lifting of the pseudo-spin degeneracy:

$$H = -\tfrac{1}{2}t\sum_\alpha\sum_{\langle ii'\rangle_\alpha}[\mathrm{e}^{-\mathrm{i}\phi_\alpha/2}u_i^\dagger + \mathrm{e}^{\mathrm{i}\phi_\alpha/2}d_i^\dagger][\mathrm{e}^{\mathrm{i}\phi_\alpha/2}u_{i'} + \mathrm{e}^{-\mathrm{i}\phi_\alpha/2}d_{i'}] + U\sum_i u_i^\dagger u_i d_i^\dagger d_i,$$

a sort of Hubbard model with spin-dependent hopping. The usual Hubbard model has isotropic spin-physics, with each bond conserving the spin on hopping. The major modification in this model is that for each bond only one component of the spin is permitted to hop and the spin is 'projected' on to this component in the process of the hop.

The use of the model is fairly clear, but the situations where it might be appropriate are much less clear. For the series $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3$, the parent compound, $x = 0$, involves single occupancy of the cubic lattice and then doping, $x > 0$, corresponds to the introduction of vacancies in the lattice. This situation is totally analogous to that in perovskite superconductors, where a half-filled antiferromagnetic insulator is doped with vacancies. In the superconductors, the hole motion is untroubled by any structural effects, because the degeneracy is spin and only couples weakly to the lattice. In the manganites the degeneracy is orbital, and is therefore very strongly coupled to the lattice leading to effects which might dominate the hole motion. Nonetheless, we will pursue the same generic paths that have been trod in the investigation of the superconductors: we will analyse the parent compound to find the preferred Mott order and then look at the role of the hole motion. The hole motion on its own can be investigated, or the motion of holes in the presence of the Mott order can be investigated.

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The order predicted in the Mott insulating limit is best found by taking the very strong coupling limit, $t/U \mapsto 0$. In this limit with single occupancy, the degeneracy is lifted by second-order degenerate perturbation theory, leading to

$$H=\frac{t^2}{U}\sum_{\alpha}\sum_{\langle ii'\rangle_\alpha}[S_i^\alpha S_{i'}^\alpha-\tfrac{1}{4}]$$

in terms of the components of pseudo-spin along the orientation of the relevant bonds

$$S^\alpha=\cos\phi_\alpha S^x+\sin\phi_\alpha S^y,$$

and the pseudo-spin operators satisfy

$$u^\dagger d\equiv S^+=S^x+\mathrm{i}S^y,\qquad d^\dagger u\equiv S^-=S^x-\mathrm{i}S^y,\qquad u^\dagger u-d^\dagger d\equiv 2S^z.$$

Each bond leads to an antiferromagnetic *Ising* interaction between the two spins, but the particular component is along the orientation of the bond.

For a Mott insulating situation, the most sensible *limiting* Hamiltonian to consider is then

$$H=-\tfrac{1}{2}t\sum_{\alpha}\sum_{\langle ii'\rangle_\alpha}[\mathrm{e}^{-\mathrm{i}\phi_\alpha/2}u_i^\dagger+\mathrm{e}^{\mathrm{i}\phi_\alpha/2}d_i^\dagger][\mathrm{e}^{\mathrm{i}\phi_\alpha/2}u_{i'}+\mathrm{e}^{-\mathrm{i}\phi_\alpha/2}d_{i'}]+\frac{t^2}{U}\sum_{\alpha}\sum_{\langle ii'\rangle_\alpha}[S_i^\alpha S_{i'}^\alpha-\tfrac{1}{4}],$$

the analogue of the t–J model in perovskite superconductivity.

3. Orbital ordering from superexchange

In this section we will investigate the Mott insulating parent compound, $\mathrm{LaMnO_3}$, under our modelling assumptions. This material finds all the manganese ions as Mn^{3+} and hence each atom has a singly occupied e_g orbital. The experimental conclusion is that an atypical *antiferromagnet* is stabilized, with ferromagnetic planes alternating in orientation as we move parallel to the z-axis. The 'standard' explanation is that the occupied d-orbitals couple ferromagnetically and reside in the x–y plane, while essentially 'empty' orbitals couple antiferromagnetically by superexchange up the z-axis. As we will see, we are not permitted the luxury of this simple explanation.

The model we have previously developed is

$$H=\frac{t^2}{U}\sum_{\alpha}\sum_{\langle jj'\rangle_\alpha}[S_j^\alpha S_{j'}^\alpha-\tfrac{1}{4}]$$

in terms of the bonding components of the pseudo-spins:

$$S_j^\alpha=S_j^x\cos\phi_\alpha+S_j^y\sin\phi_\alpha.$$

Even though we are dealing with pseudo-spin-half and quantum mechanics at its strongest, we start out looking to classical order. There appears little point in orientating pseudo-spins out of the x–y plane, and so we make the assumption that each classical spin may be described by an angle ϕ_i. The classical energy then becomes

$$H_0=\frac{t^2}{U}\sum_{\alpha}\sum_{\langle jj'\rangle_\alpha}[\cos(\phi_j-\phi_\alpha)\cos(\phi_{j'}-\phi_\alpha)-\tfrac{1}{4}].$$

The problem is solvable using the periodicity with

$$\mathrm{e}^{\mathrm{i}\phi_j}=\sum_{\boldsymbol{k}}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j}S_{\boldsymbol{k}}$$

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in terms of complex numbers $S_{\boldsymbol{k}}$. Only particular combinations appear in the Hamiltonian, which reduces to

$$H_0 = N\frac{t^2}{4U}\sum_{\boldsymbol{k}\alpha}[\gamma_{\boldsymbol{k}\alpha} - \gamma_{\boldsymbol{0}\alpha}]|T|^2_{\boldsymbol{k}\alpha}$$

in terms of the combinations

$$T_{\boldsymbol{k}\alpha} = \mathrm{e}^{-\mathrm{i}\phi_\alpha}S_{\boldsymbol{k}} + \mathrm{e}^{\mathrm{i}\phi_\alpha}S^*_{-\boldsymbol{k}}$$

and the structure factors,

$$\gamma_{\boldsymbol{k}\alpha} = \frac{1}{N}\sum_{\langle jj'\rangle_\alpha}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_j-\boldsymbol{R}_{j'})},$$

where N is the number of atoms involved. The fact that the ϕ_j are phases is then controlled by the constraints

$$\sum_{\boldsymbol{k}\alpha}T^*_{\boldsymbol{k}+\boldsymbol{q}\alpha}T_{\boldsymbol{k}\alpha} = 2N^{\mathrm{b}}\sum_{\boldsymbol{G}}\delta_{\boldsymbol{q},\boldsymbol{G}},$$

where N^{b} is the number of bond-orientations, and $\boldsymbol{G}$ denotes the reciprocal lattice. This result relies heavily on the presence of the *orbital frustration*, which appears with

$$\sum_\alpha \mathrm{e}^{2\mathrm{i}\phi_\alpha} = 0$$

and is employed in showing that the $T_{\boldsymbol{k}\alpha}$ may be used to parametrize the constraints.

As with most classical magnetism problems, the ground-state is achieved by placing the spin-density at the minimum of the structure factor. For the current system we have a bipartite lattice and consequently a unique place in reciprocal-space which minimizes the structure factor, the standard corner of the zone where unfrustrated antiferromagnetism would be expected. Interestingly, there is a *second* style of solution. We may also find that

$$T_{\boldsymbol{k}\alpha^*} = 0$$

for some particular α^* and some spin density along the line in space where the other structure factors are minimized. This peculiar style of state is present in all the systems that we have analysed.

The standard antiferromagnetic orbital ordering involves all pseudo-spins being parallel on each sublattice, and antiparallel between sublattices. Such a state corresponds to using a pair of orthogonal orbitals, one on each sublattice. At this order the choice of which particular pair of orbitals to use is *not* made and any pair remains energetically equivalent. The second style of solution involves the *orthorhombic* orbitals: each orbital points in a major direction and then has a medium and a minor direction. The major and minor directions are interlocked in a two-dimensional chequer-board arrangement, but the medium direction is equivalent for either of the two arrangements. This permits a free stacking of the two-dimensional planes parallel to the third direction.

In the real systems the orbital degeneracy is clearly lifted, and so we now investigate the natural mechanisms which lift it under the current assumptions. The most natural route is via the innate buckling which is ever-present in perovskites. Due to a mismatch of atom sizes, perovskites almost always buckle to some extent, and

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the parent compound $\mathrm{LaMnO_3}$ is no exception, although in this case a cooperative Jahn–Teller distortion is responsible for the structural change. In a tetragonal environment, the hopping matrix elements are altered with one of two natural results. If $t_3 > t_2 = t_1$, then the usual $\hat{x}^2 - \hat{y}^2$ and $3\hat{z}^2 - 1$ are stabilized, whereas if $t_3 < t_2 = t_1$ then the orthorhombic orbitals are stabilized. The real system does *not* fit into this scheme: the system becomes *antiferromagnetic* even though the dominant interactions are presumed ferromagnetic. Ferromagnetic planes are observed which are stacked antiferromagnetically along the z-axis. It is tempting to attribute this to strong ferromagnetically coupled orthorhombic orbitals in-plane, which do not couple along the z-axis, which therefore is controlled by the weaker antiferromagnetic exchange of the t_{2g} orbitals, but for the current modelling this is bogus. Using only e_g orbitals, the only way to eliminate coupling up the z-axis is to force $\hat{x}^2 - \hat{y}^2$ orbitals everywhere. This is completely opposed to the picture of *antiferromagnetic* orbital order that we have developed. If the orbitals alternate, then there is necessarily an *equal average* hopping in all three Cartesian directions. To escape from this situation, one needs to employ some s-orbital character on the transition metal ions, in order to eliminate the contributions along the z-axis, a very unpalatable inclusion, or alternatively one needs to include some hitherto ignored phenomena. It is possible that the structural energy causes the observed order and this was not modelled here, but it is also possible that the basic magnetism ideas were *wrong* and we will investigate this later.

