Magnetically induced metal-insulator transition in Pb$_2$CaOsO$_6$

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We report on the structural, magnetic, and electronic properties of two new double-perovskites synthesized under high pressure, Pb$_2$CaOsO$_6$ and Pb$_2$ZnOsO$_6$. Upon cooling below 80 K, Pb$_2$CaOsO$_6$ simultaneously undergoes a metal-to-insulator transition and develops antiferromagnetic order. Pb$_2$ZnOsO$_6$, on the other hand, remains a paramagnetic metal down to 2 K. The key difference between the two compounds lies in their crystal structures. The Os atoms in Pb$_2$ZnOsO$_6$ are arranged on an approximately face-centered cubic lattice with strong antiferromagnetic nearest-neighbor exchange couplings. The geometrical frustration inherent to this lattice prevents magnetic order from forming down to the lowest temperatures. In contrast, the unit cell of Pb$_2$CaOsO$_6$ is heavily distorted up to at least 500 K including antiferroelectric-like displacements of the Pb and O atoms despite metallic conductivity above 80 K. This distortion relieves the magnetic frustration, facilitating magnetic order which, in turn, drives the metal-insulator transition. Our results suggest that the phase transition in Pb$_2$CaOsO$_6$ is spin driven and could be a rare example of a Slater transition.

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I. INTRODUCTION

Metal-to-insulator transitions (MIT) can occur through a variety of mechanisms [1,2]. Perhaps the best known is that of the Mott insulator in which strong Coulomb interactions between electrons open up a gap at the Fermi energy [3]. In the case of weak Coulomb interactions, Slater proposed that a MIT can be driven by magnetism alone: Long-range antiferromagnetic (AFM) order changes the periodicity of the crystal potential, splitting the electronic bands and potentially leading to a MIT [4]. Such magnetically driven MITs are rare in real materials.

Over the past two decades, a number of 5d transition-metal oxides have been suggested to undergo Slater transitions, including the perovskite osmate NaOsO$_3$ (Refs. [5,6]) and the iridate and osmate pyrochlores, A$_2$Ir$_2$O$_7$, (A = Y or trivalent lanthanide), (Ref. [7]) and Cd$_2$Os$_2$O$_7$ (Ref. [8]). The extended 5d states in these systems are relatively weakly interacting as required for the Slater mechanism, but the band splitting caused by strong spin-orbit coupling can bring about Mott-like behavior instead. Indeed, later work indicated that mechanisms other than the Slater mechanism may be behind the MIT in the above-mentioned 5d oxides [2,9,10].

Recently, we have synthesized under high pressure several new double perovskites containing Os in the 5d$^2$ electronic configuration [11–14]. These materials exhibit a variety of unusual and interesting electronic and magnetic phases, such as the magnetically driven loss of centrosymmetry into a polar metal phase that occurs in metallic Pb$_2$CoOsO$_6$ [13].

Here we investigate two other members of this family, Pb$_2$CaOsO$_6$ and Pb$_2$ZnOsO$_6$. We present resistivity, susceptibility, heat capacity, neutron diffraction, and resonant inelastic x-ray scattering (RIXS) experiments and discuss
how the results shed light on the intriguing behavior of these compounds. We find that Pb$_2$CaOsO$_6$ undergoes a MIT simultaneously with the onset of magnetic order as shown in Fig. 1 and present evidence that the Slater picture might apply to this transition. Pb$_2$ZnOsO$_6$ remains metallic and paramagnetic down to 2 K, suggesting that the MIT in Pb$_2$CaOsO$_6$ is tied to the presence of magnetic order.

II. EXPERIMENT

Both polycrystalline and single-crystal samples of Pb$_2$CaOsO$_6$ were synthesized by a solid-state reaction from powders of PbO$_2$ (99.9%, High Purity Chemicals Co., Ltd., Japan), Os (99.95%, Heraeus Materials Technology, Germany), and CaO$_2$ (laboratory made). The powders were thoroughly mixed in a stoichiometric ratio, and then sealed in a Pt capsule. The procedures were conducted in an Ar-filled glove box. To generate an applied pressure of 6 GPa, static and isotropic compression of the capsule was achieved in a belt-type high-pressure apparatus at National Institute for Materials Science (Kobe Steel, Ltd., Japan). The capsule was then heated at 1500 °C for 1 h to synthesize the polycrystalline sample and at 1600 °C for 2 h to synthesize the single-crystal samples. It was then quenched to ambient temperature in less than a minute after which the pressure was released. We note that we have observed some variability in the MIT temperature between samples, possibly due to small differences in composition. In all cases examined the MIT and the magnetic transition coincide in temperature. All the results presented here are for samples in which the MIT and magnetic transition occur at 80 K.

Polycrystalline Pb$_2$ZnOsO$_6$ samples were synthesized using the same method with ZnO instead of CaO$_2$ and KClO$_4$ as an oxygen source. Excess KCl was removed by washing with distilled water.

