Electronic and magnetic transitions in a multiband model for $La_2NiO_4$

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The transition-metal oxide $La_2NiO_4$ is studied using a multiband Hubbard model with a Hund coupling $J$. We obtain its mean-field phase diagram in the $U$- ($\Delta$) plane. For $J=0$ we have a phase transition from a paramagnetic metal (PMM) to a paramagnetic insulator (PMI). On increasing $J$, the magnetic moment $M$ and the band gap $E_G$ change discontinuously at $J=J_c(U,\Delta)$. For $J=1$, the insulating phase (AFI) is antiferromagnetic, but we have, in addition, both paramagnetic (PMM) and antiferromagnetic (AFM) metallic phases. The insulator-metal (AFI-AFM) phase boundaries are first order, but the metal-metal (AFM-PMM) boundary is second order, and it seems to meet the first-order boundary at a critical end point. A reentrant PMM-AFM-PMM sequence is also seen. [S0163-1829(97)01316-7]

Considerable attention has been focused on cuprates and related oxides since the discovery$^1$ of high-$T_c$ superconductivity. However, there is a large class of other, non-superconducting oxides with interesting electrical and magnetic properties, which have not received as much attention. This includes transition-metal oxides of the type $ABO_3$ and $A_2BO_4$. Of particular interest is $La_2NiO_4$, which is isostuctural with $La_2CuO_4$. On doping with a small amount of strontium, both compounds which are antiferromagnetic insulators lose their magnetic order. However, $La_{2-x}Sr_xCuO_4$ becomes a superconductor for a range of dopant concentrations, whereas $La_{2-x}Sr_xNiO_4$ continues to be an insulator for $x<1$. In order to understand the unusual properties of $La_{2-x}Sr_xNiO_4$, a natural first step is to study the undoped parent compound, $La_2NiO_4$, which is an insulator with a band gap of about 4 eV (Ref. 2) and orders antiferromagnetically with a moment $M\approx 1.8\mu_B$.$^3$

The electronic structures of undoped transition-metal oxides have been traditionally discussed in terms of a phase diagram proposed by Zaanen, Sawatzky, and Allen (ZSA).$^3$ This well-known ZSA phase diagram was established by extensive calculations for the electronic charge-excitation gaps within the Anderson impurity Hamiltonian for every possible $d^n$ configuration. It separates the insulating regime from the metallic one by a second-order transition in the $U$-$\Delta$ plane. The use of a single transition-metal ion in the impurity model, however, precludes any possibility of describing the magnetic structure of the transition-metal compounds within this model. Hence a mean-field treatment of a multiband Hubbard model suitable for a square-planar $CuO_4$ lattice was employed$^3$ to provide a description of both charge and spin degrees of freedom. The resulting phase diagram established the existence of the covalent insulating regime, in addition to the other phases already identified by ZSA. However, the ZSA phase diagram$^4$ and its modification$^5$ are qualitatively similar, to the extent that a single continuous phase transition separates the insulating and the metallic states.

Here we show that the phase diagram for a multiband model for $La_2NiO_4$ is qualitatively different from ZSA-type phase diagrams in that it exhibits first- as well as second-order electronic transitions and even a reentrant magnetic transition. Thus the $La_2NiO_4$ class displays a much wider range of behaviors than the $La_2CuO_4$ class,$^5$ though they are isostuctural. This result emphasizes the importance of accounting for electronic configurations and electronic interaction parameters in determining the topology of the phase diagram.$^6$

In order to describe the $d^8$ electron configuration in a multiband Hubbard model, we must include an additional term in the Hamiltonian. This is the Hund coupling $J$ that favors the state with the maximum local spin. In $La_2NiO_4$ each nickel atom is surrounded by six oxygen atoms, which form a distorted octahedron, thus reducing the point-group symmetry from $O_h$ to $D_{4h}$. This lifts the degeneracy of the $d_{3z^2-r^2}$ ($a_{1g}$ symmetry) and $d_{xy}$ ($b_{1g}$ symmetry) levels. The other three Ni $d$ levels, being fully filled, do not contribute to any physical properties. Thus we have two holes distributed between the $a_{1g}$ and $b_{1g}$ levels depending on the relative strengths of the crystal-field splitting and $J$ in the ionic limit. We denote the state with two holes at the Ni site and no holes at the O sites by $d^2L^0$. Taking note of the
strong two dimensionality of the crystal structure of La$_2$NiO$_4$, we consider only the two-dimensional Ni-O plane, including the apical O atoms, so that each unit cell has one Ni and four O atoms.$^7$ There are two relevant orbitals on the Ni and three on each O, resulting in 14 orbitals (28 spin orbitals) in each unit cell. Thus the Hamiltonian is