The comparison between ferromagnetic and antiferromagnetic bonding is more complicated than might be anticipated. The physical idea is that in a ferromagnetic bond the neighbouring orbitals are orientated 'antiparallel'. One direction of motion for the oxygen electrons is then blocked and the blocking electron can hop, via the oxygen, into the empty orbital. The other directions are then expected to be 'irrelevant'. Unfortunately, the nature of the e_g orbitals is to have lobes in all directions, and consequently there are sizeable energetic contributions in all directions. The orthorhombic orbitals are expected to yield the strongest bonds in the x–y plane and be minimal along the z-axis. Direct calculation reveals that the bonding energies are

$$S_i^\alpha S_{i'}^\alpha - \tfrac{1}{4} \mapsto -\tfrac{7}{16}, -\tfrac{7}{16}, -\tfrac{1}{4}$$

and a sizeable contribution up the z-axis. This is to be compared with

$$S_i^\alpha S_{i'}^\alpha - \tfrac{1}{4} \mapsto -\tfrac{5}{16}, -\tfrac{5}{16}, -\tfrac{1}{2}$$

for the usual orbitals. The differences are small in comparison to the loss of the $-1/4$ which arises when a ferromagnetic bond is flipped to an antiferromagnetic bond. Any explanation using the current assumptions would require an artificially tuned balance between the ferro- and antiferromagnetic interactions, as we shall show.

On a fairly theoretical level, we can ask about other phenomena that might lift the orbital degeneracy in our chosen model. Since we have pseudo-spin-half, it could be that quantum fluctuations are relevant. Although we will not develop the theory here, the result of the investigation is intriguing. The usual $\hat{x}^2 - \hat{y}^2$ and $3\hat{z}^2 - 1$ orbitals are stabilized but with a surprising wrinkle. For these states, one of the three styles of bonds is *saturated*. Fluctuations cannot gain anything from these Ising bonds. The *dimensionality* of the resulting fluctuations is one lower than expected: the fluctuations are decoupled between neighbouring planes with saturated bonding. The lower-dimensional fluctuations are stronger and this is what stabilizes the phase

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with a saturated bond. The fluctuations are *so* strong, however, that they destroy the long-range order! Thermal fluctuations in two dimensions eliminate long-range order, and for our three-dimensional system, the stabilized phase involves two-dimensional fluctuations and hence would be expected to destroy the long-range order. Unfortunately, this rather pure argument is overtaken by structural distortions and a host of other important classical effects which dominate.

Due to the complete failure of our picture to describe the experimental phase, we have had to consider the possibility that the antiferromagnetic bonds are actually *dominant* and that the usual explanation in the literature is incomplete. The fact that the lattice shrinks along the antiferromagnetically coupled z-axis is good evidence that the antiferromagnetic bond is the strongest, but the lattice distortions in the x–y plane are good evidence for anisotropic orbitals in-plane which would be caused by ferromagnetic dominance. We will employ the simplest comparison between the two types of bonds to try to resolve this problem theoretically.

A simple classical calculation highlights the difficulties. Let us assume a pure cubic system and no quantum fluctuations. The orientation of the t_{2g} orbitals strongly suppresses fluctuations. A direct comparison between ferromagnetism and antiferromagnetism is easy once the orbitals have been well represented. We use the description based on equation (2.1) with arbitrary ϕ,

$$|\phi\rangle = \alpha[\cos(\phi-\phi_1)\hat{x}^2 + \cos(\phi-\phi_2)\hat{y}^2 + \cos(\phi-\phi_3)\hat{z}^2] = \frac{1}{\sqrt{2}}[\mathrm{e}^{-\mathrm{i}\phi}u^\dagger + \mathrm{e}^{\mathrm{i}\phi}d^\dagger]|0\rangle$$

for an in-plane pseudo-spin. Note that the angle ϕ is now a *classical* variable, and the quantum half-angle has been dropped. The other orthogonal orbital is

$$|\bar{\phi}\rangle = \alpha[\sin(\phi-\phi_1)\hat{x}^2 + \sin(\phi-\phi_2)\hat{y}^2 + \sin(\phi-\phi_3)\hat{z}^2] = \frac{\mathrm{i}}{\sqrt{2}}[\mathrm{e}^{-\mathrm{i}\phi}u^\dagger - \mathrm{e}^{\mathrm{i}\phi}d^\dagger]|0\rangle$$

and we can readily perform the classical calculations as a function of the type of orbital, represented through ϕ.

First let us examine the situation with antiparallel orbitals. Each of the three ferromagnetic bonds provides

$$\begin{aligned} F_\alpha &= -J_F[\cos^4(\phi-\phi_\alpha) + \sin^4(\phi-\phi_\alpha)] \\ &= -J_F + 2J_F\cos^2(\phi-\phi_\alpha)\sin^2(\phi-\phi_\alpha) \\ &= -J_F + \tfrac{1}{2}J_F\sin^2(2\phi-2\phi_\alpha) \\ &= -\tfrac{3}{4}J_F - \tfrac{1}{4}J_F\cos(4\phi-4\phi_\alpha), \end{aligned}$$

whereas each of the three antiferromagnetic bonds provides

$$\begin{aligned} A_\alpha &= -4J_A\cos^2(\phi-\phi_\alpha)\sin^2(\phi-\phi_\alpha) \\ &= -J_A\sin^2(2\phi-2\phi_\alpha) \\ &= -\tfrac{1}{2}J_A + \tfrac{1}{2}J_A\cos(4\phi-4\phi_\alpha), \end{aligned}$$

where $J_F \sim t^4\Delta^{-2}U_\mathrm{d}^{-1}$ and $J_A \sim t^4\Delta^{-2}(2\Delta+U_\mathrm{p})^{-1}$ are the relevant matrix elements for the two processes, in terms of t the hopping, Δ the cost of $\mathrm{Mn}^{3+}\mathrm{O}^{2-} \mapsto \mathrm{Mn}^{2+}\mathrm{O}^-$, U_d the cost of $\mathrm{Mn}^{3+}\mathrm{Mn}^{3+} \mapsto \mathrm{Mn}^{2+}\mathrm{Mn}^{4+}$ and U_p the cost of $\mathrm{O}^{2-}\mathrm{O} \mapsto \mathrm{O}^-\mathrm{O}^-$, and we have been careful with the combinatorics, in the sense that either of the two antiparallel electrons can hop but only one of the ferromagnetic electrons can. Since

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the two processes are mutually exclusive, we need to compare

$$
\begin{aligned}
E_0 &= A_1 + A_2 + A_3 = -\tfrac{3}{2}J_A,\\
E_1 &= A_1 + A_2 + F_3 = -J_A - \tfrac{3}{4}J_F - [\tfrac{1}{2}J_A + \tfrac{1}{4}J_F]\cos(4\phi) \mapsto -\tfrac{3}{2}J_A - J_F,\\
E_2 &= F_1 + F_2 + A_3 = -\tfrac{1}{2}J_A - \tfrac{3}{2}J_F + [\tfrac{1}{2}J_A + \tfrac{1}{4}J_F]\cos(4\phi) \mapsto -J_A - \tfrac{7}{4}J_F,\\
E_3 &= F_1 + F_2 + F_3 = -\tfrac{9}{4}J_F,
\end{aligned}
$$

where E_1 is minimized when $\phi = 0$ and we have a $3\hat{z}^2 - 1$ orbital and its orthogonal partner $\hat{x}^2 - \hat{y}^2$, whereas E_2 is minimized when $\phi = \pi/4$ and we have orthorhombic orbitals. E_0 is *never* the ground-state. E_1 is preferred when

$$-\tfrac{3}{2}J_A - J_F < -J_A - \tfrac{7}{4}J_F \quad\Rightarrow\quad J_F < \tfrac{2}{3}J_A$$

and E_2 is preferred when

$$-J_A - \tfrac{7}{4}J_F < -\tfrac{9}{4}J_F \quad\Rightarrow\quad \tfrac{2}{3}J_A < J_F < 2J_A.$$

E_3 is preferred when $2J_A < J_F$. Based on the experiments and the idea that ferromagnetic coupling is dominant, it is natural to conclude that E_2 is the winner and that we are dealing with the orthorhombic orbitals, but when we look to parallel orbitals we find difficulties with this picture.