Electrical resistivity ($\rho$) of a single crystal of Pb$_2$CaOsO$_6$ and a pressed powder of Pb$_2$ZnOsO$_6$ was measured with a DC gauge current of 0.1 mA by a four-point method in a physical properties measurement system (Quantum Design, Inc.). Electrical contacts were applied with Pt wires and Ag paste. The specific heat capacity ($C_p$) was measured in the same apparatus on polycrystalline samples by a thermal relaxation method at temperatures between 2 and 300 K. The magnetic susceptibility ($\chi$) of polycrystalline samples was measured in a magnetic properties measurement system (Quantum Design, Inc.). The measurements were conducted under field cooling and zero-field cooling conditions in a temperature range between 2 and 390 K with an applied magnetic field of 10 kOe.

A number of elastic neutron and x-ray scattering experiments on powders and single crystals of Pb$_2$CaOsO$_6$ and Pb$_2$ZnOsO$_6$ were performed. Preliminary neutron-diffraction experiments on Pb$_2$CaOsO$_6$ were carried out on the powder diffractometers SPODI operated by FRM II at the Heinz Maier-Leibnitz Zentrum (MLZ), Germany [15], and HRPD at the ISIS Neutron and Muon Facility, United Kingdom [16]. Subsequently, we obtained more complete data on the WISH diffractometer at ISIS [17,18], and these are the results presented in this paper. Finally, high-temperature x-ray powder-diffraction experiments were carried out on I11 at the Diamond Light Source, United Kingdom.

FIG. 1. Bulk measurements on Pb$_2$CaOsO$_6$ and Pb$_2$ZnOsO$_6$ as a function of temperature. (a) Resistivity, showing that Pb$_2$CaOsO$_6$ undergoes a MIT at 80 K, whereas Pb$_2$ZnOsO$_6$ remains metallic down to 2 K. The resistivity curve for Pb$_2$CaOsO$_6$ is unaffected by an external magnetic field of 7 T. (b) Inverse susceptibility together with a fit to the Curie-Weiss law at high temperatures. At 80 K there is an anomaly in Pb$_2$CaOsO$_6$, and at approximately the same temperature Pb$_2$ZnOsO$_6$ starts to deviate from the Curie-Weiss law. (c) Heat capacity showing an anomaly at around 80 K in Pb$_2$CaOsO$_6$. The inset shows the magnetic entropy of Pb$_2$CaOsO$_6$ calculated by subtracting a polynomial approximation of the lattice contribution to the heat capacity.
In the neutron powder-diffraction experiments on WISH, 4.3 g of Pb2CaOsO6 was loaded in a cylindrical Al sample holder and measured at multiple temperatures between 2 and 105 K for 20 min per run. Some 0.5 g of Pb2ZnOsO6 was loaded into a cylindrical vanadium sample holder and was measured at multiple temperatures between 2 and 300 K with runs at 2, 150, and 300 K measured for 3 h each, and the remaining temperatures measured for 20 min each. For the structure refinements presented below we used the data from banks (2 + 9) (2θ ~ 58°), (3 + 8) (2θ ~ 90°), and (5 + 6) (2θ ~ 153°). The data were reduced using MANTID [19].

In the x-ray powder-diffraction experiment on 111 at the Diamond Light Source, a series of small single crystals were crushed and ground into a micron-sized powder and then coated onto the outside of a glass capillary. This was performed in order to minimize absorption from lead and osmium. An incident energy of 25 keV was used. The capillary was rotated and a cryostream system provided a nitrogen atmosphere for heating and cooling the sample. Scans were performed at 100, 290, 350, 425, and 500 K.

To further understand the magnetism of Pb2CaOsO6 we have carried out RIXS experiments on a Pb2CaOsO6 crystal at the Os L3 edge (E = 10.877 keV, 2p → 5d) at 20 K on the ID20 spectrometer at the European Synchrotron Radiation Facility, Grenoble [20]. We measured the RIXS spectrum at a wave vector of Q = (−2.5, 7, 0) [which corresponds to (0,7,2.5) when indexed on the undistorted cell]. We used a relaxed resolution setting [ΔE = 0.40(1) eV, full width at half maximum] to measure the spectrum up to an energy loss of 11 eV and a high-resolution mode [ΔE = 0.064(1) eV] to probe the low-energy excitations.

III. RESULTS

Figure 1(a) shows the resistivity of a single crystal of Pb2CaOsO6 and a pressed powder of Pb2ZnOsO6. At room temperature the resistivity is ρ = 8 × 10−4 Ω cm for Pb2CaOsO6 and ~4 × 10−3 Ω cm for Pb2ZnOsO6. Upon cooling, the resistivity of both compounds decreases linearly with temperature, consistent with metallic conduction. At Tc ≈ 80 K, Pb2CaOsO6 undergoes a transition from a metal to an insulator with its resistivity increasing by more than four orders of magnitude between 80 and 2 K. The resistivity of Pb2CaOsO6 is unchanged by the application of a 7 T magnetic field.

Figure 1(b) shows the inverse susceptibility measured on powder samples. At high temperatures, for both materials follow the Curie–Weiss law χ = C/(T + θ) with θ = 100.7(3) K and effective moment μeff = 2.25(1)μB/Os for Pb2CaOsO6, θ = 214.4(4) K, and μeff = 2.11μB/Os for Pb2ZnOsO6. In the absence of spin-orbit coupling we would expect localized 5d2 electrons of Os6+ to form a S = 1 state with an effective moment of μeff = 2\sqrt{2} = 2.83μB. The reduction of 20–25% from the spin-only value indicates the influence of spin-orbit coupling as expected for 5d orbitals [21].

