Metal-Insulator Transition and Orbital Order in PbRuO3

Citation for published version:

Digital Object Identifier (DOI):
10.1103/PhysRevLett.102.046409

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
Physical Review Letters

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Download date: 30. Dec. 2018
Anomalous low temperature electronic and structural behavior has been discovered in PbRuO$_3$. 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 SrRuO$_3$ 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 Ru$^{4+}$ 4$d$ orbital order to distortions from Pb$^{2+}$ 6$s$6$p$ 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 6$s$6$p$ and Ru 4$d$ orbital hybridization and strong spin-orbit coupling are significant.

PACS numbers: 71.30.+h, 61.66.Fn, 71.20.Ps

DOI: 10.1103/PhysRevLett.102.046409
The itinerant ferromagnetic state is stabilized by Fermi level \([6]\), and a large exchange splitting is found. By contrast, the Ru\(_{PbRuO_3}\) measurements (Fig. 2). At ambient temperatures, the other perovskite ruthenates was discovered by resistivity virtually identical.

An unexpected difference between PbRuO\(_3\) and (b) SrRuO\(_3\) in the \(Pnma\) structure calculated by the LDA in the ferromagnetic state. Up (down) arrows refers to spin up (down). The Ru \(t_{2g}\) DOS is scaled by \(\frac{1}{3}\), and the Sr DOS is scaled by \(\frac{1}{2}\). The exchange splitting of the Ru \(t_{2g}\cdot O\) 2\(p\) bands is significantly suppressed in PbRuO\(_3\).

The \(Sr^{2+}\) states lie far from the Ru \(4d\cdot O\) 2\(p\) bands near the Fermi level [6], and a large exchange splitting is found. The itinerant ferromagnetic state is stabilized by 25 meV/f.u., in keeping with the 160 K Curie transition. By contrast, the Ru \(4d\) and \(O\) 2\(p\) states in PbRuO\(_3\) lie just between the occupied Pb \(6s\) and unoccupied Pb \(6p\) states. The Ru \(t_{2g}\)-Pb \(6s\) and Ru \(e_g\)-Pb \(6p\) hybridizations, both aided by the \(O\) 2\(p\) state, and \(t_{2g}\cdot e_g\) mixing due to the lattice distortion, significantly suppress the exchange splitting of the Ru \(t_{2g}\cdot O\) 2\(p\) conduction bands, reducing the magnetic stabilization energy to near zero (\(<4\) meV/f.u.). To confirm that the slight lattice differences between the two materials are unimportant, we also calculated the electronic structure of SrRuO\(_3\) using the PbRuO\(_3\) parameters and found that the electronic and magnetic properties were virtually identical.

An unexpected difference between PbRuO\(_3\) and the other perovskite ruthenates was discovered by resistivity measurements (Fig. 2). At ambient temperatures, the PbRuO\(_3\) has a resistivity of \(\sim 10^{-4}\ \Omega \cdot \text{cm}\) with little temperature 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), signifying a metal-insulator transition at \(T_{\text{MI}} = 90\ K\). This transition is also evident in magnetization data. The high temperature susceptibility is fitted as \(\chi = C/(T - \theta) + \chi_p\), a sum of Curie-Weiss and Pauli paramagnetic terms, respectively, with \(\chi_p = 2.09(1) \times 10^{-3}\ \\text{emu/mol}\), Curie constant \(C = 0.195\ \text{emu K/mol}\), corresponding to a paramagnetic moment of 1.25\(\mu_B\), and a Weiss temperature \(\theta = -54\ K\). Similar large temperature-independent contributions have been reported for nonperovskite ruthenates such as the pyrochlore Tl\(_2\)Ru\(_2\)O\(_7\) \(\chi_p = 2 \times 10^{-3}\ \\text{emu/mol}\) [15] close to metal-insulator instabilities. A small dip is observed in the magnetic susceptibility on cooling through \(T_{\text{MI}}\), 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). PbRuO\(_3\) remains orthorhombic down to 1.5 K; however, the lattice parameters and volume change discontinuously on cooling through the transition (Fig. 4), and, surprisingly, the \(Pnma\) superstructure 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 temperature diffraction patterns of PbRuO\(_3\), 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 diffraction 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 \(\sim 0.5\mu_B\).
The (high temperature) Pnma to (low temperature) Imma transition in PbRuO$_3$ 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 SrSnO$_3$ [16]. The Pnma-Imma “subgroup-group” transition in PbRuO$_3$ 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 4$d$ electrons.

