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Possible high-pressure orbital quantum criticality and an emergent resistive phase in PbRuO₃Anna F. Kusmartseva,^{1,2} Alexandra Sinclair,¹ Jennifer A. Rodgers,¹ Simon A. J. Kimber,³ and J. Paul Attfield^{1,*}¹*Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, King's Buildings, Mayfield Road, Edinburgh EH9 3JZ, United Kingdom*²*Department of Physics, Loughborough University, Leicestershire LE11 3TU, United Kingdom*³*European Synchrotron Radiation Facility, Boîte Postale 220, 38043 Grenoble Cedex, France*

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The orbital ordering transition in the metallic perovskite PbRuO₃ is suppressed from 90 K at ambient pressure towards zero temperature at 50 kbar, where non-Fermi liquid resistivity with a temperature exponent $n = 1.6$ is observed. This evidences a possible quantum critical point brought about by orbital fluctuations, rather than spin fluctuations as observed in Sr₃Ru₂O₇ and heavy fermion conductors. An anomalous increase of resistivity is observed at pressures above ~ 100 kbar, and a transition to a more resistive, possibly semiconducting, phase is observed at 300 kbar and ambient temperature.

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I. INTRODUCTION

Quantum critical phenomena have been reported in many correlated electron materials over the last decade.^{1,2} Tuning a phase transition towards zero temperature leads to a quantum critical point (QCP) around which quantum mechanical fluctuations dominate over thermal effects and alternative ground states such as unconventional superconducting phases are observed. New orders can emerge as the system is further tuned beyond the QCP and may persist to ambient temperature. QCPs are usually associated with suppression of a second-order transition, but are also reported at suppressed first-order transitions in some strongly correlated materials such as the heavy fermion ferromagnets UGe₂ (Ref. 3) and URhGe.⁴ Transition metal oxides show many exotic conducting states and phase transitions⁵ so a variety of quantum critical phenomena may be expected. QCPs in conducting oxides have been accessed by suppressing magnetic transitions, and are implicated in the emergence of superconductivity in doped antiferromagnetic cuprates, but the best established example is in the bilayer ruthenate Sr₃Ru₂O₇.^{6,7} This has a magnetic field-induced QCP at 8 T resulting from suppression of a metamagnetic transition. A subtle lattice distortion attributed to nematic orbital ordering correlations has recently been discovered in the 0.2-T-wide phase that emerges around the QCP.⁸

Localized Ru⁴⁺ states have spin $S = 1$ and a triple orbital degeneracy arising from the t_{2g}^4 d -electron configuration. Many ruthenate perovskites are metallic with Fermi surfaces resulting from hybridization between oxygen $2p$ and ruthenium $4d$ levels, with spin or orbital instabilities leading to diverse and competing ground states. The Ru-O-Ru bond angle has been identified as an important control parameter that may be tuned using cation substitutions or pressure;⁹ for example, layered Sr₂RuO₄ is an unconventional, p -wave superconductor¹⁰ at low temperatures, but Ca₂RuO₄ is an antiferromagnetic insulator.¹¹ There is some evidence for suppression of antiferromagnetism and emergence of superconductivity associated with a QCP in Ca₂RuO₄ around ~ 100 kbar pressure.^{12,13} Among the cubic-type ruthenate perovskites, SrRuO₃ and BaRuO₃ are itinerant ferromagnets^{14–16} but CaRuO₃ remains a paramagnetic metal with a large mass enhancement at low temperature.^{17,18} PbRuO₃ is a paramag-

netic metal and displays orbital ordering transition at 90 K, where the superstructure space group symmetry shows an unconventional increase from $Pnma$ to $Imma$ on cooling.^{19,20} No spin ordering transition is observed down to 1.5 K. A study of the Sr_{1-x}Pb_xRuO₃ system reported two possible QCPs, at $x = 0.6$ and 0.9 , based on resistivity measurements of ceramic samples.²¹ Here we report evidence for a possible QCP in PbRuO₃, induced by pressure suppression of orbital order, and the emergence of resistive correlations and a structural phase at higher pressures.

