Lattice Energetics and Correlation-Driven Metal-Insulator Transitions: The Case of Ca$_2$RuO$_4$

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Abstract: This Letter uses density functional, dynamical mean field, and Landau-theory methods to elucidate the interplay of electronic and structural energetics in the Mott metal-insulator transition. A Landau-theory free energy is presented that incorporates the electronic energetics, the coupling of the electronic state to local distortions and the coupling of local distortions to long-wavelength strains. The theory is applied to Ca$_2$RuO$_4$. The change in lattice energy across the metal-insulator transition is comparable to the change in electronic energy. Important consequences are a strongly first order transition, a sensitive dependence of the phase boundary on pressure and that the geometric constraints on in-plane lattice parameter associated with epitaxial growth on a substrate typically change the lattice energetics enough to eliminate the metal-insulator transition entirely.

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Many materials exhibit "Mott" metal-insulator transitions, primarily driven by electron-electron interactions but also involving changes in atomic positions. In the rare earth titanates and vanadates, the distortion associated with the insulating phase is a GdFeO$_3$-type octahedral rotation$^{2,3}$, in the rare earth manganites, it is an approximately volume-preserving even-parity octahedral distortion$^{1-6}$: in the perovskite nickelates, a two sublattice disproportionation of the mean Ni-O bond length$^{7-10}$ and in VO$_2$ a V-V dimerization$^{11}$. In other materials including Ca$_2$RuO$_4$$^{12}$ and V$_2$O$_3$$^{13}$ the metal-insulator transition occurs simultaneously with a crystal symmetry-preserving change of atomic positions. The association of metal-insulator and structural transitions suggests the possibility of tuning electronic behavior by strain$^{14}$, epitaxial growth, or "nonlinear phononic" effects arising from intense terahertz radiation$^{15-17}$.

While electronic aspects of the Mott transition are becoming well understood, and energies, forces, and many-body structural relaxation are now available in beyond density functional frameworks such as the density functional plus dynamical mean field methodology$^{18-20}$, the interplay between the lattice and electronic energetics has yet to be fully unraveled. A physical basis for interpreting the calculations and the experiments remains to be defined and the magnitude of the lattice contribution to the energetics of the transition has yet to be determined. Here we argue that the key point is that the electronic transition couples directly to local atomic configurations such as octahedral rotations and transition metal-oxygen bond lengths, which in turn couple directly to externally controllable variables such as strain and pressure. The response of the material to these stresses defines a lattice stabilization energy, which can in fact be large enough to dominate the energetics of the transition.

To quantify these effects we write an electronic free energy $F^e(\delta \vec{Q})$ that depends on a state variable $a$ labeling the material, on atomic coordinates, and on atomic coordinates, labeled by a vector $\delta \vec{Q}$ expressing deviations of atomic positions from a reference configuration. Expanding in $\delta \vec{Q}$ we obtain

$$F^a(\delta \vec{Q}) = F^a_0 + \vec{F}^a \cdot \delta \vec{Q} + \frac{1}{2} \delta \vec{Q}^T \cdot \mathbf{K}^a \cdot \delta \vec{Q} + ...$$ (1)

The electronic state-dependent linear term $\vec{F}^a$ specifies the force exerted by the electronic state on the atomic degrees of freedom. Typically $\vec{F}$ couples only to a subset of the lattice degrees of freedom, but this subset is coupled to other lattice coordinates by the quadratic restoring term $\mathbf{K}$. The ellipsis represents anharmonic terms that are not needed for the considerations of this Letter but may be important in other circumstances$^{4,21}$.

