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Metal-Insulator Transition and Orbital Order in PbRuO₃

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Anomalous low temperature electronic and structural behavior has been discovered in PbRuO₃. The structure (space group Pnma, a = 5.56314(1), b = 7.86468(1), c = 5.61430(1) Å) and metallic conductivity at 290 K are similar to those of SrRuO₃ and other ruthenate perovskites, but a sharp metal-insulator transition at which the resistivity increases by 4 orders of magnitude is discovered at 90 K. This is accompanied by a first-order structural transition to an Imma phase (a = 5.56962(1), b = 7.74550(1), c = 5.66208(1) Å at 25 K) that shows a coupling of Ru⁴⁺ 4d orbital order to distortions from Pb²⁺ 6s₆p orbital hybridization. The Pnma to Imma transition is an unconventional reversal of the group-subgroup symmetry relationship. No long range magnetic order is evident down to 1.5 K. Calculations show that Pb 6s⁶p and Ru 4d orbital hybridization and strong spin-orbit coupling are significant.

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Transition metal oxide perovskites display a remarkable range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1]. Perovskite-related ruthenates based on Ru⁴⁺ have proved interesting as broad range of electronic phenomena such as superconductivity, colossal magnetoresistances, and coupled charge, orbital, and spin orderings [1].
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By contrast, the Ru 4d and O 2p states in PbRuO₃ lie just
between the occupied Pb 6s and unoccupied Pb 6p states. The Ru t₂g-Pb 6s and Ru eₓ- Pb 6p hybridizations, both
aided by the O 2p state, and t₂g-eₓ mixing due to the lattice
distortion, significantly suppress the exchange splitting of the
Ru t₂g-O 2p conduction bands, reducing the magnetic
stabilization energy to near zero (∼4 meV/f.u.). To con-
firm that the slight lattice differences between the two
materials are unimportant, we also calculated the elec-
tronic structure of SrRuO₃ using the PbRuO₃ parameters
and found that the electronic and magnetic properties were
virtually identical. An unexpected difference between PbRuO₃ and the
other perovskite ruthenates was discovered by resistivity
measurements (Fig. 2). At ambient temperatures, the
PbRuO₃ has a resistivity of ∼10⁻¹ Ω cm with little tem-
perature dependence, characteristic of metallic conduction
with a resistive grain boundary contribution. However, on
cooling, the resistivity increases sharply by 4 orders of
magnitude (and was immeasurably large below 60 K), sig-
ifying a metal-insulator transition at TMI = 90 K. This
transition is also evident in magnetization data. The high
temperature susceptibility is fitted as χ = C/(T − θ) + χP,
a sum of Curie-Weiss and Pauli paramagnetic terms, re-
spectively, with χP = 2.09(1) × 10⁻³ emu/mol, Curie con-
stant C = 0.195 emu K/mol (corresponding to a paramag-
etic moment of 1.25 µB), and a Weiss temperature θ =
−54 K. Similar large temperature-independent contribu-
tions have been reported for nonperovskite ruthenates such
as the pyrochlore Tl₂Ru₂O₇ (χP = 2 × 10⁻³ emu/mol)
[15] close to metal-insulator instabilities. A small dip is
observed in the magnetic susceptibility on cooling through
TMI, showing that antiferromagnetic correlations are
present in the insulating state. However, no long range
magnetic transition is evident down to 4 K, although a
broad hump with divergence between field- and zero-field-
cooled susceptibilities is observed below 50 K.
A strong coupling of structure to the metal-insulator
transition is observed in both x-ray and neutron powder
diffraction measurements (Fig. 3). PbRuO₃ remains ortho-
rhombic down to 1.5 K; however, the lattice parameters
and volume change discontinuously on cooling through the
transition (Fig. 4), and, surprisingly, the Pnma superstruc-
ture reflections with odd (h + k + l) values disappear (see
Fig. 3 inset). No new superstructure reflections, peak
broadenings, or splittings were observed in the low tem-
perature diffraction patterns of PbRuO₃, which are indexed by the body-centered space group Imma. This describes
another common tilting superstructure of perovskites, and a
refined Imma model gives excellent fits to both x-ray and
neutron data [12]. Fits of lower-symmetry, acentric body-
centered structures were unsuccessful. No magnetic dif-
fraction peaks were observed down to 1.5 K in the GEM
time-of-flight neutron diffraction data or in subsequent
constant wavelength profiles collected from instrument E6 at the HZB reactor. We estimate the upper limit
for any ordered Ru moment to be ∼0.5 µB.
The (high temperature) *Pnma* to (low temperature) *Imma* transition in PbRuO₃ is remarkable as *Pnma* is a subgroup of *Imma*, so a continuous group-subgroup transition from *Imma* to *Pnma* is allowed in Landau theory and is observed in many simple perovskites such as SrSnO₃ [16]. The *Pnma-Imma* “subgroup-group” transition in PbRuO₃ is clearly first-order, with a small volume anomaly typical of metal-insulator transitions and a substantial hysteresis of 20 K in the cell parameters between warming and cooling experiments (Fig. 4). The subgroup-group structural contribution to the transition entropy is negative, but this is evidently outweighed by the large positive electronic contribution from the delocalization of Ru 4d electrons.