$$H = \sum_{i,l,s} \epsilon_i p_{il\sigma}^\dagger p_{il\sigma} + \sum_{i,l,s} \epsilon_j d_{il\sigma}^\dagger d_{il\sigma}$$

$$+ \sum_{i,j,l_1,l_2,s} t_{ijl_1l_2}^\dagger t_{ijl_1l_2} p_{il\sigma}^\dagger p_{jl\sigma} + \sum_{i,j,l_1,l_2,s} t_{ijl_1l_2}^\dagger t_{ijl_1l_2} d_{il\sigma}^\dagger d_{jl\sigma}$$

$$+ \sum_{i,l_1,l_2,s,s'} U d_{il_1\sigma}^\dagger d_{il_2\sigma} d_{il_1\sigma'} d_{il_2\sigma'}, - \sum_l J S^2_l, \tag{1}$$

where $d_{il\sigma}$ ($d_{il\sigma}^\dagger$) creates (annihilates) a hole with spin $\sigma$ in the $l$th $d$ orbital ($l = 1$ for $x^2-y^2$ and $l = 2$ for $3z^2-r^2$) on the Ni atom at the $i$th site. $p_{il\sigma}^\dagger$ ($p_{il\sigma}$) creates (annihilates) a hole with spin $\sigma$ in the $l$th $p$ orbital ($l = 1,2,3$ for $x,y,z$) on the O atom at the $i$th site, and $s_i$ is the total spin of the Ni atom at the $i$th site. The last term in Eq. (1) is the Hund coupling which ensures that the state with $S=1$ is lower in energy than the one with $S=0$ in the atomic limit.

The various $t_{pp}$'s and $t_{pd}$'s were determined in terms of the usual Slater-Koster parameters $t_{pp}^\dagger$, $t_{pp}^\dagger$, $t_{pd}^\dagger$, $t_{pd}^\dagger$, and $t_{pd}$. For the hopping strengths in the basal plane we used $t_{pd}^\dagger = 1.6$ eV, $t_{pp}^\dagger = -0.6$ eV, and $t_{pp}^\dagger = 0.4$ eV, which are similar to the values obtained earlier from an analysis of band-structure results; the qualitative features of the various results presented here are, however, not very sensitive to the exact values used. The hopping interaction strengths were assumed to scale with distance ($r$) as $1/r^{1+l'+1}$ where $l$ and $l'$ are the angular momenta of the orbitals involved. The $d_{3z^2-r^2}$ orbitals have an on-site hole energy ($\epsilon_{d} = \epsilon_{d_{3z^2-r^2}}$) 0.5 eV (Ref. 9) more than that ($\epsilon_{p} = \epsilon_{d_{3z^2-r^2}}$) of the $d_{x^2-y^2}$ orbitals because of crystal-field effects. The minimum energy required to transfer a hole from a nickel site to the oxygen site is the charge-transfer energy $\Delta = \epsilon_{p} - \epsilon_{d_{3z^2-r^2}} - U + J$.

We decoupled the four-fermion terms in model (1) by using a mean-field approximation and then solved self-consistently for the order parameters in $k$ space with 900 or 1600 points within the two-dimensional Brillouin zone, to ensure that our results were not affected by the finite resolution of the $k$ grid. The convergence criterion used was that the differences between the order parameters between successive iterations were less than $10^{-6}$. The band structure of the effective one-electron problem, the band gap $E_g$, the ground-state energy, and various orbital and spin related order parameters were determined after the solution had converged. The energies of various possible electronic and magnetic states were obtained at a given set of values of $U$, $\Delta$, and $J$. A comparison of the total energies of these states yielded the ground-state behavior at a given point in the $U$-$\Delta$-$J$ parameter space. Such calculations were performed at various points in the $U$-$\Delta$-$J$ space for two fixed values of $J$ ($=0$ and 1 eV) to obtain the representative phase diagrams.