II. EXPERIMENTAL RESULTS

The perovskite PbRuO₃ requires high pressures for synthesis.²² Samples were synthesized at 11 GPa and 1100 °C using a Walker-type multianvil press, as described previously.¹⁹ A high-pressure x-ray diffraction study was carried out on instrument ID09A at the European Synchrotron Radiation Facility using a wavelength of 0.414 436 0 Å. Polycrystalline PbRuO₃ was contained in a diamond anvil cell (DAC) using helium as a hydrostatic pressure transmitting medium and a ruby as a pressure calibrant. Diffraction profiles were fitted using the GSAS program.²³ However, quantitative intensities for structure refinement were not obtained due to sample granularity or pressure-induced texturing, so only lattice parameters were extracted from the data.

X-ray diffraction profiles at pressures up to 125 kbar and temperatures of 20–200 K in a He-pumped cryostat were used to explore the suppression of the transition from the high-temperature $Pnma$ superstructure (phase I) to the low-temperature, orbitally ordered $Imma$ superstructure (phase II). The I-II transition is observed at 0, 10, 15, and 30 kbar from discontinuities in lattice parameter plots (Fig. 1), and so remains first order up to at least 30 kbar, and is suppressed to below 20 K between 30 and 50 kbar. Suppression of the transition to zero temperature is predicted to be at ~ 45 – 55 kbar—linear extrapolation from the 0–30 kbar transition temperatures gives a value of 55 kbar as shown on the phase diagram in Fig. 2.

Small PbRuO₃ single crystals of approximately platelet-like geometry, with longest dimension ~ 100 – 150 μm and

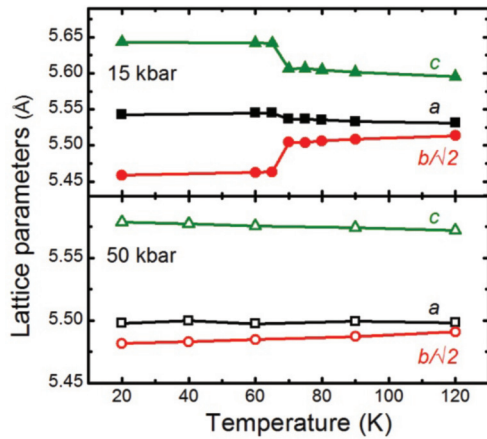


FIG. 1. (Color online) Low-temperature variation of the orthorhombic lattice parameters for PbRuO_3 at representative pressures. The discontinuity observed at 65 K in the 15 kbar data evidences the $Imma$ to $Pnma$ orbital order transition which is suppressed near 50 kbar.

thickness $\sim 50\text{--}80\ \mu\text{m}$, were isolated from some synthesis runs, and their resistivities were measured over temperatures 1.8–300 K at high pressures in several DAC experiments. A four-terminal arrangement of gold leads was used, with a two-part Stycast epoxy mixed with Al_2O_3 powder in the ratio 2:3 to insulate the steel/tungsten gaskets, and Daphne oil as the pressure medium. An apparent metal-insulator transition was originally reported at the 90 K $Pnma$ to $Imma$ transition from resistivity measurements on polycrystalline PbRuO_3 samples.¹⁹ This feature is reproducible but our subsequent studies have shown that it is a microstructural artifact caused by breaking of intergrain or grain-electrode contacts at the first-order structural transition. Application of a few kilobars of pressure suppresses this effect, and the $Imma$ phase is observed to be metallic as reported in other studies.^{20,21} This is also consistent with the small difference in minority spin electron populations of the t_{2g} orbital set

