Observation of antiferromagnetic order collapse in the pressurized insulator LaMnPO

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The emergence of superconductivity in the iron pnictide or cuprate high temperature superconductors usually accompanies the suppression of a long-ranged antiferromagnetic (AFM) order state in a corresponding parent compound by doping or pressurizing. A great deal of effort by doping has been made to find superconductivity in Mn-based compounds, which are thought to bridge the gap between the two families of high temperature superconductors, but the AFM order was not successfully suppressed. Here we report the first observations of the pressure-induced elimination of long-ranged AFM order at \( 34 \) GPa and a crossover from an AFM insulating to an AFM metallic state at \( 20 \) GPa in LaMnPO single crystals that are iso-structural to the LaFeAsO superconductor by in-situ high pressure resistance and ac susceptibility measurements. These findings are of importance to explore potential superconductivity in Mn-based compounds and to shed new light on the underlying mechanism of high temperature superconductivity.

The discovery of iron pnictide superconductor and its extended studies1-7 stimulated the investigations on Mn-based superconductors8-14. As is found in other Mn-based compounds that are iso-structural to the parent compound of iron pnictide superconductor LaFeAsO3, the physical properties of LaMnPO bear a strong resemblance to those of the parent compounds of cuprate high temperature superconductors3. Therefore, it is appropriate to study LaMnPO with the aim of uncovering the underlying mechanism of high temperature superconductivity and for seeking potential superconductivity. At ambient pressure, LaMnPO is a localized moment AFM insulator with a Ne'el temperature (\( T_N \)) about 375 K, and the \( ~3.2 \) \( \mu_B \) per Mn moment align antiferromagnetically in a checkerboard pattern that is stacked along the \( c \) axis15,16. Like doping studies of BaMn\(_2\)As\(_2\)17-20 and CaMn\(_2\)Sb\(_2\)21, long-ranged AFM order in LaMnPO is also robust upon chemical doping. The substitution of fluorine for oxygen to its solubility limit does not much alter the long-ranged AFM order state in LaMnP(O\(_{1-x}\)F\(_{x}\)), and no metallization is observed16,22. All results that are available so far demonstrate that chemical doping does not have a decisive influence on the long-ranged AFM order in these Mn-based compounds. High-pressure studies on BaMn\(_2\)As\(_2\) find evidence of metallization23, however, no experimental investigation on the variation of the long-range AFM order with pressure has been reported. In this study, we applied high pressure techniques to probe the possible elimination of the long-ranged AFM order and the potential for superconductivity in LaMnPO.

Results

Figure 1(a) displays the temperature (\( T \)) dependence of the electrical resistance (\( R \)) of a LaMnPO single crystal under different pressures. Our instrumental restrictions limit the measurement for the \( R-T \) curves at pressure lower than \( 11.7 \) GPa. The low temperature resistances at this pressure show an obvious upturn, which is suppressed remarkably with further increasing pressure. Significantly, a crossover from the insulating behavior to the metallic behavior emerges at pressures of \( 20.8 \) GPa. By careful inspection of the \( R-T \) curves measured at pressures between \( 20.8 \) GPa and \( 25.5 \) GPa, we find a sizable hump with a maximum centered at the temperature \( T^* \), as indicated by an arrow in Fig. 1b, revealing that there exists an intermediary phase in the compressed LaMnPO. The hump signals that the itinerant and localized electrons coexist and compete with each other,
suggesting the occurrence of partial electronic delocalization in LaMnPO. The hump disappears when pressure is increased above 25.5 GPa.

To determine the critical pressure for the crossover precisely, we plot the pressure dependencies of the resistance measured at different temperatures (Fig. 1c). It is noted that the temperature dependence of the resistance changes its trend at the pressure range between 19.6 and 20.8 GPa. Thus, we take the average value (20.3 GPa) as the onset pressure $P_C$ for the crossover. At pressures above 31.2 GPa, the resistance becomes almost linearly proportional to temperature (Fig. 1b), indicating that the system enters a pure metallic state.

Figure 2a shows the resistance as a function of the reciprocal temperature for the LaMnPO single crystal subjected to different pressures. We found that these Arrhenius plots are linear at high temperatures for pressures as large as 25.5 GPa. On basis of the Arrhenius equation, $\rho \sim \exp(\varepsilon_A/2k_BT)$, we can plot the activation energy for the excitation of charge carriers ($\varepsilon_A$) as a function of pressure for the sample investigated. As shown in Fig. 2b, $\varepsilon_A$ decreases rapidly with increasing pressure below 15 GPa, where the insulating behavior is systematically suppressed (Fig. 1a). It is noted that $\varepsilon_A$ remains unchanged with a value of about 60 meV in the pressure range of 16–20 GPa. We attribute this gap to the competition between the itinerant and localized electrons. As pressure is elevated above 20.3 GPa, the $\varepsilon_A$ continues to decline and the metalliclicity of the system emerges (inset of Fig. 2b). At pressure above 32 GPa, we found that $\varepsilon_A$ approaches zero, demonstrating that the gap has collapsed.