An anomaly in the susceptibility at Tc ≈ 80 K signals the transition to an antiferromagnetically ordered state in Pb2CaOsO6. At roughly the same temperature the susceptibility of Pb2ZnOsO6 deviates from the Curie-Weiss law, but no phase transition is observed. The simultaneous onset of the MIT and magnetic ordering (Tc = Tm within experimental resolution) in Pb2CaOsO6 indicates that the two phenomena are related.

The temperature dependence of the heat capacity of both compounds is presented in Fig. 1(c). The data for Pb2CaOsO6 has an anomaly close to Tc. The inset displays the magnetic entropy, calculated after subtraction of a polynomial approximation to the phonon contribution to the heat capacity. The entropy associated with this transition is S ≈ 0.3R.

We show examples of our neutron-diffraction data at 2 K on Pb2ZnOsO6 and Pb2CaOsO6 in Figs. 2(a) and 2(b),
TABLE I. The Os-O bond lengths (in angstroms) in Pb$_2$ZnOsO$_6$ and Pb$_2$CaOsO$_6$ at 2 K. The direction of the bond is given relative to the Pb$_2$ZnOsO$_6$ unit cell.

|          | (a-b)     | (a+b)     | c     |
|----------|-----------|-----------|-------|
| Pb$_2$ZnOsO$_6$ | 1.879(10) | 1.879(10) | 2.005(10) |
| Pb$_2$CaOsO$_6$Os1 | 1.833(10) | 1.933(10) | 1.919(8)  |
| Pb$_2$CaOsO$_6$Os2 | 1.924(9)  | 1.979(10) | 1.984(11) |

respectively. The red line through the data shows our refinement of the crystal structure using the fullprof suite [22], and the tick marks indicate the positions of Bragg peaks. In addition to the Pb$_2$ZnOsO$_6$ main phase we also account for the vanadium sample holder in Fig. 2(a). In Fig. 2(b) the tick marks indicate the Pb$_2$CaOsO$_6$ main structural phase, the magnetic phase, and a few percent of Pb$_2$Os$_2$O$_7$ [23]. We have established that Pb$_2$Os$_2$O$_7$ remains paramagnetic at temperatures down to 2 K (see Appendix A), so its presence has no effect on any of the results we present. We also observe small peaks from the A1 sample holder and trace amounts of unreacted PbO$_2$, neither of which scatter strongly enough to warrant inclusion as separate phases in the refinement.

We find that Pb$_2$ZnOsO$_6$ crystallizes in space-group $P2_1/n$ with lattice parameters $a = 5.6329(2)$, $b = 5.6059(2)$, $c = 7.9201(2)$ Å, $\beta = 89.96(1)^\circ$ at 2 K, similar to Pb$_2$CoOsO$_6$ [13] (see Table II for a list of all the refined structural parameters). The monoclinic structure of Pb$_2$ZnOsO$_6$ is typical for many double perovskites [24] and combines octahedral tilting.

![FIG. 3. Temperature dependence of the lattice parameters for Pb$_2$ZnOsO$_6$ determined from neutron powder-diffraction measurements. The statistical uncertainty on the parameters is smaller than the markers.](image)

(a$+b^-b^-$ tilting pattern in the Glazer notation [25]) and rock-salt ordering of Zn and Os in the B-site perovskite position. There is no evidence of short- or long-range magnetic order down to 2 K. No anomalies are seen in the lattice parameters between 2 and 300 K (see Fig. 3), and we find no evidence for oxygen vacancies. Figure 4(a) shows the crystal structure of Pb$_2$ZnOsO$_6$ as viewed down the $b$ axis.

Pb$_2$CaOsO$_6$ also crystallizes in space-group $P2_1/n$ but in a significantly distorted cell with lattice parameters $a = 10.0812(3)$, $b = 5.689(1)$, $c = 11.837(4)$ Å, $\beta = 125.32(2)$ (Pb$_2$CaOsO$_6$), and $a = 5.6329(2)$, $b = 5.6059(2)$, $c = 7.9201(2)$ Å, $\beta = 89.96(1)^\circ$ (Pb$_2$ZnOsO$_6$).

![FIG. 4. The unit cell of (a) Pb$_2$ZnOsO$_6$ and (b) Pb$_2$CaOsO$_6$. The distortion in Pb$_2$CaOsO$_6$ is mainly seen in the oxygen octahedra which are tilted and deformed.](image)
The distortion is most pronounced in the oxygen atoms and causes the oxygen octahedra surrounding the Ca and Os sites to tilt and deform. The Os-O bond lengths at 2 K are listed in Table I for both compounds. The bond directions are given with respect to the Pb$_2$ZnOsO$_6$ unit cell. The oxygen octahedra in Pb$_2$ZnOsO$_6$ are elongated along $c$. Notably, in Pb$_2$CaOsO$_6$ there are two different Os sites with different local surroundings. The octahedron surrounding Os$_1$ is compressed along (a-b), whereas the Os$_2$ octahedron is close to ideal. There is also a significant distortion of the local coordination of the Pb atoms in the two compounds as detailed in Appendix B.