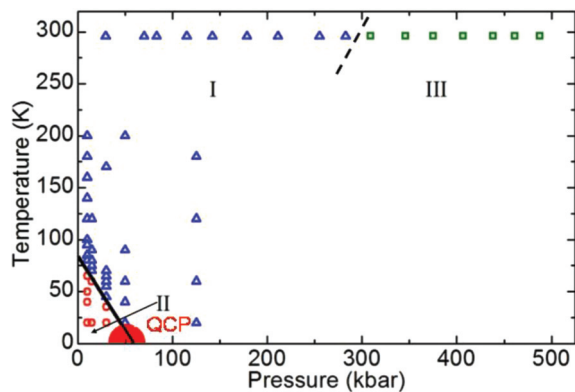


FIG. 2. (Color online) High-pressure phase diagram for PbRuO_3 showing the ambient metallic $Pnma$ phase I, the low-temperature orbitally ordered metallic $Imma$ phase II, and the poorly metallic or semiconducting phase III discovered at high pressures. The I-III transition has only been measured at 300 K so a nominal boundary is shown as a broken line. The critical region around the proposed 50 kbar QCP is also shown.

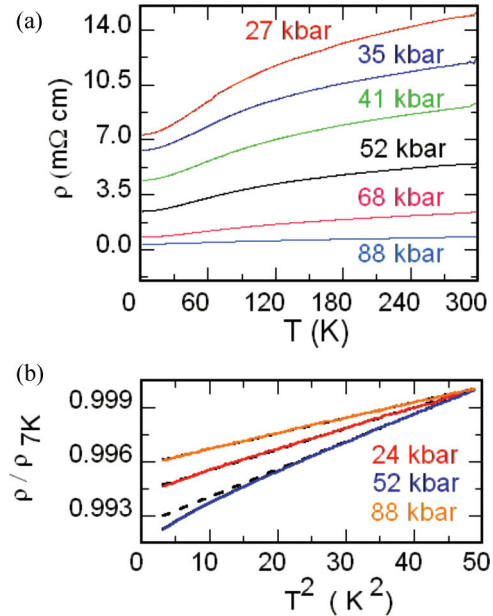


FIG. 3. (Color online) (a) Resistivity of PbRuO_3 as a function of temperature at representative pressures between 20 and 90 kbar. (b) Plots of 1.8–7 K resistivities relative to 7 K values against T^2 , showing good Fermi liquid behavior at 24 and 88 kbar, but a significant deviation at 52 kbar close to the identified QCP.

calculated for the $Imma$ structure.¹⁹ Hence the I-II transition in PbRuO_3 is identified as an orbital ordering in a metallic oxide (a band Jahn-Teller distortion) without an associated spin order or charge localization. The order parameter is the difference in minority spin populations between the d_{xy} and d_{xz}, d_{yz} orbitals. Orbitorally ordered metallic states are reported in other perovskite oxides, for example, $\text{PrBaMn}_2\text{O}_6$ and $\text{NdBaMn}_2\text{O}_6$.²⁴

Resistivities of a PbRuO_3 crystal between 20 and 90 kbar pressure are shown in Fig. 3. Smooth temperature variations are obtained without a discontinuity at the I-II orbital ordering transition. Resistivity decreases with increasing pressure in this range, and the residual values of $<1\ \text{m}\Omega\ \text{cm}$ above ~ 60 kbar approach those of a good metal. A change in the low-temperature resistivity variation evidences quantum critical behavior around the ~ 50 kbar suppression of orbital ordering. All of the results we show in Figs. 3 and 4 are from one DAC experiment, to ensure comparability of data, but measurements on other crystals show the same 50 kbar discontinuity. At pressures well above or below 50 kbar [shown for 24 and 88 kbar data in Fig. 3(b)], resistivity ρ has a quadratic $\rho \sim T^2$ variation with temperature T , as expected for a conventional Fermi liquid. However, resistivity deviates from T^2 behavior at an intermediate pressure of 52 kbar. To explore this change further, resistivities in the range 1.8–7.0 K from 12 separate measurements at 30–90 kbar were fitted as $\rho = \rho_0 + AT^n$. Values of the residual resistivity ρ_0 and thermal exponent n shown in Fig. 4 were obtained from these fits in which $\rho_0, n,$ and A were varied. A clear discontinuity in n is observed in Fig. 4, as the exponent falls from $n \approx 1.8$ at pressures near 30 kbar to a minimum value of $n = 1.6$ at 50 kbar which evidences non-Fermi liquid behavior. Conventional Fermi liquid behavior is recovered as the pressure is increased