The evolution of the Ru-O bond distances (Fig. 4) reveals an important aspect of the metal-insulator transition. At room temperature, the RuO$_6$ 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 $d_{xz}^2d_{yz}^2$ orbital ordering of the Ru$^{4+}$ electronic configuration in the insulating Imma phase, creating planes of minority-spin-occupied $d_{xy}$ orbitals, as shown in Fig. 4. Pb$^{2+}$ 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 $d_{xy}$ and $d_{xz}/d_{yz}$ levels of ~50 meV. Our LSDA + $U$ + SOC calculations gave an insulating ground state with a small gap of ~0.1 eV, verifying that PbRuO$_3$ is in the vicinity of a metal-insulator transition. The minority spin electron has a 0.46(1 + $i$)$d_{xy} - 0.38(1 - i)(d_{xz} + d_{yz})$ orbital state which consists of 42% $d_{xy}$, 29% $d_{xz}$, and 29% $d_{yz}$, with $d_{xy}$ 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 PbRuO$_3$ is anomalous in comparison to the other A$\text{RuO}_3$ perovskites ($A =$ Ca, Sr, Ba), which remain metallic to the lowest temperature. This is not due to a size effect as CaRuO$_3$ has the most tilted Pnma superstructure but is stable to orbital order. (The combination of small Ca$^{2+}$ and an imposed tetragonal symmetry in layered Ca$_2$RuO$_4$ 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 4$d$-Pb 6$s$-$p$-$O$ 2$p$ hybridizations are evident in the above band structure calculations. This Pb$^{2+}$ covalency is sometimes manifest as a lone pair distortion resulting in ferroelectricity, e.g., in PbTiO$_3$, but lone pair distortions are not observed in either the Pnma or the
Imma phases of PbRuO₃. Another consequence of covalency is the stabilization of lower Pb⁶⁺ 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 PbRuO₃ to five, described above, in the Imma phase. The metal-insulator transition in PbRuO₃ is thus driven by electronic instabilities of both cations as the orbital order of t²₂gRu⁴⁺ is coupled to an order of s²p⁰Pb⁵⁺ hybrid states. By contrast, Ru-orbital order is suppressed, and the metallic state remains stable in the other ARuO₃ 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 La₄Ru₂O₁₀ [20,21] and possible Haldane chains in Tl₂Ru₂O₇ [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 25 K and the lack of a long range magnetic transition down to 1.5 K, which in conjunction with a Weiss temperature of $-54 \text{ K}$ corresponds to a frustration factor $|\theta/T_\text{c}| > 36$, shows that PbRuO₃ does not have a conventional ordered magnetic ground 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°) 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 PbRuO₃ show that normally hidden orbitally ordered states such as that of degenerate t²₂gRu⁴⁺ 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 4d and 5d 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 PbRuO₃, and further experiments and theoretical work will be needed to elucidate the magnetic ground state.

We acknowledge EPSRC for support and the provision of ESRF and ISIS beam time and the Leverhulme trust for additional support. H.W. and D.I.K. are supported by DFG through SFB 608. We thank J.W.G. Bos (Edinburgh), P.G. Radaelli (ISIS), and N. Stier, A. Buchsteiner, and D.A. Tennant (HZB) for assistance with diffraction measurements and useful discussions.

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[12] Refined x, y, and z coordinates and isotropic U factors for neutron refinements of PbRuO₃ in space group Pnma at 290 K [and in Imma at 25 K where different]; Pb: 0.0110 (5) [0], 0.25, 0.9955(4) [0.9868(1)], and 0.0075(3) Å² [0.0001(1) Å²]; Ru: 0, 0, 0.5, and 0.0026(3) Å² [0.0010(1) Å²]; O₁: 0.4991(1) [0.5], 0.25, 0.0638(5) [0.0705(2)], and 0.0077(5) Å² [0.0032(2) Å²]; O₂: 0.2745(4) [0.25], 0.0359(2) [0.0456(1)], 0.7255(4) [0.75], and 0.0084(4) Å² [0.0034(1) Å²]. 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. 
[19] Hence a high pressure is needed to increase the Pb oxygen coordination from 8 in the ideal pyrochlore structure of PbRuO₃ to 12 in the ideal perovskite arrangement, while SrRuO₃ is thermodynamically stable at ambient pressure. This effect is also evident in the room temperature Pnma perovskite structures. The lattice parameters of PbRuO₃ are slightly larger than those for SrRuO₃ ($a = 5.535$, $b = 7.851$, $c = 5.752$ Å), but the three short (<2.6 Å) Pb-O distances in PbRuO₃ (2.47 Å×3) are shorter than the corresponding Sr-O distances in SrRuO₃ (2.51×1 and 2.52×2 Å).