Minimizing the terms written in Eq. (1) gives $F = F^a_0 - \frac{1}{2} \vec{F}^a \cdot \mathbf{K}^{-1} \cdot \vec{F}^a$ defining the stabilization energy

$$F^a_{\text{stabil}} = -\frac{1}{2} \vec{F}^a \cdot \mathbf{K}^{-1} \cdot \vec{F}^a$$ (2)

so that if the lattice is free to relax, the transition between phases $a = 1, 2$ will occur when $F^a_0 + F^a_{\text{stabil}} = F^2_0 + F^2_{\text{stabil}}$ corresponding to a shift in the transition point relative to a frozen lattice calculation and a lattice change across the transition $\delta \vec{Q}^1 - \delta \vec{Q}^2 = -\mathbf{K}^{-1} (\vec{F}^1 - \vec{F}^2)$.

We now apply these generic considerations to Ca$_2$RuO$_4$, which exhibits a correlation-driven paramagnetic metal to paramagnetic insulator transition as the temperature is decreased below a critical value about 350 K$^{12}$. The transition is accompanied by a large amplitude, symmetry preserving lattice distortion$^{22,23}$. Below about 140 K there is an onset of antiferromagnetic order$^{22,23}$, which is not relevant to our present considerations. Ca$_2$RuO$_4$ crystallizes in a $Pbca$-symmetry structure with four formula units in each crystallographic unit cell. The basic structural unit is the Ru-O$_6$ octahedron;
these form corner-shared planes separated from adjacent Ru-O$_6$ planes by layers involving Ca atoms. The left panel of Fig. 1 shows one unit cell with four formula units. The $Pbca$ structure is derived from the ideal tetragonal $n = 1$ Ruddlesden-Popper structure by rotations of the Ru-O$_6$ octahedrons about the apical Ru-O(2) bonds, tilts of this axis with respect to the Ru-O(1) plane, as well as an additional distortion that makes the two in-plane Ru-O bond lengths slightly different. The apical [Ru-O(2)] and the average over the two in-plane directions [Ru-O(1)] Ru-O bond lengths are the crucial variables in the electronic energetics. Their values across the metal-insulator transition are presented in Table I. The bond lengths continue to evolve as temperature is varied.

We will be interested here in structures where the $c$-axis lattice parameter is relaxed for given values of the octahedral bond lengths. Thus the lattice degrees of freedom in our theory are the average Ru-O(1) and Ru-O(2) lengths. We parametrize the Ru-O bond lengths in terms of changes $\delta x, \delta y, \delta z$ with respect to a reference state, which we take to be the 400 K metallic state, and we express these in terms of the octahedral coordinates

$$\delta Q_0 = \frac{1}{\sqrt{3}}(\delta z + \delta x + \delta y) \quad \delta Q_3 = \frac{1}{\sqrt{6}}(2\delta z - \delta x - \delta y) \quad (3)$$

which we assemble into the vector $\delta \vec{Q} = (\delta Q_3, \delta Q_0)$. $K$ in Eq. (1) is defined from the dependence of energies on $\delta Q_3$ and $\delta Q_0$, with the c-axis lattice constant relaxed for each value of $\delta \vec{Q}$. We used density functional plus U (DFT+U) calculations and observed phonon frequencies (which give energetics of Ru-O bond length changes without lattice relaxation) to estimate the entries of $K$ (see Supplemental Material [24]), finding $K_{33} = 17.7, K_{03} = 7.6, K_{30} = 46.2$ eV/A$^2$ per formula unit. The observation$^{25-27}$ that the changes in optical phonon frequencies across the transition are about 2%, justifies the harmonic approximation and the independence of $K$ on the electronic phase.

We now turn to the electronic degrees of freedom. The relevant frontier electronic states are $t_{2g}$-derived Ru-4d oxygen 2$p$ antibonding states which we refer to as Ru $d$ states, following standard practice$^{28-32}$. The $t_{2g}$-derived bands are well separated from the other bands, so we may focus our treatment of the correlation problem on them, treating the other bands as inert$^{30-32}$. The tetragonal symmetry splits the $t_{2g}$-derived triplet into a singlet ($d_{xy}$) and a doublet ($d_{xz}$ and $d_{yz}$). The octahedral rotations and other distortions ($\alpha$) provide small additional rearrangements of the level structure (in particular lifting the $xz/yz$ degeneracy), but as long as the orbitals are defined with respect to the local octahedral symmetry axes, the deviations from the perfectly tetragonal structure do not significantly affect the on-site level splitting, basic energetics, or assignment of orbital character. Spin-orbit coupling ($\lambda_{SOC} \approx 0.1$ eV) is important for lower $T$ magnetic properties of the insulating state$^{27,33,34}$ but is not relevant to the physics we consider here since the spin-orbit energy scales are small compared to the orbital level splitting and electron interactions.