Now let us examine the situation with parallel orbitals. Each of the three ferromagnetic bonds provides

$$f_\alpha = -2J_F\cos^2(\phi - \phi_\alpha)\sin^2(\phi - \phi_\alpha) = -\tfrac{1}{4}J_F + \tfrac{1}{4}J_F\cos(4\phi - 4\phi_\alpha),$$

whereas each of the three antiferromagnetic bonds provides

$$a_\alpha = -4J_A\sin^4(\phi - \phi_\alpha) = -\tfrac{3}{2}J_A + 2J_A\cos(2\phi - 2\phi_\alpha) - \tfrac{1}{2}J_A\cos(4\phi - 4\phi_\alpha)$$

using the same parametrization as before. The corresponding comparison is

$$
\begin{aligned}
e_0 &= a_1 + a_2 + a_3 = -\tfrac{9}{2}J_A,\\
e_1 &= a_1 + a_2 + f_3 = -3J_A - \tfrac{1}{4}J_F - 2J_A\cos(2\phi) + [\tfrac{1}{2}J_A + \tfrac{1}{4}J_F]\cos(4\phi)\\
&\quad \mapsto -\tfrac{7}{2}J_A - \tfrac{1}{2}J_F - \frac{J_A^2}{J_A + J_F/2},\\
e_2 &= f_1 + f_2 + a_3 = -\tfrac{3}{2}J_A - \tfrac{1}{2}J_F + 2J_A\cos(2\phi) - [\tfrac{1}{2}J_A + \tfrac{1}{4}J_F]\cos(4\phi)\\
&\quad \mapsto -4J_A - \tfrac{3}{4}J_F,\\
e_3 &= f_1 + f_2 + f_3 = -\tfrac{3}{4}J_F,
\end{aligned}
$$

where e_1 is minimized when $\cos(2\phi) = J_A/(J_A + J_F/2)$ and e_2 is minimized when $\phi = \pi/2$ and we have the $\hat{x}^2 - \hat{y}^2$ orbital. e_0 is *never* the ground-state. e_1 is preferred when

$$
\begin{aligned}
&-\tfrac{7}{2}J_A - \tfrac{1}{2}J_F - \frac{J_A^2}{J_A + J_F/2} < -4J_A - \tfrac{3}{4}J_F\\
&\qquad\qquad\qquad\Rightarrow\quad \tfrac{1}{2}(J_A + \tfrac{1}{2}J_F)^2 < J_A^2 \quad\Rightarrow\quad J_F < 2(\sqrt{2} - 1)J_A,
\end{aligned}
$$

and e_3 is never preferred so e_2 is preferred when $J_F > 2(\sqrt{2} - 1)J_A$. Comparing with the previous antiparallel orbitals

$$
\begin{aligned}
e_2 - E_3 &= -4J_A + \tfrac{3}{2}J_F < 0 &&\Rightarrow &&J_F < \tfrac{8}{3}J_A,\\
e_2 - E_2 &= -3J_A + J_F < 0 &&\Rightarrow &&J_F < 3J_A,\\
e_2 - E_1 &= -\tfrac{5}{2}J_A + \tfrac{1}{4}J_F < 0 &&\Rightarrow &&J_F < 10J_A,
\end{aligned}
$$

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e_2 wins when $2(\sqrt{2}-1)J_A < J_F < 8J_A/3$, and when $8J_A/3 < J_F$ then E_3 wins. When e_1 beats e_2, the antiparallel orbitals are well separated in energy.

The final picture is

$$\begin{aligned}
J_F < 2(\sqrt{2}-1)J_A \quad &\Rightarrow \quad e_1 = -\tfrac{7}{2}J_A - \tfrac{1}{2}J_F - \frac{J_A^2}{J_A + J_F/2} \\
&\qquad \text{with } \cos(2\phi) = \frac{J_A}{J_A + J_F/2}, \\
2(\sqrt{2}-1)J_A < J_F < \tfrac{8}{3}J_A \quad &\Rightarrow \quad e_2 = -4J_A - \tfrac{3}{4}J_F \text{ with } \phi = \pi/2 \\
\tfrac{8}{3}J_A < J_F \quad &\Rightarrow \quad E_3 = -\tfrac{9}{4}J_F \text{ with any } \phi.
\end{aligned}$$

The experiment is consistent with only one case: all the orbitals should be $\hat{x}^2 - \hat{y}^2$ and we find ferromagnetic bonding in the x–y plane together with *dominant* antiferromagnetic bonding along the z-axis. The restriction $0.83J_A < J_F < 2.67J_A$ is not too strenuous and translates into $0.83U_\mathrm{d} < 2\Delta + U_\mathrm{p} < 2.67U_\mathrm{d}$, although the actual numbers would be only approximate.

The physical causes of our result are easy to understand. The antiferromagnetic bonds are much more anisotropic than the ferromagnetic bonds. It is quite easy to replace very weak antiferromagnetic bonds with ferromagnetic bonds, but there are no weak ferromagnetic bonds. Parallel orbitals are preferred by the antiferromagnetic bonds, which prefer neighbouring orbitals to be empty, and antiparallel orbitals are preferred by ferromagnetic bonds, which require an electron to hop across from a filled into an empty orbital. If the ferromagnetic energy dominates, then the system goes ferromagnetic. If the antiferromagnetic energy wins, then the system *always* has some residual ferromagnetic bonds which are orientated along directions for which the antiferromagnetic bonds are very weak. In the proposed experimental phase, the antiferromagnetic bonds which survive are *sixteen* times as strong as the bonds which are turned ferromagnetic.

After all this analysis, we arrive at the unpalatable realization that using the current assumptions we *cannot* explain the experiments. Indeed, the structural Jahn–Teller distortions dominate *energetically* and the orbital order is *not* controlled by the motion. The experimentally proposed picture (Goodenough 1955) is that of strongly distorted octahedra with $3\hat{x}^2 - 1$ and $3\hat{y}^2 - 1$ orbitals stabilized in-plane. The ferromagnetic energy is *not* optimized, being

$$F_1 = -\tfrac{3}{4}J_F, \qquad F_2 = -\tfrac{3}{4}J_F, \qquad F_3 = -\tfrac{3}{8}J_F,$$

and the antiferromagnetic energy is also not optimized, being irrelevant in-plane and $A_3 = -9J_A/4$ up the z-axis. We are forced into the assumption that the Jahn–Teller energy dominates and that

$$J_F < 6J_A, \qquad 2\Delta + U_\mathrm{p} < 6U_\mathrm{d},$$

a not very stringent condition. Even if the antiferromagnetic interaction were dominant, the structural distortion effectively switches it off.

We finish off this section with a simple-minded model for the orbital-degeneracy lifting coming from the structural source, to assess whether the experimental explanation makes sense. The simplest model arises from second-order perturbation theory, where an electron hops back and forth between an oxygen ion and a manganese ion. We presume that when an oxygen ion is moved, there is a linear change in the hopping matrix element, and further we presume that there is a quadratic ‘structural’

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energy opposing the motion. We provide each manganese atom with an e_g electron in a fixed orbital described by

$$|\phi\rangle = \alpha[\cos(\phi-\phi_1)\hat{x}^2 + \cos(\phi-\phi_2)\hat{y}^2 + \cos(\phi-\phi_3)\hat{z}^2] = \frac{1}{\sqrt{2}}[\mathrm{e}^{-\mathrm{i}\phi}u^\dagger + \mathrm{e}^{\mathrm{i}\phi}d^\dagger]|0\rangle$$

as before and then remark that the hopping takes place into the orthogonal orbital. We arrive at the simple model

$$\begin{aligned} H = S\sum_\alpha \sum_{\langle ii'\rangle_\alpha} \delta^2_{\langle ii'\rangle_\alpha} \\ - \frac{t^2}{\Delta}\sum_\alpha \sum_{\langle ii'\rangle_\alpha} [(1+\delta_{\langle ii'\rangle_\alpha})^2 \sin^2(\phi_i-\phi_\alpha) + (1-\delta_{\langle ii'\rangle_\alpha})^2 \sin^2(\phi_{i'}-\phi_\alpha)], \end{aligned}$$

where S is a structural energy and $\delta_{\langle ii'\rangle_\alpha}$ is proportional to the displacement of the oxygen orbital. The displacements can quite simply be minimized to provide

$$E = -\frac{t^2}{\Delta}\sum_\alpha \sum_{\langle ii'\rangle_\alpha} \left[1 + \frac{(\sin^2(\phi_i-\phi_\alpha) - \sin^2(\phi_{i'}-\phi_\alpha))^2}{\Delta S/t^2 - \sin^2(\phi_i-\phi_\alpha) - \sin^2(\phi_{i'}-\phi_\alpha)}\right]$$

when the displacements satisfy

$$\delta_{\langle ii'\rangle_\alpha} = \frac{\sin^2(\phi_i-\phi_\alpha) - \sin^2(\phi_{i'}-\phi_\alpha)}{\Delta S/t^2 - \sin^2(\phi_i-\phi_\alpha) - \sin^2(\phi_{i'}-\phi_\alpha)}$$

and this is minimized for reasonable values of $S\Delta \gg t^2$ by making the neighbouring orbitals antiparallel. The overall quantization direction for the orbitals is *not* lifted by this interaction, and so one would need to look to the magnetism or some less coarse structural effect for an explanation. The energy gain from this orbital ordering is on a scale $t^2/\Delta\delta \sim t^4/(\Delta^2 S)$, which depends on the quantity S, which is also likely to be a function of t. This simple argument would suggest that the structural energy would prefer antiparallel orbitals and *not* the previously suggested orbitals.

These rather rudimentary structural arguments suggest that the *orthorhombic* orbitals are the natural candidates. We can have optimal strain energy, freedom to stack the ferromagnetic planes in a way that will enhance the desired perovskite buckling and the possibility of the experimentally observed magnetic state if $2J_A/3 < J_F < 2J_A$, or, alternatively, $2U_\mathrm{d}/3 < 2\Delta + U_\mathrm{p} < 2U_\mathrm{d}$, which does appear rather stringent. It is clear that the rather complicated distortions experimentally observed have been ignored, and further that weaker magnetic interactions involving the t_{2g} and p_π orbitals, and interactions which are not Hund's rule-preferred and a host of other not insignificant effects have been ignored here.