The temperature dependence of the lattice constants and ordered magnetic moment of Pb$_2$CaOsO$_6$ determined from neutron powder-diffraction measurements. The vertical line marks the metal-insulator and magnetic ordering transitions, which coincide at $T_c = T_N = 80$ K. In (d) the moment is shown for the noncollinear model up to 500 K, which confirms that it is not directly related to the MIT at $T_c = 80$ K.

More insight into the structure of Pb$_2$CaOsO$_6$ can be obtained by decomposing the structure in terms of symmetrized displacive modes of the parent cubic perovskite structure with $Pm\bar{3}m$ symmetry. This allows us to identify the primary distortions and compare them with other perovskite structures. The result of the decomposition made with the ISODISTORT software [26,27] is summarized in Appendix D Table V for Pb$_2$ZnOsO$_6$ and Table VI for Pb$_2$CaOsO$_6$.

Similar to Pb$_2$ZnOsO$_6$, Pb$_2$CaOsO$_6$ contains the $R_1^+(k = 1/2, 1/2, 1/2)$ and $M_3(k = 1/2, 1/2, 0)$ irreducible representations (Irreps), which yield the $a^+b^-b^-$ Glazer tilt pattern. In Pb$_2$CaOsO$_6$, however, the largest distortion is $\Lambda_1(k = 1/4, 1/4, 1/4)$. The distortions associated with $\Lambda_3$ are less common but were also observed in several Bi$_3^{3+}$-containing perovskites, such as BiCrO$_3$ [28], BiScO$_3$ [29], and BiFe$_{1/2}$Sc$_{1/2}$O$_3$ [30]. We will discuss the significance of the $\Lambda_3$ distortion in the next section.

The distortion is most pronounced in the oxygen atoms and causes the oxygen octahedra surrounding the Ca and Os sites to tilt and deform. The Os-O bond lengths at 2 K are listed in Table I for both compounds. The bond directions are given with respect to the Pb$_2$ZnOsO$_6$ unit cell. The oxygen octahedra in Pb$_2$ZnOsO$_6$ are elongated along $c$. Notably, in Pb$_2$CaOsO$_6$ there are two different Os sites with different local surroundings. The octahedron surrounding Os$_1$ is compressed along (a-b), whereas the Os$_2$ octahedron is close to ideal. There is also a significant distortion of the local coordination of the Pb atoms in the two compounds as detailed in Appendix B.

The temperature dependence of the lattice parameters of Pb$_2$CaOsO$_6$ for $T \leq 105$ K is shown in Fig. 5. The $a$ and $c$ parameters, and to a lesser extent the $b$ parameter, exhibit anomalies at $T_c$. The fact that the lattice relaxes when magnetic order sets in indicates a significant magnetoelastic coupling as also found in NaOsO$_3$ (Ref. [6]). Such an effect could be the result of the spatially extended 5$d$ orbitals of Os bonding covalently with their environment. Importantly, we observe no symmetry changes in the crystal structure and no abrupt changes in, e.g., the oxygen octahedra. We conclude from these results that no structural phase transition accompanies the MIT. We observe no further anomalies in the lattice parameters for temperatures above $T_c$ up to 500 K.

At temperatures below $T_N$ we observe the emergence of additional resolution-limited peaks in the neutron powder diffraction data on Pb$_2$CaOsO$_6$. The peak positions are consistent with magnetic order with propagation vector $k = (1/2, 1/2, 1/2, 0)$. The magnetic intensity, which is much weaker than the nuclear scattering, can be isolated by plotting the difference between the data recorded at 2 and 105 K as shown in the inset to Fig. 2(b). The subtraction is imperfect due to the change in lattice constant around $T_N$, but several magnetic peaks are clearly visible despite this complication, with $(1/2, 1/2, 0)$ being the strongest.

There are no symmetry constraints on the magnetic structure (the magnetic space group is $P1_1$) (see Appendix C for details). The absence of symmetry restrictions substantially complicates the analysis of the magnetic structure, making unambiguous determination of the spin configuration, based on the available powder-diffraction data impossible. To reduce the number of parameters in the refinement, we restricted our consideration to two cases: (i) When all spins are constrained to lie along a single direction (collinear model) and the moments on the symmetry-independent sites (Os1 and Os2) are allowed to adopt different magnitudes; (ii) when both Os1 and Os2 sites are constrained to have identical moment sizes but canting between the sublattices is allowed (noncollinear model). Both models can reproduce the observed magnetic intensities accurately and cannot be discriminated based on the quality of the agreement with the data. The collinear model was tested assuming that the magnetic moments are confined either within the $ac$ plane or along the $b$ axis and only the former provided a good fit. The refinement converged with substantially different moment sizes on Os1 and Os2, 0.87(1)$\mu_B$ and 0.26(1)$\mu_B$, respectively, and this difference is essential to achieve a good fit. The refinement in the noncollinear model converged with moment size 0.64(1)$\mu_B$ and canting angle 56° between the Os1 and Os2 spins. Figure 6 illustrates the structure of the noncollinear model. The average...
ordered moment per site is similar for both models; 0.57(1)μB in the collinear model and 0.64(1)μB in the noncollinear model. The temperature dependence of the ordered moment in the noncollinear model is plotted in Fig. 5(d), and saturates at 0.64(1)μB/Os at 2 K.