To ensure that the model (1) is indeed relevant for La$_2$NiO$_4$ and related compounds, we compare the physical properties of La$_2$NiO$_4$, as calculated from our mean-field theory, with those obtained experimentally. The values of the other interaction parameters, namely, $U$ and $\Delta$, have been estimated from high-energy spectroscopies to be about 8 eV and 4 eV, respectively. If we set $J = 1$ eV, we find a band gap of about 4 eV and a magnetic moment $M = 1.7 \mu_B$. The experimental band gap is $\approx 4$ eV (Ref. 2), and the magnetic moment $M = 1.8 \mu_B$; thus there is good agreement between our results and experiments.

In Fig. 1 we show the phase diagram in the $U$-$\Delta$ plane for $J=0$, with the inset illustrating typical variations of the gap as a function of $\Delta$ (for $U=8$) and $U$ (for $\Delta = 9.5$). In each
case, the band gap is found to decrease continuously to zero, indicating that there is always a continuous transition between a paramagnetic insulator and a paramagnetic metal for \( J=0 \). The paramagnetic states, throughout the \( J=0 \) plane, are easy to understand, since, in the absence of the Hund rule (or intraatomic exchange) coupling, the crystal-field splitting always favors the \( S=0 \) state with spins paired at each site. The metal-insulator transition (MIT) in the phase diagram of Fig. 1 is qualitatively similar to the ZSA diagram or the modified-ZSA diagram, insofar as there is only one second-order phase boundary.

Since La\(_2\)NiO\(_4\) is an antiferromagnetic insulator, which does not appear in the phase diagram of Fig. 1, we must allow for \( J>0 \) in model (1). We begin by investigating the effect of \( J \) on the band gap \( E_G \) and the magnetic moment \( M \) at the Ni site at a given point in the \( U-\Delta \) plane, namely, \( U=5 \) eV and \( \Delta=4.5 \) eV. We find that both change discontinuously at a critical value, \( J=J_c=0.6 \) eV (Fig. 2), signifying a first-order transition. The reason for the discontinuous changes as a function of \( J \) can be understood easily in the ionic limit. For small values of \( J \), the two holes reside on the \( d_{2z^2-r^2} \) orbital giving rise to the \( S=0 \) state because of the finite crystal-field splitting. Once \( J \) becomes greater than the crystal-field splitting, the two holes adopt a parallel spin configuration (\( S=1 \)) by distributing themselves equally in the \( d_{2z^2-r^2} \) and \( d_{3z^2-r^2} \) orbitals, with \( J \) more than compensating for the crystal-field splitting. This shows that the first-order transition between the paramagnetic \( S=0 \) state and the magnetic \( S=1 \) state occurs at \( J_c=(e_2^G-e_1^G)=0.5 \) eV in our model in the ionic limit. In the presence of hopping \( J_c \) changes somewhat, since the \( d_{2z^2-r^2} \) and \( d_{3z^2-r^2} \) orbitals hybridize differently with the oxygen orbitals because of the distortions of the NiO\(_6\) octahedron. However, \( J_c \) appears to depend only weakly on other electronic interaction parameters, since \( J_c=0.6 \) eV for the parameters of Fig. 2 and at various other points in the \( U-\Delta \) plane not shown here.

In Fig. 3 we show the mean-field phase diagram of model (1) for \( J=1 \) eV. Note that it is qualitatively different from the phase diagram of Fig. 1 in that it shows a paramagnetic metal (PMM) phase and two antiferromagnetic phases, one an antiferromagnetic insulator (AFI) and the other an antiferromagnetic metal (AFM). The topology of this phase diagram is such that the metallic phases (PMM and AFM) are separated from the insulating phase (AFI) by a first-order phase boundary (solid line), whereas the phase transition between the metallic phases (AFM-PMM transition) is a con-
tinuous one (dashed line). The simplest way in which the first- and the second-order phase boundaries can meet is at a critical end point (shaded circle); however, such numerical studies are not accurate enough to rule out more complicated topologies with combinations of other multicritical points (like tricritical points), which might well arise from further-neighbor interactions. Note that the AFM-PMM phase boundary curves in a way that allows the reentrance sequence PMM-AFM-PMM with changing $\Delta$ or $U$ over a limited range of our parameter space.