4. Orbital ordering from double-exchange

Unlike the previous section, where the modelling assumptions are overtaken by physical interactions omitted from the outset, in this section the modelling is more physically reasonable. The double-exchange is a *second*-order hopping process, and so ought to be much stronger than the weaker *fourth*-order superexchange and hence more able to compete with the omitted structural interactions. The phase diagrams involve a *cubic* phase in the ferromagnetic metallic regions, which suggests that no

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static Jahn–Teller distortion is present, and that the motion of the electrons is dominating the structural effects.

We simply take our chosen double-exchange representation

$$H_1 = -\tfrac{1}{2}t \sum_{\alpha} \sum_{\langle ii'\rangle_\alpha} [\mathrm{e}^{-\mathrm{i}\phi_\alpha/2} u_i^\dagger + \mathrm{e}^{\mathrm{i}\phi_\alpha/2} d_i^\dagger][\mathrm{e}^{\mathrm{i}\phi_\alpha/2} u_{i'} + \mathrm{e}^{-\mathrm{i}\phi_\alpha/2} d_{i'}]$$

and attempt to solve it at low temperatures using the experience with the Hubbard model as a guide.

Our first elementary theory is that of mean-field theory in the strong-coupling limit. As the on-site energy, U, is permitted to become large, charge fluctuations are eradicated. In a non-interacting state of mean-field theory, this forces each site to orientate its permitted pseudo-spins along a fixed quantization axis. The pseudo-spin representation,

$$H_1 = -t \sum_{\alpha} \sum_{\langle ii'\rangle_\alpha} |i, \pi/2, \phi_\alpha\rangle\langle i', \pi/2, \phi_\alpha|,$$

is very convenient for this limit providing

$$\begin{aligned} H_1 &= -t \sum_{\alpha} \sum_{\langle ii'\rangle_\alpha} \langle \pi/2, \phi_i | \pi/2, \phi_\alpha\rangle\langle \pi/2, \phi_\alpha | \pi/2, \phi_{i'}\rangle c_i^\dagger c_{i'} \\ &= -t \sum_{\alpha} \sum_{\langle ii'\rangle_\alpha} \cos\tfrac{1}{2}(\phi_i - \phi_\alpha) \cos\tfrac{1}{2}(\phi_{i'} - \phi_\alpha) c_i^\dagger c_{i'}, \end{aligned}$$

where $c_i^\dagger$ creates an electron with the chosen orientation on site i, and we have used the usual spin-half representation to evaluate the matrix elements. This is more complicated than the usual Hubbard model result, which can be seen from

$$\cos\tfrac{1}{2}(\phi_i - \phi_\alpha) \cos\tfrac{1}{2}(\phi_{i'} - \phi_\alpha) = \tfrac{1}{2}[\cos(\tfrac{1}{2}(\phi_i + \phi_{i'}) - \phi_\alpha) + \cos(\tfrac{1}{2}(\phi_i - \phi_{i'}))],$$

where the second term occurs in the isotropic Hubbard model and prefers all the orientations to be parallel. The first term involves the bond orientations and might be expected to average out to zero. We will simply assume that the orbitals all align and simply calculate the preferred orbital for the motion.

This mean-field theory is *not* very valuable for the Hubbard model, because of the freedom to use the spin degrees of freedom to avoid Fermi statistics around loops. In these orbital models the particles find it much more difficult to exchange around loops and the results might be expected to be more relevant.

The calculation reduces to a comparison of different dispersions. For each choice of orbital we find a dispersion

$$\epsilon_{\boldsymbol{k}} = -\tfrac{2}{3} \sum_{\alpha} \cos^2\tfrac{1}{2}(\phi - \phi_\alpha) \cos k_\alpha$$

in terms of ϕ the orientation of the orbital. For each band-filling, one can evaluate the energies for different values of ϕ and compare. The result is depicted in figure 1. At the edges of the band the $\hat{x}^2 - \hat{y}^2$ is preferred, whereas near half-filling the $3\hat{z}^2 - 1$ orbital is preferred. The first result is easy to understand once the densities of states are plotted (figure 2). The $\hat{x}^2 - \hat{y}^2$ orbital has motion restricted to two dimensions and as such has a higher density of states near the edge of the band than the essentially three-dimensional $3\hat{z}^2 - 1$ orbital. The second result is rather more subtle and is

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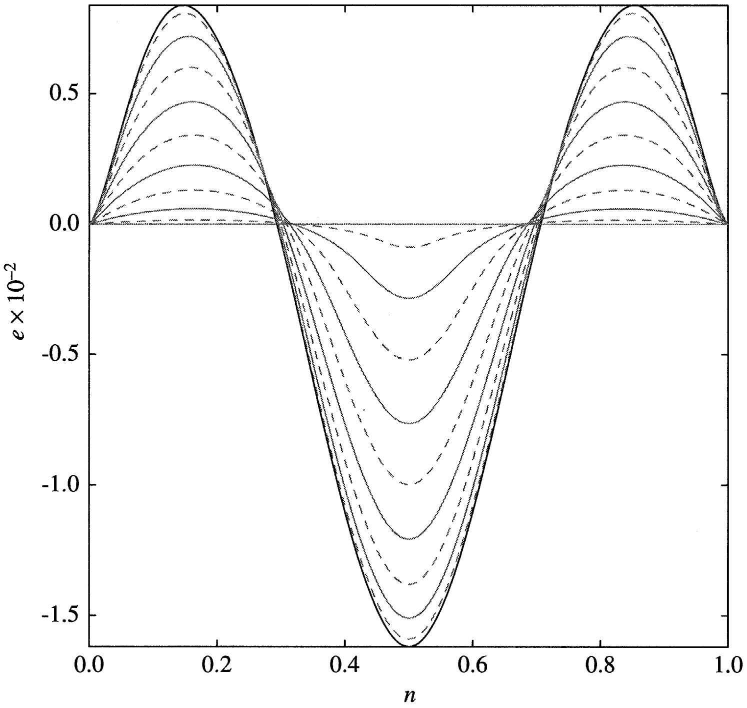

Figure 1. A plot of the energy differences between the ground-state energy of the $\hat{x}^2-\hat{y}^2$ orbital and a sequence of other possible orbitals culminating in the $3\hat{z}^2-1$ orbital. The plot is for double-exchange energy as a function of the electron number, which corresponds to the variable x in the experimental system.

associated with the more one-dimensional motion of the $3\hat{z}^2-1$ orbital along the z-axis being preferred in avoiding the other particles over the true two-dimensional behaviour of the $\hat{x}^2-\hat{y}^2$ orbital.

There is patchy experimental evidence for this picture (Wollan & Koehler 1955). The two-dimensional state is *only* present in the phase diagram if we ignore the antiparallel orbitals in the parent compound. The magnetic state is not inconsistent with the proposed motion, although it is clear that all the orbitals would have to be reorientated into planes of aligned $\hat{x}^2-\hat{y}^2$ orbitals. Indeed, one would need to provide an explanation for why the antiferromagnetism would be broken down! Also, in the planar $La_{1.2}Sr_{1.8}MnO_7$ compounds there is excellent experimental evidence for this phase (Argyriou *et al.* 1997), and this for rather more obvious reasons. The $3\hat{z}^2-1$ phase with its linear motion does have some possible justification in the vicinity of $La_{0.2}Ca_{0.8}MnO_3$, where lines of ferromagnetically coupled atoms are seen (the so-called C-phase (Wollan & Koehler 1955)), but these alternate antiferromagnetically in the other two directions. Once again, the antiferromagnetic bonds which we have ignored in our modelling have surfaced to become relevant. Near half-filling the charges actually localize, another effect not predicted by the model. Obviously, the strain energies from moving the oxygen atoms around are very relevant at these commensurate band-fillings.

The parent compound, $LaMnO_3$, has the correct spin-arrangement to allow our proposed motion, but has the wrong orbital alignment. We would expect the weakly

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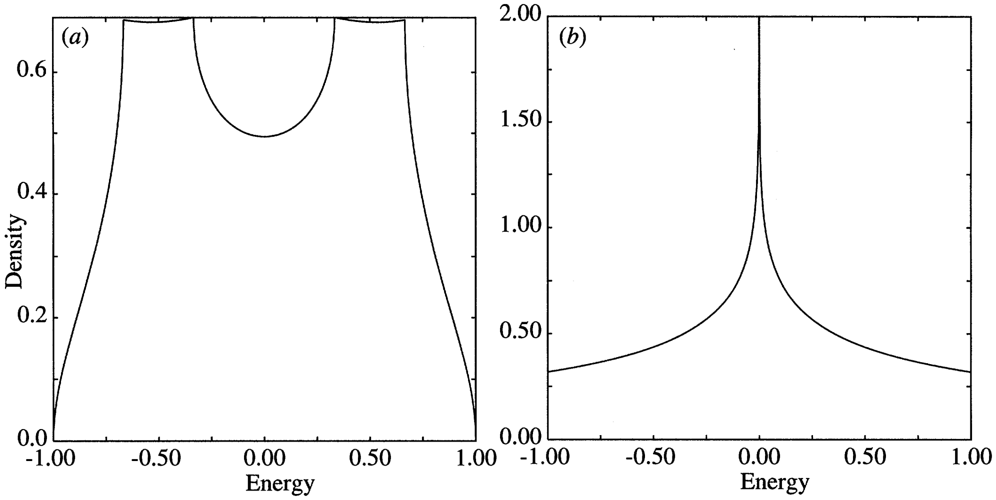

Figure 2. Densities of states for double-exchange electron motion in systems with fixed orbitals on each site: (a) $3\hat{z}^2 - 1$, (b) $\hat{x}^2 - \hat{y}^2$.

doped charge carriers to be localized in the ferromagnetic planes and then their motion would be expected to compete against the structural energy. In the vicinity of a hole, namely a Mn^{4+}, we would expect the orbitals to reorientate to the double-exchange preferred order, in a form of polaronic distortion.