We have performed DFT and DFT+DMFT calculations (see Supplemental Material$^{35}$). We find, in agreement with previous work$^{30}$, that a calculation at room temperature with the experimentally determined 400 K structure produces a moderately correlated metallic solution while using the 295 K structure produces a Mott insulator. The metallic state is characterized by an approximately equal occupancy of the three $t_{2g}$ orbitals.

![Image](59x603 to 132x714)

**FIG. 1.** Left panel: Representation of the unit cell of Ca$_2$RuO$_4$. Gray balls are ruthenium atoms, red balls oxygen atoms and blue balls calcium atoms. Right panel: Orbitally resolved many-body densities of states for structures interpolating between experimental 295 and 400 K structures. Upper panel: $xy$ orbital; lower panel: $yz$ orbital ($xz$ is very similar). $\alpha = 0$ is the 295 K structure; $\alpha = 1$ is the 400 K structure; $\alpha = 0.4$ is in the metallic phase but very close to the transition point; the $\alpha = 0.6, 0.8$ spectra are very similar to the 400 K spectra and are omitted for clarity.

| $K$ | $\delta Q_0$ | $\delta Q_3$ | $\delta Q_{xy}$ | $\delta Q_{yz/xx}$ |
|-----|---------|---------|------------|----------------|
| 400 K | 2.042 | 1.95 | 0.0 | 0.671 | 0.665 |
| 295 K | 1.995 | 1.99 | 0.0196 | -0.069 | 0.982 | 0.508 |

$K_{ij}$ denotes the electronic phase. Their values across the transition are about 2%, justifies the harmonic approximation and the independence of $K$ on the electronic phase.
The approximately equal orbital occupancy is not protected by any symmetry and is due to the strong electron–electron scattering. The insulating state is orbitally dis-proportionated, with an essentially fully filled $xy$ band and half filled, much narrower, $xz/yz$ bands with upper and lower Hubbard bands separated by a gap (Fig. 1 right panel with blue dashed lines). Calculated orbital occupancies are given in Table 1.

The right-hand panels of Fig. 1 present the orbitally resolved densities of states obtained from DFT+DMFT calculations at room temperature, performed for a series of structures linearly interpolated between the $T=295$ ($\alpha=0$) and $T=400$ K ($\alpha=1$) structures. As the interpolation parameter $\alpha$ changes from 1 to 0.4, the state remains metallic but the bands and occupancies ($n_{xy},n_{xz},n_{yz}$) change from $\approx (4/3,4/3,4/3)$ to $\approx (5/3,7/6,7/6)$. A first order MIT occurs as $\alpha$ is decreased below a critical value $\approx 0.4$. Further changes of structure within the insulating phase ($\alpha=0$, 0.2) do not affect the orbital occupancies but do lead to an approximately 0.1 eV shift upward of the $xz/yz$ band relative to the $xy$ band. We have also performed calculations in which one starts from the DFT+U relaxed insulating phase atomic positions with in-plane lattice constants fixed to 5.44 Å and the $c$-axis parameter is then gradually stretched. The results are very similar to the first group. Although the transition is first order we have not observed coexistence of metal and insulator phases at any of the lattice configurations we have studied.

Fig. 2 plots the DFT+DMFT energy of the correlated bands in two series of structures: the linearly interpolated structures between the experimentally observed metallic 400 K and insulating 295 K structures (solid points, blue) and a series obtained by starting from an relaxed insulating structure with $a=b=5.44$ Å and stretching the $c$-axis (open symbols, red). The bold dashed black line stands for the linear fit in Eq. (4) and the light dashed line shows the phase boundary. The error bars are statistical errors from the Monte Carlo solution of the DMFT equations.