It is known from the studies of cuprate and iron pnictide superconductors that the full suppression of long-ranged AFM order is a crucial step to realize superconductivity, and one can ask what the case looks like in LaMnPO. We probed the evolution of the onset AFM transition temperature $T_N$ with pressure by in-situ high pressure ac susceptibility measurement. Since the $T_N$ of LaMnPO at ambient pressure is about 375 K, which is out of the measuring range of our instrument, we cannot detect the $T_N$ at pressures less than 7.3 GPa, above the pressure of which the AFM transition becomes apparent as shown in Fig. 3. We can see that the $T_N$ shifts to lower temperature with increasing pressure, and then vanishes at pressure close to 34 GPa eventually. The disappearance of the $T_N$ indicates that pressure drives the system undergoing an AFM-PM transition and all electrons related to the AFM order are delocalized. This is in excellent agreement with our high-pressure resistance data, i.e. at pressures above 32 GPa, the system exhibits metallic behavior over the entire temperature range (Fig. 1b). This is the first observation of the collapse of long-ranged AFM order in a Mn-based compound that is iso-structural to the iron pnictide superconductors, an event that was predicted by our previous calculations.

**Discussion**

To demonstrate the overall behavior of pressurized LaMnPO clearly, the electronic phase diagram of the LaMnPO is presented in Fig. 4. $T_N$ is indicated by filled triangles, which is systematically suppressed upon increasing pressure. At ~ 20 GPa, the system enters a mixed state (referred to as the M’ phase), in which the insulating (I) and metallic (M) states coexist, therefore the long-ranged AFM order is still retained. The AFM-M’ regime that is delineated by the resistance hump and the $T_N$ lies in the pressure range 20–32 GPa. At pressures close to 34 GPa, there is no indication of AFM order, demonstrating
that the long-ranged AFM order has collapsed and that the localized/moment-bearing electrons are now fully delocalized. We note that the system becomes fully metallic (Fig. 1b) only at pressures where the long-ranged AFM order at $T = 0$ has collapsed, implying that the insulating behavior of the intermediary phase requires at least some form of AFM short range order. These results, in particular the resistance hump observed at intermediate pressures, are reminiscent of the experimental findings in compressed $A_2Fe_4Se_5$ ($A = K$ or Tl substituted on Rb). The coexistence of localized and delocalized carriers in these systems has been suggested to be the origin of the hump. In the present study, no superconductivity is found in LaMnPPO above the temperature of 1.5 K. However, the observations of the long-ranged AFM order collapse and the novel intermediary phase provide fresh information for exploring potential superconductivity in Mn-based compounds and provide new insight into the underlying mechanism of high temperature superconductivity.

**Methods**

The single crystals of LaMnPO were grown by the NaCl-KCl eutectic flux method, as described in Ref 22 and 28. Diamond anvil cells (DACs) were used to create high pressure. The anvil diameter is about 300 μm. High-pressure electrical resistance experiments were carried out in a DAC using the standard four-probe technique. High-pressure alternating current (ac) susceptibility measurements were conducted...
using home-made coils that were wound around a diamond anvil \textsuperscript{29,30}. The nonmagnetic rhenum gasket was preindented down to a 50 μm thickness for different runs of high-pressure resistance and magnetic measurements. A thin plate sample with dimensions of around 80 × 80 × 10 μm, cleaved from the LaMnPO single crystal, was loaded into the gasket hole in a DAC for the resistance measurements. To detect the T\textsubscript{N} with stronger signal under pressure, several more plates than resistance measurements were loaded into the gasket hole sitting in a different DAC for ac susceptibility measurements. Pressure was determined by ruby fluorescence\textsuperscript{31}.

Figure 4 | The P-T electronic phase diagram of LaMnPO. The open triangle represents the AFM transition temperature (T\textsubscript{N} = 375 K) at ambient pressure, taken from neutron diffraction measurements\textsuperscript{15,16}. The filled triangles correspond to values of T\textsubscript{N} obtained from our high pressure ac susceptibility measurements. The open circles represent temperatures T', where the resistance is at a maximum, taken from different independent runs. There is no indication of AFM order at ∼ 34 GPa, as displayed by the dashed open triangles. The acronyms AFM-I and AFM-M' stand for antiferromagnetic insulating and antiferromagnetic mixed state regimes, respectively. PM-I and PM-M represent paramagnetic insulating and paramagnetic metallic states, respectively.

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Additional information
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