The phase diagram of Fig. 3 is based on various scans through the $U$-$\Delta$ plane which examine the variations of $E_G$ and $M$ with $\Delta$ at fixed $U$ or vice versa. Three representative scans are shown in Figs. 4(a) and 4(b) for $E_G$ and $M$, respectively. (1) For $\Delta=1.5$ eV (full triangles), $M$ [Fig. 4(b)] rises continuously from 0 at the PMM-AFM transition at $U=0.9$ eV, but $E_G$ [Fig. 4(a)] remains at 0 till $U=2.7$ eV, signifying a second-order transition between the metallic states. For larger values of $U$, a finite band gap develops, indicating a metal-insulator transition [see Fig. 4(a)]. This transition between the metallic (AFM) and the insulating (AFI) phases is first order, though the resolution of the figure is not adequate to show the discontinuity. Therefore we have shown the variations in the moment in the band gap over a very narrow range of the parameter space near the transition point in the inset of Fig. 4(a). This clearly shows a discontinuous change in the moment at the transition point. We have checked the order of this AFM-AFI transition at several points along the phase boundary by carrying out similar calculations over very fine grids in the parameter space and have indeed confirmed that it is always a first-order transition. (2) For $\Delta=0$ (full inverted triangles), we have a clear first-order PMM-AFI transition as can be seen from the jumps in both $E_G$ [Fig. 4(a)] and $M$ [Fig. 4(b)] at $U=4.4$ eV. With decreasing $U$, we find that a finite moment develops for $U$ less than about 4.0 eV [see Fig. 4(b)], but the band gap remains zero, indicating a transformation from the PMM to the AFI phase. Eventually $M$ disappears for $U$ less than about 2.6 eV, showing a reentrant PMM phase. Within our numerical accuracy, the PMM-AFI boundary appears to be second order. (3) If we increase $\Delta$ at $U=5$ eV (full squares), we only encounter the first-order PMM-AFI transition at $\Delta=0.23$ eV.

It is worth noting that our phase diagram (Fig. 3) exhibits all categories of insulators discussed in the ZSA and modified-ZSA contexts, namely, charge-transfer, Mott-Hubbard, and covalent insulators (see the variation of $E_G$ in the inset of Fig. 1). In addition, our model (1) also shows a Slater insulator at $U=0$ for $\Delta>4.7$ eV; this is made possible by the presence of a finite $J$ in the system.

To summarize, our study of La$_2$NiO$_4$ shows that a two-dimensional, multiband Hubbard Hamiltonian can describe the low-energy physics of the undoped compound if we include the Hund coupling. We have shown this yields quantitative agreement between experimental and calculated band gaps and the magnetic moment. The $U$-$\Delta$ phase diagram for $J=0$ shows a continuous transition between PMI and PMM phases. This topology persists for $0<J<J_\ast$. For $J>J_\ast$ the phase diagram is qualitatively different from the ZSA type. Specifically, for $J=1$ eV, the phase diagram shows an AFI phase for large $U$ and $\Delta$, which persists even for $U=0$ when $\Delta>\Delta_\ast=4.7$ eV. AFM and PMM phases also appear in this phase diagram, which has a rich topology including first-order and continuous phase boundaries meeting at a critical end point. The phase diagram also shows an intriguing PMM-AFM-PMM reentrant sequence for small values of $\Delta$. Thus the electronic and magnetic phase diagrams for transition-metal compounds of the A$_2$BO$_4$ type are determined not only by the various electronic strengths, but also depend explicitly on the electron configuration and lattice geometry. It would be interesting to see if phase diagrams like Fig. 3 can be obtained by studying a whole class of such oxides, each member of which will be characterized by different coupling strengths in model (1), although it might be hard to resolve the topologies of such phase diagrams near multicritical points.

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10 Of course one must ascertain whether terms other than those in model (1) are important in different A$_2$BO$_4$ systems. Examples of such terms include full multiplet interactions within the intraatomic terms and extended Hubbard interactions.