Information about the electronic ground state of Pb2CaOsO6 was sought from RIXS. Figure 7(a) shows a RIXS map measured with relaxed energy resolution. There are four features, labeled I–IV in the figure, which resonate at slightly different energies. Based on results from other osmates with Os in octahedral coordination [31,32], these processes can be assigned as follows: I is below 1 eV and corresponds to intra-t2g excitations; II and III at around 4 and 7 eV correspond to t2g → eg transitions; IV corresponds to charge-transfer excitations. Figure 7(b) shows a cut through this data for incident energy Ei = 10.876 keV which clearly displays the four broad features. The splitting of the t2g and eg levels by 10Dq ~ 4 eV (excitation II) is similar to that in other osmates [31].

In Fig. 7(c) we show high-resolution RIXS data recorded at Ei = 10.872 keV in order to further investigate the intra-t2g excitations. Even in the high-resolution setting, we observe only a single broad peak centered around 0.7 eV. The lack of distinct peaks precludes further analysis of the spectrum. The width of the peaks, which far exceeds the energy resolution, is an indication of the itinerant nature of the 5d electrons as found also in NaOsO3 [32,33].

FIG. 7. RIXS data on Pb2CaOsO6 at \( Q = (-2.5, 7, 0) \) at \( T = 20 \) K. (a) shows a map with four distinct excitations. (b) A scan through the map at \( E_i = 10.876 \) keV. (c) A high-resolution scan through \( E_i = 10.972 \) keV to look at the intra-t2g levels.

IV. DISCUSSION

We first consider the crystal structures of Pb2ZnOsO6 and Pb2CaOsO6 in more detail. For Pb2ZnOsO6, the Goldschmidt tolerance factor, which describes the mismatch between the size of the A and B sites [34] is \( t = 1.001 \). The sizes of the Pb\(^{2+}\), Zn\(^{2+}\), and Os\(^{5+}\) ions are, thus, almost perfectly matched for the double perovskite structure. Despite this, the oxygen octahedra in Pb2ZnOsO6, are tilted (mainly by the \( R_1^{2}\) and \( M_1^{2}\) modes), and the space group is not cubic but \( P2_1/n \). This distortion is probably caused by the interaction between the Pb lone pair and the surrounding oxygen, which is known to cause structural distortions, for example, in PbO (Ref. [35]) and Pb2MnTeO6 (Ref. [36]).

The tolerance factor for Pb2CaOsO6 is \( t = 0.941 \), which indicates that the large ionic radius of Ca does not fit as well in the Pb2OsO6 structure as the smaller Co or Zn ions. In Pb2CaOsO6 the crystal structure is heavily distorted up to temperatures of, at least, 500 K, and due to this distortion it is questionable if it can even be classified as a double perovskite. The structure of Pb2CaOsO6 appears to be unique among double perovskites as it is not shared by any of the over thousand double perovskites surveyed in Ref. [37]. The structural distortion in Pb2CaOsO6 is most likely caused by the combined efforts of the large Ca ionic size and the Pb lone pair.

The lone pair electronic instability is well known for many Pb\(^{2+}\)-based perovskite systems, and this instability is responsible for their ferroelectric (e.g., PbTiO3 and PbVO3, Refs. [38,39]) and antiferroelectric (e.g., PbZrO3 and Pb2MnWO6, Refs. [40,41]) properties. Its effect is most clearly elucidated by analyzing the displacement modes in Pb2CaOsO6. In addition to tilting of the oxygen octahedra by the \( R_1^{2}\) and \( M_1^{2}\) modes, the \( \Lambda_3 \) mode has significant amplitude for both the oxygen and the Pb atoms (see Appendix D, Table VI).

The \( \Lambda_3 \) distortion is also found in certain Bi-containing perovskites where it results in complex antiferroelectric displacements of Bi and O attributed to the stereochemical activity of the lone electron pair on the Bi\(^{3+}\) cations [42]. Given that lone pair instabilities are also observed in Pb\(^{2+}\)-based perovskites, it seems very likely that there are antiferroelectriclike distortions of the Pb and O in Pb2CaOsO6. This is a particularly interesting observation because the structural transition in Pb2CaOsO6 is continuous and occurs in the metallic phase. Therefore, at temperatures above \( T_N \) Pb2CaOsO6 can be classified as a “metallic antiferroelectric.”

In 2013, the first example of a “metallic ferroelectric” was reported [42] and attracted considerable attention because the electrostatic mechanisms that drive electric dipole formation and ferroelectric distortions are usually suppressed in metals due to screening by conduction electrons. The antiferroelectric state is also associated with a spatial charge separation and formation of well-correlated electric dipoles and expected to be uncommon in metals. It would be of interest, therefore, to understand what drives the antiferroelectriclike structural distortion in Pb2CaOsO6.