The most interesting phase, in the vicinity of $La_{0.7}Sr_{0.3}MnO_3$, *does* remain ferromagnetic and shows no obvious static structural phenomena, and so this is the phase which is most relevant for our modelling. Sadly there is no evidence for either of the two phases suggested. The only positive statement that can be made is that the choice of which orbital is at its most difficult when the compound is at its most interesting, and this might be mildly relevant.

Perhaps the most remarkable feature of the phase diagram of $La_{1-x}Sr_xMnO_3$ is its lack of any reflection symmetry. The physical interactions at the Mn^{3+} end must be very different from those at the Mn^{4+} end. The simplest interpretation is the difference between the spin interactions between like species: the ferromagnetic interaction between pairs of Mn^{3+} and the antiferromagnetic interaction between pairs of Mn^{4+}. In the intermediate doping regime, however, double-exchange is presumed to dominate and moreover to have a larger innate energy scale. Does this asymmetry mean that the double-exchange never really dominates? To address this issue, we have had a detailed look at whether or not particle-hole symmetry is likely to hold in our chosen model.

The mean-field theory to the Hubbard model is very limited and suffers from some well-known defects. The biggest problem is that it is very susceptible to classical order. Indeed, we have investigated solely the classical ordering so far and determined that this preferred order would be subject to changes. The problem may be characterized as the inability for the approximation to describe quantum fluctuations. The experimental systems appear to remain cubic in the most interesting ferromagnetic phase and hence our previous mean-field analysis was unlikely to predict this. If our modelling is to become useful, then we need to assess whether or not the mean-field solution is relevant to the physics when doping away from the Mott insulating phase.

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Unfortunately, it is extremely difficult to model quantum fluctuations, and we have only tackled the most basic of physical questions.

The simplest approach is to analyse and compare single-particle with single-hole motion. The local on-site repulsion between electrons is allowed to diverge, eliminating any competition with the superexchange phenomena, and the motion via double-exchange is all that remains. A single particle in this model suffers no interactions, and hence the previous band-structure picture is exact. When many particles are added, it is easy to believe that this picture remains essentially correct and the motion will be dominantly two-dimensional. When a single hole is doped into the otherwise singly occupied Mott insulating phase, quite different considerations are required. The previous mean-field model would suggest extracting an electron from one x–y plane, but this proves quite wrong.

The single-hole in the otherwise singly occupied Mott insulator, which lifts the degeneracy through its motion, is known as the Nagaoka problem (Nagaoka 1966), after the solver of this problem for the Hubbard model. The solution for a bipartite lattice is that of ferromagnetism, whereas that for a geometrically frustrated lattice is as yet not well understood. For the current system we do not have the isotropic spin-symmetry, and so the hole motion needs also to decide upon an overall quantization direction for our pseudo-spins. This additional complication makes the problem very taxing mathematically. We have not been able to solve this problem, although we can show that the single-hole motion is very different to that predicted in the mean-field solution. The orbital frustration eliminates the state where all the orbitals align, and we predict a fairly complicated orbital configuration.

We start out by analysing the problem of a single square plane of atoms perpendicular to the z-axis. This might be expected to mimic $La_{1.2}Sr_{1.8}MnO_3$, which has a similar but double-plane structure. The orbital frustration is *no longer present*, and

$$\sum_{\alpha} e^{i\phi_\alpha} = -1 = e^{i\pi},$$

which leads to a preference for $\phi \sim \pi$ and pseudo-spins orientated antiparallel to the x-axis. This in turn corresponds to $\hat{x}^2 - \hat{y}^2$ orbitals. As might be expected, the orbitals lie in the plane of their motion, maximizing the double-exchange. Note that this is also the mean-field solution on the cubic lattice, which predicts an electron localized in a single plane of atoms. The state with all the pseudo-spins orientated parallel to the x-axis is *not* an eigenstate, and the ground-state involves the hole travelling about with a polaronic distortion in its vicinity. The pseudo-spins exhibit short-range correlations which align the neighbouring spins along the local bond angles, thereby enhancing the hopping. This local polaronic distortion is half in the form of the Jahn–Teller distortions: before the system metalizes, there is an interesting competition between the Jahn–Teller and double-exchange interactions. The hole gains about 10% extra energy from this local polaronic distortion although it is fair to say that the basic physical picture is that of the mean-field solution. When we move on to the actual double-plane structure of $La_{1.2}Sr_{1.8}MnO_3$, we find a surprise: the hole gains another 10% of the mean-field energy by polarizing the second plane. Instead of using the second plane for similar motion to the first, the hole polarizes the second plane in the *positive* pseudo-spin direction, i.e. with $3\hat{z}^2 - 1$ orbitals. The hole shows strong two-dimensional delocalization in one of the two planes and hops briefly on to the other plane and back without delocalizing coherently!

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Extending from two to three planes reinforces the broken symmetry. The hole delocalizes along the central plane, carrying its polaronic distortion along with it, but polarizes the two outer planes in the $3\hat{z}^2 - 1$ direction. The energy gain from this perpendicular motion is now of order 20% of the original.

The full three-dimensional problem is much more complicated, the full frustration is present, and there is no intrinsic orbital direction to simplify expectations. We believe that a similar picture to the bi- and tri-layer systems occurs, and that the hole selects a plane to delocalize in, and then polarizes the *rest* of the lattice with the perpendicular orbital. The situation with many such holes behaving as polarons is an impressively sophisticated situation to consider modelling, and we will complete this section with a brief discussion of the simpler free-electron orbital-degeneracy lifting at the end of this section.

The cause of the transition to a cubic ferromagnetic state has now emerged in the modelling: although the mean-field solution suggests no competition between the parent phase and that preferred by the double-exchange, the fluctuation effects yield a sizeable gain in energy from orientating orbitals in perpendicular directions. When the energy gain from the motion along the perpendicular direction outweighs the superexchange energy one would expect a phase transition. The experiments indicate that this transition occurs at about 10% doping, which would require that the double-exchange was very strong indeed.

The problem of a single hole lifting the pseudo-spin degeneracy is theoretically very difficult. In order to simplify things we have considered some related but more elementary models. The idea here is to separate out the effect of the choice of orbital, i.e. the choice of pseudo-spin quantization direction, from the statistical forces between particles. This is accomplished by allowing the bonding angles, ϕ_α, to become perpendicular and not just 120°. The electronic motion cannot then *exchange* two electrons and the statistical forces become equivalent to on-site Pauli exclusion. The orbital degeneracy is still present and is lifted by the hole motion. This restriction is best understood by observing that all *geometric loops* are eliminated by this assumption, and the orbital degeneracy amounts to a choice of *geometry* for the hole. This style of model predicts this idea of coherent motion in low dimensions combined with weak tunnelling perpendicular to the coherent motion into orbitals aligned to receive the hole. The point to these simple models is that one can come close to a *rigorous proof* of this behaviour, thereby demonstrating its source.

Our final task in this section is to briefly review the non-interacting solution, and to explain how the orbital degeneracy is lifted in this case. The elementary double-exchange Hamiltonian is easily transformed into reciprocal-space,

$$H_1 = -t \sum_{\boldsymbol{k}} \begin{bmatrix} u_{\boldsymbol{k}}^\dagger & d_{\boldsymbol{k}}^\dagger \end{bmatrix} \begin{bmatrix} a_{\boldsymbol{k}} & b_{\boldsymbol{k}} \mathrm{e}^{-\mathrm{i}\phi_{\boldsymbol{k}}} \\ b_{\boldsymbol{k}} \mathrm{e}^{\mathrm{i}\phi_{\boldsymbol{k}}} & a_{\boldsymbol{k}} \end{bmatrix} \begin{bmatrix} u_{\boldsymbol{k}} \\ d_{\boldsymbol{k}} \end{bmatrix},$$

in terms of the quantities

$$a_{\boldsymbol{k}} = \cos k_1 + \cos k_2 + \cos k_3, \qquad b_{\boldsymbol{k}} \mathrm{e}^{\mathrm{i}\phi_{\boldsymbol{k}}} = \omega \cos k_1 + \omega^2 \cos k_2 + \cos k_3.$$

This Hamiltonian is readily diagonalized with

$$X_{\boldsymbol{k}\tau}^\dagger = \frac{1}{\sqrt{2}} (\mathrm{e}^{-\mathrm{i}\phi_{\boldsymbol{k}}/2} u_{\boldsymbol{k}}^\dagger + \tau \mathrm{e}^{\mathrm{i}\phi_{\boldsymbol{k}}/2} d_{\boldsymbol{k}}^\dagger),$$

where $\tau = \pm 1$ to provide

$$H_1 = -t \sum_{\boldsymbol{k}\tau} X_{\boldsymbol{k}\tau}^\dagger X_{\boldsymbol{k}\tau} (a_{\boldsymbol{k}} + \tau b_{\boldsymbol{k}}).$$