The evolution of the Ru-O bond distances (Fig. 4) reveals an important aspect of the metal-insulator transition. At room temperature, the RuO₆ octahedra are almost regular with Ru-O bond lengths of 2.00–2.01 Å, but, below *T*ₘᵢ, a Jahn-Teller distortion is apparent in the *Imma* structure, with two short Ru-O1 bonds (1.97 Å) aligned approximately along *z* and four long Ru-O2 bonds (2.02 Å) in the xy plane. To a first approximation, this corresponds to a *dₓ²₋* / *dᵧ²₋* / *dᵢz*, orbital ordering of the Ru⁴⁺ / Ru⁴⁺ configuration in the insulating *Imma* phase, creating planes of minority-spin-occupied *dₓᵧ* orbitals, as shown in Fig. 4. Pb²⁺ shows an unusual *A*-site distortion, having a near-regular square pyramidal coordination with five short Pb-O bonds (Pb-O1, 2.51 Å × 1; Pb-O2, 2.50 Å × 4), while other Pb-O distances are >2.82 Å. The O1-Ru-O2 angle of 122.5° shows that this is not a lone pair effect, for which an angle of <90° is expected. The Pb and Ru distortions are cooperative as O1 forms short bonds to Ru and only one short bond to Pb, whereas O2 has long bonds to Ru and four short bonds to Pb.

To clarify the orbitally ordered state, we have carried out LSDA + *U* calculations for the *Imma* phase with an effective Hubbard *U* = 3.5 eV [17]. Spin-orbit coupling (SOC) was also included since this ~160 meV interaction is large relative to the calculated crystal field splitting between the *dₓᵧ* and *dᵢz*, *dᵧz* levels of ~50 meV. Our LSDA + *U* + SOC calculations gave an insulating ground state with a small gap of ~0.1 eV, verifying that PbRuO₃ is in the vicinity of a metal-insulator transition. The minority spin electron has a 0.46(1 + *i*) *dₓᵧ* - 0.38(1 - *i*)(*dᵢz* + *dᵧz*) orbital state which consists of 42% *dₓᵧ*, 29% *dᵢz*, and 29% *dᵧz*, with *dₓᵧ* being dominant as expected from the above structural results. Different magnetic solutions lie close in energy; e.g., the lowest *G*-type antiferromagnetic state is only 6.8 meV/f.u. below the ferromagnetic state, in keeping with the observed lack of magnetic order discussed below.

The insulating, orbitally ordered ground state of PbRuO₃ is anomalous in comparison to the other ARuO₃ perovskites (*A* = Ca, Sr, Ba), which remain metallic to the lowest temperature. This is not due to a size effect as CaRuO₃ has the most tilted *Pnma* superstructure but is stable to orbital order. (The combination of small Ca²⁺ and an imposed tetragonal symmetry in layered Ca₂RuO₄ is sufficient to induce a weak orbital order [18], but this phase is a Mott insulator.) The electronic nature of Pb is a key factor, and Ru 4d-Pb 6s⁷p-O 2p hybridizations are evident in the above band structure calculations. This Pb²⁺ covalency is sometimes manifest as a lone pair distortion resulting in ferroelectricity, e.g., in PbTiO₃, but lone pair distortions are not observed in either the *Pnma* or the
Imma phases of PbRuO$_3$. Another consequence of covalency is the stabilization of lower Pb$^{2+}$ coordination numbers than expected from cation size arguments [19] as shown by the change from three short (2.47 Å) Pb-O bonds in the Pnma structure of PbRuO$_3$ to five, described above, in the Imma phase. The metal-insulator transition in PbRuO$_3$ is thus driven by electronic instabilities of both cations as the orbital order of $t_{2g}^2$Ru$^{4+}$ is coupled to an order of $s^2p^0$ Pb$^{2+}$ hybrid states. By contrast, Ru-orbital order is suppressed, and the metallic state remains stable in the other ARuO$_3$ perovskites that lack A-cation instabilities.

