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Local moments and symmetry breaking in metallic PrMnSbO

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We report a combined experimental and theoretical investigation of the layered antimonide PrMnSbO which is isostructural to the parent phase of the iron pnictide superconductors. We find linear resistivity near room temperature and Fermi liquidlike T^2 behavior below 150 K. Neutron powder diffraction shows that unfrustrated C-type Mn magnetic order develops below ~ 230 K, followed by a spin flop coupled to induced Pr order. At $T \sim 35$ K, we find a tetragonal to orthorhombic (T-O) transition. First-principles calculations show that the large magnetic moments observed in this metallic compound are of local origin. Our results are thus inconsistent with either the itinerant or frustrated models proposed for symmetry breaking in the iron pnictides. We show that PrMnSbO is instead a rare example of a metal where structural distortions are driven by f-electron degrees of freedom.

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The discovery[1] of high-temperature superconductivity in $LaFeAsO_{1-x}F_x$ has reignited interest in the role of magnetism in this phenomenon. The characteristic feature of the parent, nonsuperconducting, iron pnictides is a tetragonal-orthorhombic (T-O) structural phase transition, which accompanies or precedes striped magnetic order.[2] Optimal T_C is reached after this transition is completely suppressed by alovalent or isovalent doping,[2,3] or by the application of pressure.[4] Despite metallic electrical conduction and even reports of quantum oscillations,[5] the origins of the magnetism in the iron pnictides are currently controversial.[6] The key experimental observations of a strongly reduced magnetic moment and symmetry breaking of the square FeAs substructure, can to some degree, be explained by two competing viewpoints. The first, is based on itinerant models of magnetism[7] while the second is based upon local-moment exchange as the iron lattice maps onto a frustrated J_1-J_2 model.[8] Currently consensus seems far away but what is not disputed is that magnetism, structural distortion, and superconductivity are related. Understanding the correlations between structure, magnetism, and transport properties in the whole family of oxypnictide materials[9] is thus of great topical interest.

In this Rapid Communication we report a combined experimental and theoretical investigation of PrMnSbO, which is isostructural to the LaFeAsO parent phase of the iron pnictide superconductors.[10,11] We find strong evidence for localized magnetic moments which coexist with a sea of conduction electrons and a T-O structural phase transition at 35 K. Even though Mn spin order is found at extremely high temperature (T_N=230 K), this barely couples to the lattice showing that neither the itinerant nor frustrated models for the iron arsenides are appropriate. Instead, the symmetry-breaking transition is apparently driven by single-ion Pr^{3+} degrees of freedom. While many other isostructural materials with f-electron degrees of freedom are known,[12–15] none have previously been shown to undergo structural phase transitions except the iron pnictide parent phases.

We synthesized polycrystalline samples of PrMnSbO using the previously reported method[11] and measured a range of physical properties. Magnetic susceptibility measurements [Fig. 1(a)], performed with a Quantum Design magnetic properties measurement system in a 1 T field, show an anomaly near ~ 250 K and an antiferromagnetic (AFM) transition at around 40 K. The inverse susceptibility was well fitted by a Curie-Weiss term over a wide temperature region, and gave an effective moment of 4.99(2) μ_B and a Weiss constant of −85(1) K, implying strong antiferromagnetic correlations. Assuming Pr^{3+} has the expected free ion moment (in agreement with the neutron-diffraction results below) of 3.58 μ_B, then the paramagnetic Mn moment is 3.47 μ_B. This value is consistent with the very strong Mn-Sb hybridization in this class of materials which stabilizes an intermediate spin configuration.[16] Transport measurements [Fig. 1(b)] were performed on PrMnSbO using a physical properties measurement system and showed a low room-temperature resistivity of 0.011 Ω m. The temperature dependence was metallic with a residual resistivity of $\rho/\rho_{300\ K}=0.09$. Fermi liquidlike T^2 behavior was found over a wide temperature regime (2–150 K) with a crossover at higher temperatures to quasilinear behavior. An anomaly in $d^2\rho/d^2T$ was found at 230 K [Fig. 1(b)]. As shown below, this corresponds to the Mn ordering temperature. The linear resistivity at higher temperatures could therefore be a result of Mn spin fluctuations. Intriguingly, the succession of magnetic and structural transitions which occur at lower temperatures, have no further effect on the transport properties. These are however, clearly visible in the specific heat [inset, Fig. 1(b)], which has a sharp peak at 35 K and a broader feature centered at 80 K. The 230 K transition is not clearly distinguished, probably due to the very large phonon contribution to $C_p(T)$ at high temperature.