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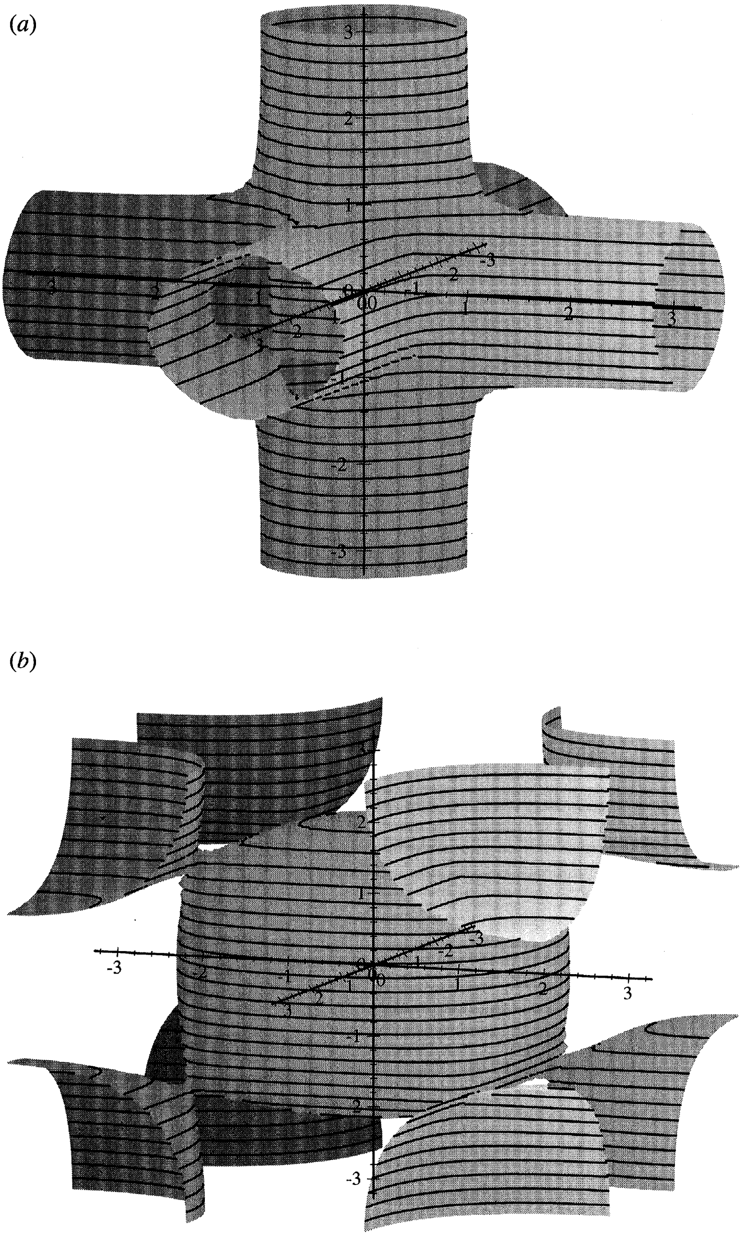

Figure 3. Fermi surface for chemical potentials of (*a*) $\mu = 0.8$ and (*b*) $\mu = 0$ using the scaling $(\cos k_2 - \mu)(\cos k_3 - \mu) + (\cos k_3 - \mu)(\cos k_1 - \mu) + (\cos k_1 - \mu)(\cos k_2 - \mu) = 0$.

When either both states are filled or both states are empty, then there is no orbital-degeneracy lifting, but when only one is occupied then only one of the two orbitals is occupied and the orbital-degeneracy is strongly lifted. The form of the eigenstates is very instructive: the hopping energy only couples to pseudo-spins in the x–y plane, and we see that the style of orbital is completely controlled by the $\boldsymbol{k}$-dependent angle $\phi_{\boldsymbol{k}}$, which corresponds absolutely directly to the quantum pseudo-spin orientation of

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§ 2. A typical low-doping Fermi surface is depicted in figure 3*a*, and there is a second, hidden, fairly spherical Fermi surface in the centre. The regions of single occupancy are to be found in the 'arms', and for an arm in the z-direction, $\boldsymbol{k} \sim (0, 0, k_z)$, we find the occupied orbital corresponds to $\phi \sim \pi$ and the $\hat{x}^2 - \hat{y}^2$ orbital is preferred. Obviously, the other 'arms' correspond to a preference for the symmetrically related $\hat{y}^2 - \hat{z}^2$ and $\hat{z}^2 - \hat{x}^2$ orbitals. It is clear that planar motion is preferred using orbitals orientated in the chosen plane, and the orthogonal $3\hat{z}^2 - 1$ orbitals which are filled preferentially near $\boldsymbol{k} \sim (\pi, \pi, k_z)$ are usually swamped. Near to half-filling these more one-dimensional orbitals do become more relevant in sympathy with the strong correlations mean-field result, as is depicted in figure 3*b*.

The orbital order for the free-electron case is lifted on the double-exchange energy scale, and is experimentally observable via the Fermi surface in angle-resolved photoemission. It remains to be seen whether the strong correlations leave the weak-coupling picture intact at this level.

5. Conclusions

(*a*) *General*

There exists a class of orbital-degeneracy problems which exhibit a form of geometrical frustration. We describe the orbital degeneracy using a pseudo-spin and then consider a hopping Hamiltonian,

$$H_1 = -t \sum_{\alpha} \sum_{\langle ii' \rangle_\alpha} |i, \hat{\boldsymbol{r}}_\alpha\rangle\langle i', \hat{\boldsymbol{r}}_\alpha|,$$

where $|i, \hat{\boldsymbol{r}}\rangle$ is a state with the pseudo-spin on site i orientated in the direction $\hat{\boldsymbol{r}}$, and $\hat{\boldsymbol{r}}_\alpha$ is a fixed orientation associated with the bond which is the component allowed to hop along the bond. The geometric frustration occurs when

$$\boldsymbol{R}_i = \sum_{\alpha} \sum_{\langle ii' \rangle_\alpha} \hat{\boldsymbol{r}}_\alpha = \boldsymbol{0}$$

and the average bonding vanishes for each site. When we are dealing with pseudo-spins and bonds in the x–y plane, then

$$0 = \left\langle i, \phi \middle| \sum_{\alpha} \hat{\boldsymbol{r}}_\alpha \cdot \hat{\boldsymbol{\sigma}} \middle| i, \phi \right\rangle = \sum_{\alpha} \cos(\phi - \phi_\alpha),$$

and if the bonds are equally spaced angles forming roots of unity, then

$$\sum_{\alpha} \mathrm{e}^{\mathrm{i}\phi_\alpha} = 0 \qquad \Rightarrow \qquad \sum_{\alpha} \mathrm{e}^{2\mathrm{i}\phi_\alpha} = 0$$

and we get the form used in the main text.

This class of models occurs when only one out of the different degenerate orbitals can hop across each of the bonds. This occurs in the manganites because one of the e_g orbitals has d-symmetry as seen by an electron hopping from a neighbouring oxygen atom, which consequently has no overlap. Normal situations involve both types of orbital being able to hop, but often with disparate matrix elements. The frustration occurs because the point-group symmetry of the orbital is mismatched to the lattice: the bond orientations in space correspond to phases of the orbital

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which cancel out on average. In the manganites the three Cartesian directions pick up cube-roots of unity on hopping, which clearly cancel out. Other natural analogue models include p-electrons on the honeycomb lattice (an almost identical problem in two dimensions) and p-electrons on the square or cubic lattices (similar problems but without coupling between the different pseudo-spin directions).

The Mott insulating limit provides an elementary Ising model,

$$H = \frac{t^2}{U} \sum_{\alpha} \sum_{\langle ii' \rangle_\alpha} [S_i^\alpha S_{i'}^\alpha - S^2],$$

where only the component along the bond direction interacts

$$S_i^\alpha = \hat{\boldsymbol{r}}_\alpha \cdot \hat{\boldsymbol{\sigma}} = |i, \hat{\boldsymbol{r}}_\alpha\rangle\langle i, \hat{\boldsymbol{r}}_\alpha|$$

in terms of the pseudo-spin operators $\hat{\boldsymbol{\sigma}}$. For a bipartite lattice the classical ground-state involves the classical Néel state, $\phi_i = \phi^* + \boldsymbol{R}_i \cdot \boldsymbol{Q}$ and then

$$E = -\frac{S^2 t^2}{U} \sum_{\alpha} \sum_{\langle ii' \rangle_\alpha} [\cos^2(\phi^* - \phi_\alpha) + 1] = -\frac{3S^2 t^2}{2U} NZ,$$

where Z is the coordination number and N is the number of atoms involved. This result relies on the frustration and indicates that the quantization direction is *not* decided at this order. There is an additional style of ground-state which occurs when $\phi^* = \phi_{\alpha^*} \pm \pi/2$ for some value of α^*. These bonds, in the chosen direction, then provide no energy and one can choose the ± randomly between pieces which are disconnected by the irrelevant bonds. When quantum fluctuations are considered in these models, quite generally the states with $\phi^* = \phi_{\alpha^*}$ are stabilized. The chosen bonds are saturated, and hence fluctuations cannot gain from them. Fluctuations in the unsaturated bonds, which form a reduced geometry, are stronger because of the lower connectivity which is the stabilization energy. If the reduced connectivity leads to a reduced dimension, as happens in all the cases we have studied, then the lower dimensional fluctuations can actually eliminate the order in an analogous way to the way thermal fluctuations destroy long-range order. When the system is disordered, however, the opposite result is predicted with $\phi^* = \phi_\alpha \pm \pi/2$ being preferred. Since the unsaturated bonds are shared out most evenly, the classical distortion around the disorder is strongest.