Orbital order lowers magnetic dimensionality relative to the structural dimensionality, and this can open a spin gap in some nonperovskite ruthenates, e.g., a singlet dimerized phase in La$_4$Ru$_2$O$_{10}$ [20,21] and possible Haldane chains in Tl$_2$Ru$_2$O$_7$ [15]. This seems not to be the case here; however, the observation of a broad susceptibility maximum at 25 K and the lack of a long range magnetic transition down to 1.5 K, which in conjunction with a Weiss temperature of $-54$ K corresponds to a frustration factor $|\theta/|T_c| > 36$, shows that PbRuO$_3$ does not have a conventional ordered magnetic state. The divergence of field- and zero-field-cooled susceptibilities evidences some glassy character to the ground state, but there is no obvious source for structural disorder. One possibility is that the combination of orbital order and octahedral tilting (which gives a Ru-O-Ru angle of 159.8$^\circ$) weakens nearest neighbor antiferromagnetic superexchange interactions in the $xy$ plane so that they become comparable to the next nearest neighbor couplings. This frustrates spin order in the $xy$ plane, leading to one-dimensional ($z$ direction) magnetic behavior in the three-dimensional perovskite lattice imposed by orbital order.

In summary, the low temperature properties of PbRuO$_3$ show that normally hidden orbitally ordered states such as that of degenerate $t_{2g}^2$Ru$^{4+}$ ions in ruthenate perovskites may be stabilized by coupling to electronic instabilities of other cations. This may provide a strategy for accessing orbitally ordered states of other 4$d$ and 5$d$ transition metal oxide networks. The combined order of Pb $s$ and $p$ hybridized orbitals, Ru $d$ orbitals, and O-centered octahedral tilting instabilities results in an anomalously high symmetry ground state structure that inverts the usual subgroup symmetry descent. These distortions also suppress long range spin order in PbRuO$_3$, and further experiments and theoretical work will be needed to elucidate the magnetic ground state.

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12 Refined x, y, and z coordinates and isotropic U factors for neutron refinements of PbRuO$_3$ in space group Pnma at 290 K [and in Imma at 25 K where different]: Pb: 0.0120 (5) [0], 0.25, 0.9955(4) [0.9868(1)], and 0.0075(3) Å$^2$ [0.0001(1) Å$^2$]; Ru: 0.0, 0.0, 0.5, and 0.0026(3) Å$^2$ [0.0010(1) Å$^2$]; O1: 0.4991(1) [0.5], 0.25, 0.0638(5) [0.0705(2)], and 0.0075(5) Å$^2$ [0.0032(2) Å$^2$]; O2: 0.2745(4) [0.25], 0.0359(2) [0.0456(1)], 0.7255(4) [0.75], and 0.0084(4) Å$^2$ [0.0034(1) Å$^2$]. Cell parameters are shown in the abstract. Reduced chi-squared = 1.27 [1.77] and weighted profile residual $R_{wp} = 0.022$ [0.026].
14 P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k code, http://www.wien2k.at. The muffin-tin sphere radii were 2.5, 2.1, and 1.5 Bohr for Pb(Sr), Ru, and O, respectively, the cutoff energy of the plane wave expansion was set at 16 Ryd, and 1600 k points were used for integration over the Brillouin zone. Structural relaxations gave lattice constants only 1.2% smaller than the experimental ones and atomic displacements $\leq 0.02$ Å.
17 $U$ was calculated following G. K. H. Madsen and P. Novák, Europhys. Lett. 69, 777 (2005).
19 Hence a high pressure is needed to increase the Pb oxygen coordination from 8 in the ideal pyrochlore structure of PbRuO$_3$($c$) to 12 in the ideal perovskite arrangement, while SrRuO$_3$ is thermodynamically stable at ambient pressure. This effect is also evident in the room temperature Pnma perovskite structures. The lattice parameters of PbRuO$_3$ are slightly larger than those for SrRuO$_3$ ($a = 5.535$, $b = 7.851$, $c = 5.572$ Å), but the three short (<2.6 Å) Pb-O distances in PbRuO$_3$ (2.47 Å $\times$ 3) are shorter than the corresponding Sr-O distances in SrRuO$_3$ (2.51 $\times$ 1 and 2.52 $\times$ 2 Å).