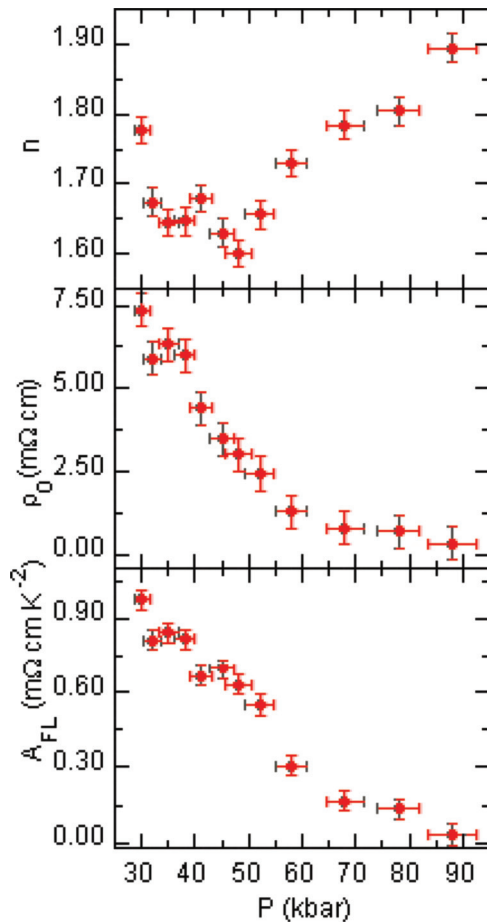


FIG. 4. (Color online) Pressure evolution of parameters extracted from fitting 1.8–7 K resistivity data as $\rho = \rho_0 + AT^n$: (a) thermal exponent n ; (b) residual resistivity ρ_0 ; and (c) coefficient $A = A_{FL}$ obtained when n is fixed to the Fermi liquid $n = 2$ value at the lowest temperatures. Anomalies in all these parameters evidence an order parameter change and possible QCP at a critical pressure of $p_c \approx 50$ kbar.

above p_c and the resistivity exponent approaches the Fermi liquid value of $n = 2$. The minimum in n is observed at 48 kbar, close to the expected suppression of the I-II structural and orbital ordering transition, and thus evidences a possible QCP at a critical pressure $p_c \approx 50$ kbar.

A separate series of fits in which the thermal exponent was fixed at $n = 2$ were used to extract values of the coefficient A_{FL} in the Fermi liquid limit from the resistivity data for PbRuO_3 . The fitting range was significantly reduced around the critical pressure $p_c \approx 50$ kbar to allow convergence of A_{FL} . Peaklike anomalies in the coefficient A_{FL} and the residual resistivity ρ_0 are predicted at QCPs associated with suppressed magnetic transitions in metallic materials.²⁵ These result from a significant increase of conduction electron (quasiparticle) mass m^* near a QCP due to slow, long-range magnetic fluctuations. Peaklike anomalies in A_{FL} and ρ_0 were seen from analysis of single crystal resistivities for metamagnetic $\text{Sr}_3\text{Ru}_2\text{O}_7$ ⁶ and the heavy fermion ferromagnet UGe_2 (Ref. 3) at their QCPs. However, different behaviors are apparent in our PbRuO_3 data (Fig. 4), as an anomalous decrease in A_{FL} and a change of slope of ρ_0 with pressure are observed