Despite being a metal, the magnetic susceptibility of Pb2ZnOsO6 follows the Curie-Weiss law for temperatures above about 80 K. The Weiss temperature of 214 K indicates strong antiferromagnetic interactions between localized...
magnetic moments. However, we observe no sign of magnetic order in susceptibility or neutron diffraction down to 2 K, indicating that the sample is strongly frustrated. At low temperatures the susceptibility deviates from the Curie-Weiss law. Possible reasons for this deviation include the presence of a small concentration of paramagnetic impurity and the buildup of short-range magnetic correlations.

In a perfectly cubic double perovskite the Os atoms would form a face-centred-cubic (fcc) lattice, which for AFM nearest-neighbor interactions is frustrated and has no unique magnetic ground state [43,44]. As discussed above, Pb$_2$ZnOsO$_6$ is distorted compared to the ideal cubic symmetry and, thus, the Os only approximately forms a fcc lattice but nevertheless remains significantly frustrated. In Pb$_2$CaOsO$_6$, the magnetic frustration is nearly fully relieved as evidenced by the onset of magnetic order at 80 K, close to the Weiss temperature of 101 K (which is only half that of Pb$_2$ZnOsO$_6$). The additional distortion away from the ideal fcc lattice in Pb$_2$CaOsO$_6$ could be what relieves the frustration. It is not surprising that the lower-symmetry, less-frustrated, structure has the greater tendency for magnetic order, but it has been noted previously that in other 5$d^2$ double-perovskites it seems that decreasing symmetry (and increasing spin-orbit coupling) destabilizes magnetic order, the opposite of our results here [45].

The average ordered magnetic moment in Pb$_2$CaOsO$_6$ is only around 0.6$\mu_B$/Os at 2 K, and the entropy associated with the magnetic transition is $S_{\text{mag}} \approx 0.3R$, consistent with such a small moment. A similar reduction in the ordered moment was found in Sr$_2$MgOsO$_6$ [21]. In that material, density functional theory calculations attributed the reduction in the ordered moment to strong spin-orbit coupling as well as to hybridization with the neighboring oxygen atoms which carry up to 40% of the moment. Such a hybridized moment would contribute to the susceptibility and heat capacity but less so to neutron-diffraction due to the magnetic form factor. Hybridized would explain the strong exchange interactions between the Os ions and the broadening of the transitions in our RIXS data.

A noncollinear magnetic order in Pb$_2$CaOsO$_6$ would be quite surprising. Most other 5$d^2$ double-perovskites have nonmagnetic or spin-glass ground states or collinear ferro- or antiferromagnetic long-range magnetic orders [45]. The main difference between Pb$_2$CaOsO$_6$ and these other double-perovskites seems to be the structural distortion, which results in two crystallographically distinct Os sites. The splitting of the $f_{2g}$ levels is, thus, expected to be different for the two sites, which could contribute to the broadening of the peaks in our RIXS data and might result in different magnetic moments on the two sites. It is also possible that the average charge on the two different sites is different as reported for some perovskites [46].

We conclude by discussing the possible origins of the MIT in Pb$_2$CaOsO$_6$. The MIT coincides with the transition to magnetic order, indicating that the two phenomena are related. We observe anomalies in the lattice constants at the transition, but no change in the crystal symmetry to within the precision of our diffraction measurements. The low degree of frustration makes it unlikely that the structural anomalies are driven by relief of frustration, in contrast to what is proposed for Pb$_2$CoOsO$_6$ [13]. On the other hand, the presence of magnetoelectric coupling indicates that the orbitals could play a role in the MIT as has been suggested in frustrated multiorbital 5$d^3$ double-perovskites [47].

In some respects the MIT in Pb$_2$CaOsO$_6$ resembles that in NaOsO$_3$, which was initially proposed to be a Slater transition [48]. In both compounds, a transition from a Curie–Weiss metal to an insulator or bad metal occurs simultaneously with AFM order, and the ordered moment is much smaller than the paramagnetic moment. In NaOsO$_3$, the MIT occurs over a temperature range of some 400 K, and such a continuous transition has been argued to be a signature of a spin-driven Lifshitz transition rather than a Slater transition [9]. The electronic configuration of Os in NaOsO$_3$ is 5$d^3$ corresponding to half-filled $t_{2g}$ states, whereas it is 5$d^2$ in Pb$_2$CaOsO$_6$. Hence, the effect of spin-orbit coupling is expected to be larger in Pb$_2$CaOsO$_6$, and as a result the mechanism of the MIT may be different from that in NaOsO$_3$.

The pyrochlore-structure 5$d$ oxides Cd$_2$Os$_2$O$_7$ and A$_2$Ir$_2$O$_7$ also have metal-to-insulator transitions which coincide with magnetic order, but these cannot be Slater transitions because the magnetic order has propagation vector $\mathbf{k} = 0$ which does not change the periodicity of the crystal potential [10,49–52]. The magnetic order in Pb$_2$CaOsO$_6$, on the other hand, has propagation vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$. This magnetic order results in a doubling in the periodicity of the crystal potential, consistent with one of the requirements of a Slater transition [4].