The consistency of the model can be verified via a computation of the pressure dependence of the transi-
tion. This is obtained by adding to Eq. (1) a term
\[ +PdV = P_3^c(ab\delta c + ac\delta b + bc\delta a) = P(\beta_3\delta Q_3 + \beta_0\delta Q_0) \]
with \((\beta_3, \beta_0) = (-0.3281, -0.1861)\) eV/(GPa Å formula unit), so that applied pressure is in effect a linear term shifting the position and value of the energy minimum. We find \(P_\text{exp} = 3.6 - 0.011T\) (Gpa) which is comparable to \(P_\text{exp} = 2.3 - 0.0067T\) (Gpa) fitted from published data\(^{36}\). More details are in the Supplemental Material\(^{15}\).

In Fig. 3 we plot the free energy landscape at different temperatures in the plane of Ru-O bond length coordinates \(\delta x = 1/\sqrt{3}\delta Q_0 - 1/\sqrt{6}\delta Q_2\) and \(\delta z = 1/\sqrt{3}\delta Q_0 + \sqrt{6}/3\delta Q_3\), using force terms estimated in Eq. (5). We chose the metallic state at \(T > T_{M-I}\) as the reference. At high temperature, there is no global minimum in the insulating phase. For \(T \leq T_{M-I}\), an insulating energy minimum as in Eq. (2) appears and becomes more stable. The stabilization energy defined in Eq. (2) is \(-0.048\) eV/Ru at \(T_{M-I}\).

We now turn to epitaxially grown films. While epitaxial films are strained with respect to bulk, strain is not the key issue. Rather, the tight association of the in-plane lattice parameter and the Ru-O(1) bond length means that epitaxy implies a constraint: instead of freely minimizing Eq. (1) over the full space of structural variables, the system can explore only a one-dimensional cut across the energy landscape, corresponding to a fixed Ru-O(1) bond length. The solid and dashed lines in Fig. 3 show the one-dimensional cuts which can be explored under different epitaxy conditions. Because the curves typically do not pass near the global minimum, the phase transition becomes much more expensive and in most cases is eliminated. Only in a small range of compressive strains around \(-1.0\%\) (relative to 295 K structure) can a metal-insulator transition occur in a reasonable temperature range. For a larger compressive strain the system is always a metal while for a tensile or small compressive strain the material is always an insulator. This is consistent with recent experimental observations\(^{37,38}\) that thin films of Ca\(_2\)RuO\(_4\) grown epitaxially on NdGaO\(_3\) (+0.3% strain) and NSAT (-0.48%) remain insulating up to 550 K while films grown on NdAlO\(_3\) (-3.0%) remain metallic down to lowest temperature. Only films grown on LaAlO\(_3\) (-1.6%) exhibit a transition to a weakly insulating phase at \(T \approx 200\) K.

In summary, we demonstrated the importance of lattice energetics in the Mott metal-insulator transition, elucidating the crucial interplay between the local octahedral distortions and long wavelength strains, and the previously unappreciated role of epitaxial constraints. We focused on Ca\(_2\)RuO\(_4\), which has two simplifying features: the metal and insulator have the same symmetry and oc-tahedral rotations are of minor importance, so the order parameter couples linearly to strains and the in-plane Ru-O bond lengths determine the Ru-Ru spacing. Performing a complete DFT+DMFT structural relaxation study and providing a less phenomenological treatment of the electronic and, especially, lattice entropies are also important directions for future research. Most importantly, a generalization of the theory to cases where octahedral rotation is important (perovskite titanates and vanadates) or the insulating phase breaks a translation symmetry (manganites and nickelates) so that strain couples via nonlinear terms in the elastic theory, is urgently needed.

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See Sec. I for details of DFT+U calculation and estimation of stiffness matrix $\mathbf{K}$, which includes Refs. 39–42 not cited in the main text.

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