The motion of the electrons in the strong-coupling limit is by no means as simple as the classical orbital ordering at half-filling. Even the Nagaoka problem is too difficult, due to the implicit frustration of the orbitals. We have no general results on this more interesting problem.

(b) *Particular*

The problem we have investigated is: Which physical phenomena lift the orbital degeneracy in the compounds $La_{1-x}Sr_xMnO_3$, and what resulting order is expected? The major theoretical difficulty with this modelling is the host of different physical phenomena, all on very similar energy scales. We have been forced into the belief that:

1. double-exchange motion is dominant;

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2. structural Jahn–Teller effects are next most important;

3. either ferromagnetic or antiferromagnetic interactions come last.

We can rationalize these beliefs in perturbation theory by arguing that the double-exchange occurs at order t^2/Δ, the Jahn–Teller effect involves interfering with the t^2/Δ energy at an order of a small fraction, by moving the oxygen atoms around and promoting the Mn–O bonding in preferred directions, and the magnetic interactions involve $t^4/(\Delta^2 U)$ and are correspondingly weaker. We know that $t < \Delta$ because the parent compound is a localized Mott insulator. We have also provided complementary evidence by assuming that the superexchange phenomena dominate and have shown that any resulting phases are not consistent with the experiments.

Our modelling of the parent compound has not proven very useful. If we assume that the superexchange phenomena are dominant, then we have two options: after the first oxygen electron has hopped to a neighbouring oxygen, either a second electron hops to the other neighbouring manganese, or an electron on that manganese atom replaces the oxygen electron which departed. The first process provides an antiferromagnetic exchange, whereas the second provides a ferromagnetic exchange from the Hund's rule coupling of the Mn^{2+}. One might expect that the relative expense of the $\mathrm{Mn}^{4+}\mathrm{O}^{2-}\mathrm{Mn}^{2+}$ state over the $\mathrm{Mn}^{2+}\mathrm{O}^{0}\mathrm{Mn}^{2+}$ state would control the magnetism. Although in global terms this is true, the different ways that these two processes are affected by the orbital degeneracy is crucial to the argument. The antiferromagnetic interaction is much more anisotropic, and hence it is highly susceptible to the orbital order. One would therefore expect that if the ferromagnetic interaction wins then the system would go fully ferromagnetic, whereas if the antiferromagnetic interaction wins it could quite easily be partly replaced with some weaker ferromagnetic bonds. In practice, the structural energies control the orbital-degeneracy lifting, and the preferred state in the literature appears to completely eliminate the antiferromagnetic interactions in the x–y plane, which therefore goes ferromagnetic. The coupling up the z-axis is then seen to be antiferromagnetic experimentally, which means that the oxygen superexchange must be sizeable. The restriction is not too strict, amounting to $2\Delta + U_{\mathrm{p}} < 6U_{\mathrm{d}}$ under the simplest modelling assumptions. Our simple arguments tend to indicate that one would expect the *orthorhombic* orbitals to be preferred. Both the structural and ferromagnetic energies are preferred, although the observed antiferromagnetic arrangement is much less easy to obtain, $2U_{\mathrm{d}}/3 < 2\Delta + U_{\mathrm{p}} < 2U_{\mathrm{d}}$, being the most naive restriction.

Over most of the phase diagram, the material is not a very good metal. This probably means that structural effects are important and one is dealing with a competition between local distortions and the double-exchange. Our modelling assumptions omitted the structural effects, and hence we do not obtain any real progress in describing the host of exotic antiferromagnetic phases with their associated orbital orderings. This leaves only one possible phase accessible, the ferromagnet.

In the limit of low doping, one would expect a conflict between the structural Jahn–Teller distortions and the double-exchange motion. The softening of the transitions to the distorted state upon doping and their subsequent eradication upon entering the ferromagnetic state indicate that in the ferromagnetic state the double-exchange is deciding both the spin *and* orbital-degeneracy lifting. The model that we have developed is therefore much more relevant for this case.

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The model we propose is the pseudo-spin hopping model,

$$H_1 = -\tfrac{1}{2}t\sum_{\alpha}\sum_{\langle ii'\rangle_\alpha}[\mathrm{e}^{-\mathrm{i}\phi_\alpha/2}u_i^\dagger + \mathrm{e}^{\mathrm{i}\phi_\alpha/2}d_i^\dagger][\mathrm{e}^{\mathrm{i}\phi_\alpha/2}u_{i'} + \mathrm{e}^{-\mathrm{i}\phi_\alpha/2}d_{i'}],$$

subject to the strong-coupling restriction that one can only have either one or no fermions per site, in this case electrons. The motion requires to decide both the overall quantization direction, as well as the relative orientations between orbitals as in the usual spin-degenerate hopping problems. One can analyse this problem in a progression of more sophisticated ways. First, one can ignore correlations and analyse the 'band-structure' solution; this was shown to break the orbital degeneracy on the hopping energy scale, and to provide orbitals appropriate to the direction of motion. Secondly, one can analyse Hartree–Fock mean-field theory. This calculation was performed for the strong-coupling limit, and phase transitions between an $\hat{x}^2-\hat{y}^2$ phase at the edges of the band and a $3\hat{z}^2-1$ phase in the middle of the band was predicted. Since this mean-field theory promotes ordered solutions, and the experiments show a lack of static structural distortions, it seems clear that the fluctuations play an important role. More sophisticated methods of analysis are required.

There are two physical phenomena competing in the model, which makes it rather hard to solve. First, the different bond angles, ϕ_α, lead to strong local forces aligning orbitals in directions to promote hole motion. The orbital frustration makes this aspect particularly complicated. Secondly, the choice of orbitals can be used to interfere with the *statistics* of the charge-carriers. If two particles meet in a pseudo-spin singlet, then they can freely exchange without the strong fermionic repulsion encountered by electrons in parallel orbitals. The second force is the only one present in the Hubbard model, and promotes a highly complicated paramagnetic phase dominated by quantum mechanics, which is impressively difficult to describe formally. We have devoted some effort in this paper to the first force, that attributable to the competition between the different bond angles. We have been able to isolate this contribution by altering the bond angles until they are at right-angles. With this assumption the statistical exchange is eliminated and the quantum fluctuations of this type disappear. Using these models we have found that a complicated polaron is formed. A low-dimensional subset of the original geometry is selected, usually combined with a symmetry breaking, and the holes move coherently in this subset using the appropriate choice of orbitals. The remainder of the system then polarizes with different orbitals which are appropriate for motion in the directions perpendicular to the coherent direction. For the original manganite system, where there are also quantum fluctuations, we appear to predict that there is a natural two-dimensional motion with in-plane $\hat{x}^2-\hat{y}^2$ orbitals, combined with out-of-plane $3\hat{z}^2-1$ orbitals, permitting weaker incoherent motion perpendicular to the chosen plane.

Our double-exchange results *still* involve an unhealthy amount of classical order which is not obviously present in the experiments. It may well be that an even more quantum fluctuation dominated phase is stabilized due to the orbital frustration. It is also possible that some remnant of the free-electron solution remains, as is the case with perovskite superconductors.

One physical point which has been theoretically very obvious but also appears experimentally relevant, is that the Jahn–Teller distortions do *not* interfere with the spin-physics whereas the double-exchange interactions do. The extra entropy loss in using the double-exchange makes it relevant at a lower temperature. Once the spins

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become disordered at higher temperature, the Jahn–Teller distortions can recur as a useful energy saving in the absence of the magnetism. The smearing out-of-the-phase transition by a magnetic field could then be used to explain why the sharp 'either-or' structural phenomena are lost with the consequent smoothing out of the resistance which is observed in the colossal magnetoresistance phenomenon.

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Discussion

D. KHOMSKII (*University of Groningen, The Netherlands*). I disagree with Dr Long's statement that the electronic mechanism of superexchange is hardly relevant for this problem as compared with Jahn–Teller. In the old days, when we worked with K. Kugel on the problem of orbital ordering, I was very much worried by this problem myself: how to discriminate between different mechanisms. In real materials, they act simultaneously, and usually they lead to the same type of orbital ordering. But recently it has become possible to check it by careful numerical calculations. Corresponding calculations carried out by A. Liechtenstein, V. Anisimov and Y. Zaanen have shown that at least for such compounds ($KCuF_3$) you get correct orbital ordering even when you fix the cubic lattice. It was checked that you can, for instance, take a fixed lattice, a cubic lattice, and you are still able to reproduce direct orbital ordering for one of these compounds. Of course, when you release the lattice later on, when you make proper distortions, you still decrease the energy by about 20–30%. Thus you can say that 70–80% of the energy gain is due to a purely electronic effect and 20–30% due to the Jahn–Teller effect later on.

A. J. MILLIS (*The Johns Hopkins University, USA*). Following on from Dr Khomskii's comment: precisely for the manganites the Japanese group, Hamada, Terakura and Solovyev, did the same calculations and concluded that almost all of the energy in fact came from the structural distortion and that you had to add a modest U.

D. KHOMSKII. This calculation is a different method; it is simply the LDA method with some corrections, but I am talking about LDA plus U, which is really quite

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good at reproducing orbital ordering. But of course you can doubt which method is better and the numerical accuracy of all the calculations. I cannot really guarantee that it is 70%, but in any case they were able to reproduce orbital ordering for this potassium cuprate; and even more for this 50% charge-ordered state (PrCa) they got both charge ordering and orbital ordering simultaneously without doing anything to the lattice. They reproduced the correct CE magnetic structure and charge ordering; that was done quite recently by Korotin of the same group.