V. CONCLUSION

Our study has revealed that Pb$_2$ZnOsO$_6$ exhibits no phase transitions between 2 and 350 K and remains a paramagnetic metal throughout this temperature range. By contrast, Pb$_2$CaOsO$_6$ is found to have several unusual and interesting phases. It undergoes a structural transition at high temperatures (above 500 K) to a distorted phase with antiferroelectriclike displacements of the Pb and O atoms despite having metallic conductivity. Therefore, it could be classified as an antiferroelectric metal, in the same sense that LiOsO$_3$ (Ref. [42]) is referred to as a ferroelectric metal (a term originally coined by Anderson and Blount [53]). It also exhibits a metal-to-insulator transition (at 80 K) coincident with the onset of antiferromagnetic order which doubles the periodicity of the crystal potential. Our data suggest that the transition is spin driven, which makes it a candidate for a Slater-type MIT. Angle-resolved photoemission measurements combined with electronic structure calculations to determine the Fermi surface and locate the band gap in momentum space would be very valuable to constrain the mechanism of the MIT in Pb$_2$CaOsO$_6$ with greater certainty.

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APPENDIX A: MAGNETIC SUSCEPTIBILITY OF POLYCRYSTALLINE Pb2Os2O7.

The temperature dependence of the magnetic susceptibility of Pb2Os2O7 is shown in Fig. 8. There is no evidence for any magnetic transitions in the measured temperature range between 2 and 400 K.

APPENDIX B: STRUCTURAL PARAMETERS FROM NEUTRON POWDER DIFFRACTION

Structural parameters of Pb2CaOsO6 and Pb2ZnOsO6 are given in Table II. The coordination of the Os sites is discussed in the main text. As illustrated in Fig. 9, the local environment of the Pb atoms is significantly distorted relative to the cubic parent in which the 12 nearest oxygen atoms form a cuboctahedron with Pb at the center. Table III gives the corresponding Pb-O distances for Pb2ZnOsO6 and Pb2CaOsO6. In Pb2CaOsO6, the Pb-O distances deviate from the mean by up to 0.6 Å, and the Pb1 and Pb2 atoms are displaced from the center of the surrounding oxygens by 0.052 and 0.038 Å, respectively. In Pb2ZnOsO6, the deviation is up to 0.4 Å, and the displacement from the center is 0.019 Å.

APPENDIX C: IRREDUCIBLE REPRESENTATIONS

For the space-group $P2_1/n$ and $k=(\frac{1}{2}, \frac{1}{2}, 0)$ in Table IV, the magnetic representation $\Gamma_{mag}$ for the two

| Pb2ZnOsO6 | Pb2CaOsO6 |
|-----------|-----------|
| Atom      | Pb-O      | Atom      | Pb1-O      | Atom      | Pb2-O      |
| O1a       | 2.710(11) | O11a      | 2.434(11)  | O12a      | 3.107(10)  |
| O1b       | 2.481(9)  | O12b      | 2.805(13)  | O11b      | 2.334(13)  |
| O1c       | 2.955(11) | O11c      | 3.425(11)  | O12c      | 2.591(10)  |
| O1d       | 3.158(9)  | O11d      | 3.752(12)  | O12d      | 3.072(12)  |
| O2a       | 2.461(17) | O21a      | 3.108(9)   | O22a      | 2.533(8)   |
| O2b       | 2.8468(18)| O22b      | 2.803(13)  | O21b      | 3.397(13)  |
| O2c       | 3.244(17) | O21c      | 2.895(9)   | O22c      | 3.298(9)   |
| O2d       | 2.735(16) | O21d      | 2.432(13)  | O22d      | 3.027(13)  |
| O3a       | 2.748(15) | O31a      | 2.385(9)   | O32a      | 3.416(9)   |
| O3b       | 3.255(17) | O32b      | 3.349(14)  | O31b      | 3.441(12)  |
| O3c       | 2.842(18) | O31c      | 3.426(8)   | O32c      | 2.499(9)   |
| O3d       | 2.457(17) | O31d      | 2.649(12)  | O32d      | 2.459(13)  |
Os sites (Wyckoff positions 2a and 2c) decomposes into the irreducible representations,

$$\Gamma_{\text{mag}} = \Gamma_2^3 + \Gamma_4^1.$$  

Both representations are three dimensional and complex, and the corresponding basis functions are summarized in Table VI. The basis functions that transform as $\Gamma_2$ and $\Gamma_4$ are complex conjugates and must be combined to obtain real moments on the Os sites.