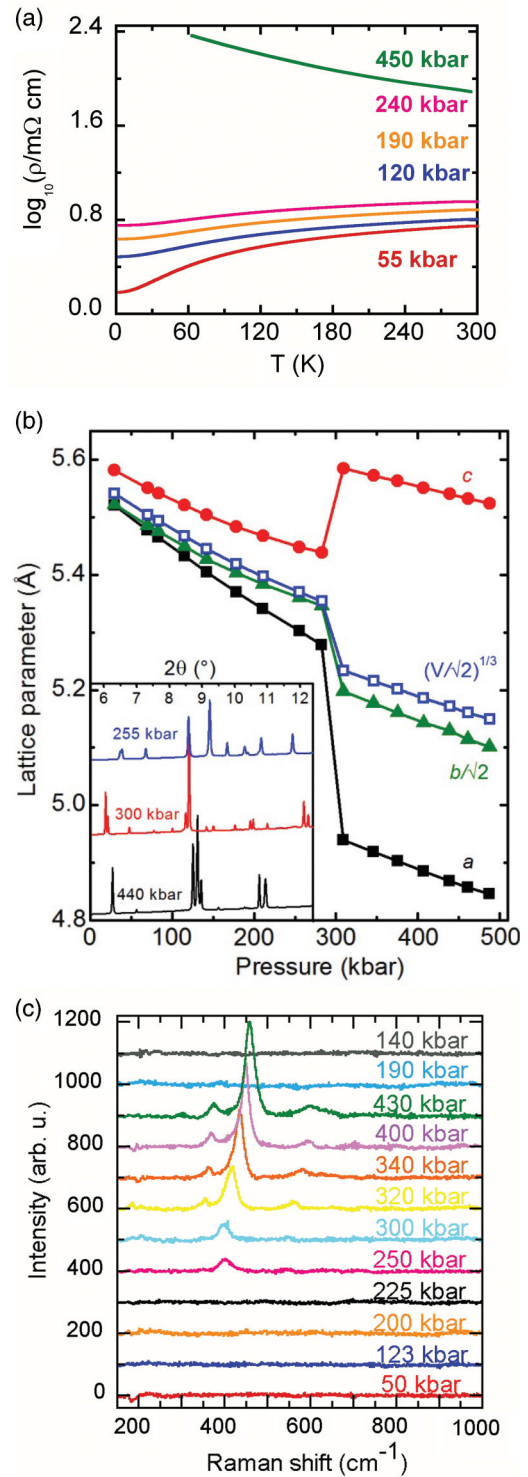


FIG. 5. (Color online) High-pressure measurements across the I-III phase boundary for PbRuO_3 at 300 K. (a) Log(resistivity) data showing an increase of resistivity within the metallic phase I up to 240 kbar, and apparent semiconducting behavior at 450 kbar for phase III. (b) Orthorhombic cell parameters showing a discontinuity and volume reduction at the transition, with representative x-ray diffraction patterns shown in the inset. (c) Raman spectra on compression from 50 to 430 kbar and during decompression (top two spectra). The appearance of peaks at pressures >250 kbar corroborates the poorly metallic or semiconducting nature of phase III.

at ~ 55 kbar. This may signify the emergence of some different scattering mechanism in the vicinity of an orbital QCP, or indicate that a more simple change in an order parameter is occurring. However, the underlying changes may not be observed as impurity scattering can mask possible QCP anomalies, as high-pressure growth does not yield high-purity PbRuO₃ crystals [residual resistance ratios $R(300\text{ K})/R(2\text{ K})$ are <10 in our crystals, whereas ratios >100 were reported for floating-zone crystals of Sr₃Ru₂O₇ (Ref. 6)]. Although the intrinsic A_{FL} and ρ_0 behaviors are unclear, the pressure variation of n clearly suggests that suppression of orbital order, without an associated magnetic order, leads to a QCP-like feature in metallic PbRuO₃. The observed minimum value of $n = 1.6$ is close to the $n = 5/3$ prediction for three-dimensional ferromagnets²⁶—this may be applicable to PbRuO₃ as the *Imma* structure is the orbital analog of a ferromagnet, with a ferro-orbital order of excess t_{2g} electron density in d_{xy} orbitals at all Ru sites.¹⁹ Whether the first-order orbital order transition becomes second order between 30 kbar and p_c , or remains first order as observed in some correlated electron ferromagnets,^{3,4} is not clear and will require further low-temperature structural measurements close to the quantum critical region.