M. W. LONG. The main cause of this question is a lack of clarity in the sources and assignment of the different energies in this system. In the atomic limit, the different contributions are quite easy to annotate: at order t^2/Δ (where t is the manganese–oxygen hopping), there is an *electronic* energy that, when combined with an appropriate orbital ordering, gives rise to an induced structural distortion. This interaction is spin independent. At fourth order, t^4/Δ^3, there are various superexchanges both magnetic and non-magnetic. Although in the atomic limit the magnetic contributions may be separated out, in any calculation like that suggested by Khomskii, it is not trivial to do this. I will complete this response by addressing two issues: the fundamental physical ideas and the role of experiment.

The physical cause of the Jahn–Teller distortions is blocking. The e_g electron on a Mn^{3+} atom blocks, by Pauli exclusion, electrons on the surrounding oxygen atoms. An isolated Mn^{3+} with any orbital blocks equally as any other to leading order. When a pair of neighbouring Mn^{3+} atoms are considered, however, by orientating the orbitals in 'opposite' directions one can ensure that each oxygen atom has a dominant blocker and a preferred Mn^{3+} to hybridize with. This saves energy because no oxygen atom is required to serve two masters simultaneously. Since the magnetic interactions involve just such multiple interactions, the minimization of blocking reduces the magnetic contributions. A careful comparison shows that the non-magnetic contributions excluding lattice effects are almost always stronger than the magnetic interactions and hence if we compare magnetic versus non-magnetic interactions, then non-magnetic will win and furthermore be enhanced by lattice distortions. If, on the other hand, one compares superexchange with lattice energies, then the issue is unclear and is likely to be comparable in all transition metal systems.

The comparison between magnetic and non-magnetic interactions is clearly experimentally accessible in the two transition temperatures: the non-magnetic interactions order the structure at 800 K, whereas the magnetic superexchange orders at 100 K with only a weak additional structural rearrangement. The comparison between lattice and superexchange interactions is not experimentally accessible.

Note that the theory suggests that non-magnetic superexchange provides the wrong orbital ordering from the fluctuations and hence that structural effects are required to explain the observed experimental structure.

T. VENKATESAN (*University of Maryland, USA*). Dr Long mentioned that in the Ruddlesden–Popper structure the frustration is lifted. In what way does his theoretical ideas explain the experimental data?

M. W. LONG. If one were to jump straight in with full cubic symmetry of the lattice, then one would need to cope with any spontaneous symmetry breaking. By using the idea that the cubic system is the $n \to \infty$ limit of the Ruddlesden–Popper phases, each of which lifts the symmetry, one can control the symmetry breaking aspect.

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The symmetrically related states which are degenerate in the limit are separated by an energy which usually exponentially decays in n. When we actually performed the calculation at the one hole level, however, we found that only the $n = 1$ system is special and that the $n > 1$ systems all exhibit the properties anticipated for the $n \to \infty$ limit: a single plane is selected for coherent motion and the other planes provide incoherent 'cul-de-sacs'. Since the $n > 2$ systems behave in a similar way to $n \to \infty$, I have no difficulty in reconciling the transport experiments which also show the $n = 1$ phase as the only 'special' case.

D. McK. Paul (*University of Warwick, UK*). I would like to ask a general question which is probably for all the theoreticians: as an experimentalist, I have a tendency to look at phonons and the vibrational modes of these systems. Nobody is doing that, of course, because it is a very difficult problem to start off on, the number of branches is enormous, and so on. But which branches should we be looking at? Just the breathing modes of the system, or are there other phonons which are going to be of crucial importance?

M. W. Long. After consideration, I would say that the shape of the orbital controls the phonon response. An $\hat{x}^2 - \hat{y}^2$ and $3\hat{z}^2 - \hat{\psi}^2$ have quite clear preferred local deformations. One needs to model the phonons around this picture. As the electrons move, they carry this deformation, smearing it out both spatially and energetically. In this sense it is messy and difficult to predict.

D. McK. Paul. Well, localized vibrations you can still see if it's a very flat mode.

M. W. Long. Only if they are really localized in that sense—they'll be pushed all over the park by local configurations.

D. McK. Paul. They will not decay into a phenomenological system then?

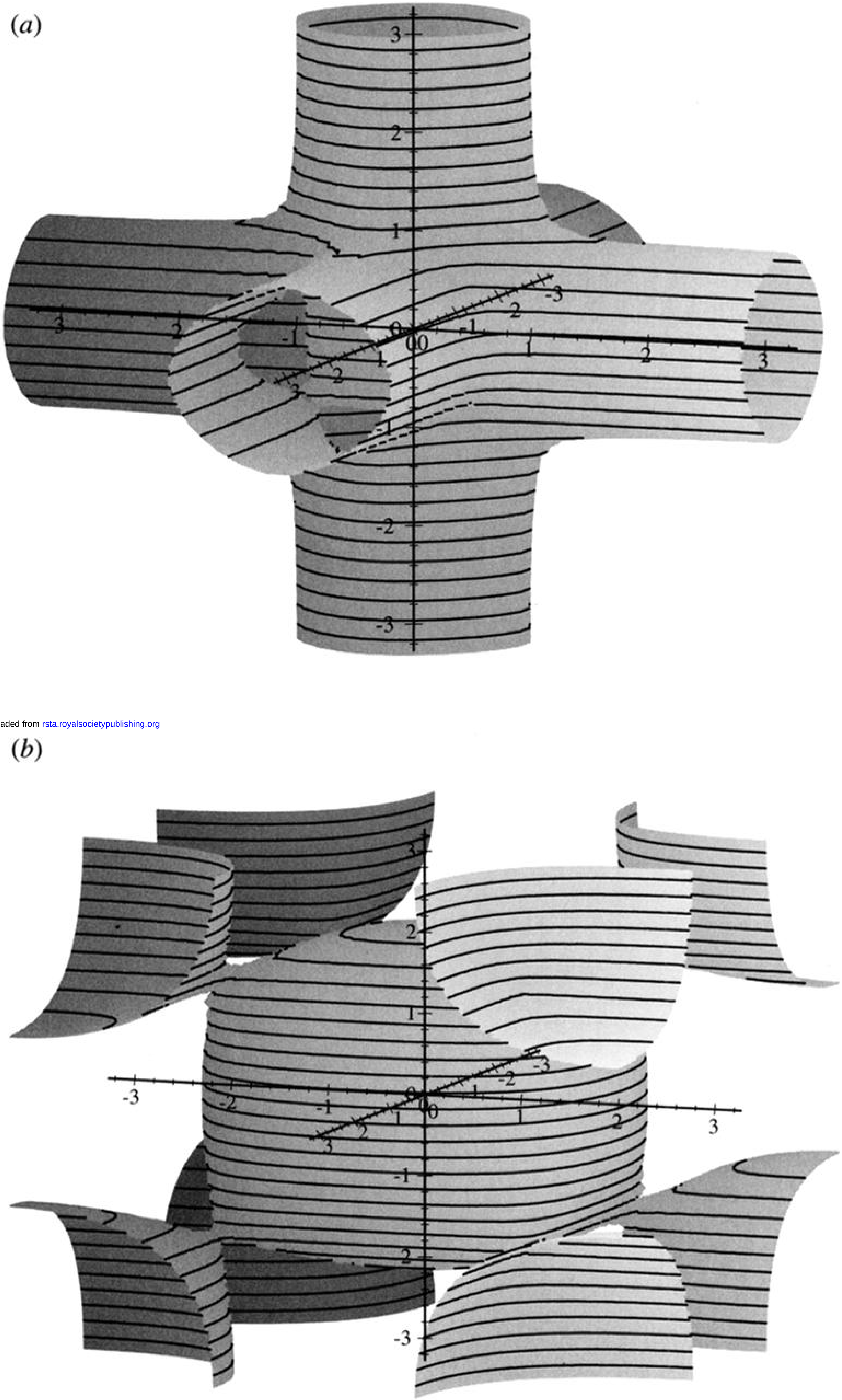
M. W. Long. My only answer would be that I think it would be a mess experimentally.

D. McK. Paul. It'll come through as a lifetime on some mode.

A. J. Millis. In my paper (this volume) I show information about the static lattice disorder. Now the question is about the vibration spectrum. If you really believe this picture, then in the paramagnetic insulating phase above T_C there are large amplitude local lattice distortions and some of them are Jahn–Teller in nature and break the local symmetry. So, you have to ask what is the time-scale on which these guys change? I think I can estimate for this, and then if you do a measurement which is fast on that time-scale, what you want to look for is a line which is forbidden on a symmetrical structure and allow that you actually have a Jahn–Teller distortion. So I'd like to see lines in Raman or something and, assuming that you can make the measurement fast enough, which disappear below T_C as the lattice distortions unwind themselves. You would also imagine that if you are really changing bond lengths by the order of 10% then the frequency of small oscillations about that has to change so you'd also expect phonon frequencies to change from above to below T_C. Those are the two things really to look for.

D. McK. Paul. Well, it wouldn't change anyway if it's a first-order transition.

A. J. Millis. But many of these have second-order transitions, but of course it's not a subtle thing. We're looking for very gross changes between very high temperature and very low temperature not precisely accurate.



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igure 3. Fermi surface for chemical potentials of (*a*) $\mu = 0.8$ and (*b*) $\mu = 0$ using the scaling $(\cos k_2 - \mu)(\cos k_3 - \mu) + (\cos k_3 - \mu)(\cos k_1 - \mu) + (\cos k_1 - \mu)(\cos k_2 - \mu) = 0$.