**APPENDIX D: DECOMPOSITION OF STRUCTURES**

In Tables V and VI we show the decomposition of the Pb$_2$ZnOsO$_6$ and Pb$_2$CaOsO$_6$ structures into the symmetrized displacive modes of the parent cubic $Pm\overline{3}m$ structure.

| Irrep ($k$) | Order parameter | Site irrep | Amplitude |
|------------|-----------------|------------|-----------|
| $\Gamma_1^+$ (0, 0, 0) | $e_{xx} + e_{yy} + e_{zz}$ | $T_{1u}(a)$ | 0.00001 |
| $\Gamma_3^+$ (0, 0, 0) | $-e_{xx} - e_{yy} + 2e_{zz}$ | $T_{1u}(a)$ | 0.00277 |
| $\Gamma_1^+$ (0, 0, 0) | $e_{yy} + e_{zz}$ | $T_{1u}(a)$ | 0.00056 |
| $\Gamma_3^+$ (0, 0, 0) | $e_{yy} + e_{zz}$ | $T_{1u}(a)$ | 0.201 |
| $R_1^+$ (1/2, 1/2, 1/2) | $a$, $b$, $b$ | $T_{1u}(a)$ | 0.20079 |
| $R_2^+$ (1/2, 1/2, 1/2) | $a$, $0$ | $A_{2u}(a)$ | 0.04084 |
| $R_2^+$ (1/2, 1/2, 1/2) | $0$, $a$, $-a$ | $E_{u}(a)$ | 1.1013 |
| $R_2^+$ (1/2, 1/2, 1/2) | $a$, $b$, $b$ | $E_{u}(a)$ | 0.03593 |
| $X_1^+$ (0, 1/2, 0) | $0$, $0$, $a$, $a$ | $E_{u}(a)$ | 0.05556 |
| $M_2^+$ (1/2, 1/2, 0) | $a$, $0$, $0$ | $A_{2u}(a)$ | 0.11566 |
| $M_2^+$ (1/2, 1/2, 0) | $a$, $0$, $0$ | $E_{u}(a)$ | 0.00112 |
| $M_2^+$ (1/2, 1/2, 0) | $a$, $0$, $0$ | $E_{u}(a)$ | 0.69843 |
| $M_2^+$ (1/2, 1/2, 0) | $a$, $a$, $0$, $0$ | $E_{u}(a)$ | 0.03369 |
| Irrep (k)       | Order parameter | Site irrep | Amplitude |
|-----------------|-----------------|------------|-----------|
| $\Gamma^+_1(0, 0, 0)$ | $(a), e_{xx} + e_{yy} + e_{zz}$ | $(a)$ | 0.00024 |
| $\Gamma^+_2(0, 0, 0)$ | $(a, \sqrt{3}a), 2e_{xx} - 1e_{yy} - 1e_{zz}$ | $(a)$ | 0.00182 |
| $\Gamma^+_3(0, 0, 0)$ | $(a, b, -a), e_{xz} - 1e_{yz}$ | $(a)$ | 0.00783 |
| $\Gamma^+_5(0, 0, 0)$ | $(a, b, -a), e_{xy}$ | $(b)$ | -0.02793 |

Pb displacement

| $\Lambda_1(1/4, 1/4, 1/4)$ | $(0, 0; 0, 0; 0, 0; a, 0)$ | $T_{0a}(a)$ | 0.12338 |
| $\Lambda_3(1/4, 1/4, 1/4)$ | $(0, 0, 0, 0; 0, 0, 0, b, -b, \sqrt{3}b, \sqrt{3}b)$ | $T_{0a}(a)$ | 0.23899 |

Ca displacement

| $X^+_2(0, 1/2, 0)$ | $(0, 0; -a; 0, 0)$ | $T_{0a}(a)$ | -0.09609 |

O displacement

| $\Lambda_1(1/4, 1/4, 1/4)$ | $(0, 0; 0, 0; 0, 0; a, 0)$ | $A_{2a}(a)$ | 0.00671 |
| $\Lambda_2(1/4, 1/4, 1/4)$ | $(0, 0; 0, 0; 0, 0; a, 0)$ | $E_{2}(a)$ | -0.00284 |
| $\Lambda_3(1/4, 1/4, 1/4)$ | $(0, 0, 0, 0; 0, 0, 0, a, 0; -a, -1/\sqrt{3}a, -1/\sqrt{3}a; a, -b, \sqrt{3}b, \sqrt{3}b)$ | $A_{2a}(a)$ | -0.30797 |

| $R^+_1(1/2, 1/2, 1/2)$ | $(a)$ | $A_{2a}(a)$ | -1.0125 |
| $R^+_2(1/2, 1/2, 1/2)$ | $(a, \sqrt{3}a)$ | $A_{2a}(a)$ | 0.04599 |
| $R^+_3(1/2, 1/2, 1/2)$ | $(a, 0, a)$ | $E_{2}(a)$ | 1.6103 |
| $R^+_4(1/2, 1/2, 1/2)$ | $(a, b, -a)$ | $E_{2}(a)$ | 0.00755 |

| $X^+_2(0, 1/2, 0)$ | $(0, 0; -a; 0, 0)$ | $E_{2}(a)$ | -0.2628 |
| $M^+_2(1/2, 1/2, 0)$ | $(0; 0; a)$ | $A_{2a}(a)$ | -0.04517 |
| $M^+_3(1/2, 1/2, 0)$ | $(0; 0; a)$ | $E_{2}(a)$ | 0.50508 |
| $M^+_4(1/2, 1/2, 0)$ | $(0, 0; 0, 0; a, -a)$ | $E_{2}(a)$ | -0.1971 |

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