To explore the possible emergence of a new electronic order above p_c , further DAC resistivity measurements were made at pressures >100 kbar [Fig. 5(a)]. Surprisingly, these revealed that PbRuO₃ becomes more resistive between 120 and 240 kbar. Measurements at higher pressures are challenging, but a successful experiment using small culet diamonds at 450 kbar found a negative ρ - T slope in the measured 70–290 K range, evidencing semiconducting behavior with an energy gap of ~ 10 meV. The electron-electron correlations responsible for the rise in resistivity beyond 100 kbar do not immediately drive a transition to a new long-range order, as no unexpected distortion of the *Pnma* phase was observed between 20 and 300 K at 120 kbar (Fig. 2). However, further DAC synchrotron diffraction data recorded at 300 K and pressures up to 480 kbar reveal a further structural phase transition at 300 kbar [Fig. 5(b)]. The lattice parameters of this high-pressure phase III are still those of a $\sqrt{2} \times 2 \times \sqrt{2}$ perovskite superstructure, but with a far greater dispersion of magnitudes than in phases I or II showing that the perovskite arrangement is highly distorted. A substantial (11%) volume reduction is observed at the first-order I-III structural transition. The x-ray diffraction peaks from the >300 kbar phase III have reflection conditions consistent with primitive orthorhombic space group *Pnna*. However, it was not possible to refine a structural model because of the granularity or texturing effects noted above, and further studies will be needed to determine the full structure of phase III.

The I-III transition in PbRuO₃ is confirmed by Raman spectroscopy [Fig. 5(c)]. Spectra from polycrystalline PbRuO₃ in a Merrill–Bassett-type DAC cell were recorded at 300 K with a 4:1 mixture of ethanol and methanol as the pressure medium and a ruby as a pressure calibrant. The spectrum

of the ambient *Pnma* phase I is featureless in the 100–1000 cm⁻¹ frequency range, but sharp peaks emerge at the 250–300 kbar approach to the I-III transition and persist to the highest measured pressure of 430 kbar. This corroborates the change from metallic to a more resistive behavior found in transport measurements [Fig. 5(a)]. The changes observed in the Raman spectra are reversible, as shown at the top of Fig. 5(c), confirming that they have not resulted from sample amorphization or decomposition.

The increased resistivity upon pressurization and possible opening of a gap at 300 kbar in PbRuO₃ is very unusual as displacive transitions driven by pressure usually result in more highly conducting phases. The resistivity measurements in Fig. 5(a) show that resistive correlations are evident above pressures of at least 120 kbar, and so may emerge from the vicinity of the implied 50 kbar QCP. Full structure determination of the high-pressure phase III is needed to identify the emergent order. A (non-ferro-) orbital order, perhaps coupled to Ru⁴⁺ spin order, or an array of Ru-O-Ru spin singlet dimers like those in La₄Ru₂O₁₀ (Ref. 27) are possible ground states.

III. CONCLUSIONS

This study demonstrates that PbRuO₃ may exemplify a long-range orbital ordering transition driven to a QCP in an itinerant electron material. The observed minimum value of the temperature exponent as the ferro-orbital order is suppressed is close to the $n = 5/3$ prediction for three-dimensional ferromagnets. The possibility for new orbital physics is demonstrated by an anomalous increase in resistivity at pressures beyond p_c , and the emergence of a further superstructure phase III that may be a poor metal or a semiconductor. The origin of the proposed QCP in PbRuO₃ is different from those in Sr₃Ru₂O₇ and heavy fermion metals, which are usually accessed by driving a magnetic transition towards zero temperature. However, the presence of strong-spin orbit coupling in such materials suggests that spin and orbital quantum criticality are ultimately connected, as illustrated by the recently reported emergence of nematic orbital order around the QCP in Sr₃Ru₂O₇.⁸ Hence, magnetism may be involved around the QCP or in the high-pressure phase III of PbRuO₃. Further experimental studies of PbRuO₃ may help to guide theories of orbital criticality²⁸ and their application to other orbitally ordered materials such as iron pnictide superconductors,²⁹ but they present challenges to growing cleaner crystals and measure resistivity and magnetization accurately at high pressures.

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