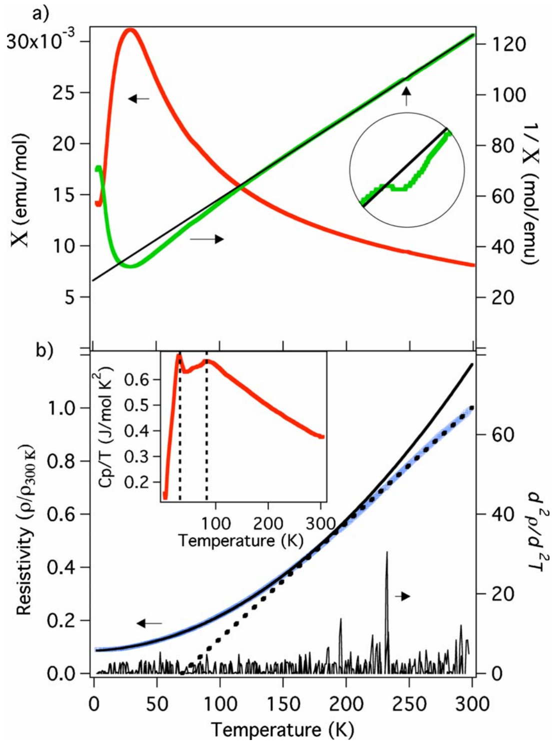

FIG. 1. (Color online) (a) dc-magnetic susceptibility of PrMnSbO measured as a function of temperature in a 1 T field; (b) resistivity of polycrystalline PrMnSbO measured in zero field, solid line shows fit to T^2 behavior over range $2<T<150$ K, dashed line shows linear behavior near room temperature. Inset shows specific heat from 2–300 K.

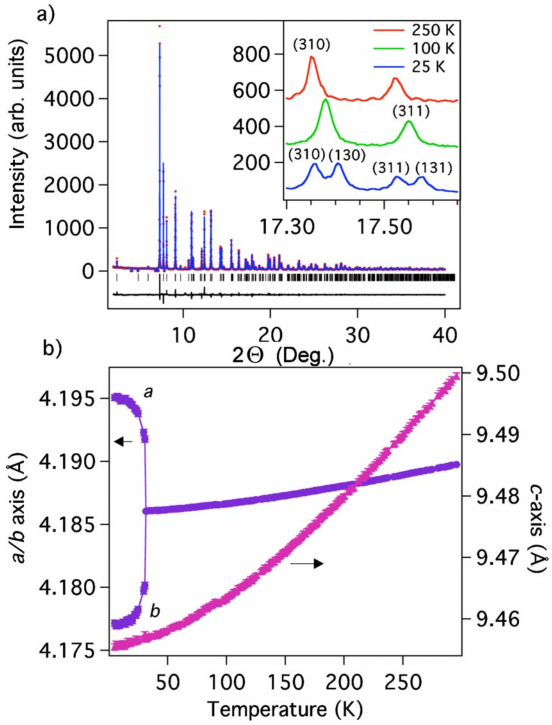

FIG. 2. (Color online) (a) Observed, calculated and difference profiles for Rietveld fit to synchrotron x-ray diffraction profile of PrMnSbO at 20 K. The refinement converged with $R_{wp}=0.067$, $R_p=0.052$, and $\chi^2=2.89$. The inset shows the orthorhombic peak splitting as a function of temperature. (b) Refined lattice parameters of PrMnSbO as a function of temperature from the neutron powder-diffraction experiment.

At room temperature, Rietveld analysis[17] of extremely high-resolution x-ray powder-diffraction data collected using ID31 at the ESRF, Grenoble, were consistent with the reported[11] $P4/nmm$ structure and no evidence for disorder or deficiencies was detected. Below ~35 K, a clear orthorhombic splitting is seen [inset, Fig. 2(a)]. Unlike LaFeAsO, this does not lead to an enlarged centered cell. Here the structure was solved and refined in the subgroup *Pmmn* with a small distortion in the *ab* plane.[18] No change in the nearest-neighbor Mn-Mn distance was found, however, the Pr site point-group symmetry is reduced from 4*mm* to *mm*2. This is consistent with the rare-earth magnetism driving the structural distortion as confirmed below. The temperature dependence of the cell parameters is shown in Fig. 2(b). Clearly, the manganese spin-ordering transition at 230 K has little or no coupling to the lattice as no anomalies are seen. We note that the absolute magnitude of the distortion in the *ab* plane at 35 K (4.2%) is only slightly smaller than that found[19] in PrFeAsO (4.8%), although the latter undergoes the T-O phase transition at significantly higher temperatures (136 K).

Our neutron powder-diffraction measurements were made using D20 at the ILL, Grenoble,[20] and showed evidence of magnetic order below 230 K. All reflections could be indexed with the primitive unit cell, i.e., $k=(0,0,0)$. The peaks showed an unusual temperature dependence [Fig. 3(a)] with several reaching a peak at 100 K with more complex behavior on further cooling. Above 100 K, the data could be accounted for using ordered Mn spins only [region I in Fig. 3(b)]. Representational analysis of the possible magnetic structures allows AFM solutions with moments along all three axes. However, only a z component was necessary to fit the data. The magnetic structure corresponds to nearest-neighbor AFM coupling in the plane and ferromagnetic stacking of layers (i.e., C-type order). The refined moment reached a peak of ~3 μ_B at 100 K, which compares to a value of ~5 μ_B expected for spin-only Mn^{2+}. Notably, this relative reduction (~40%) in moment from that expected in a local-moment picture, is much less than that seen in iron pnictides such as LaFeAsO ($\mu/\mu_{exp}\sim 0.1$). In the region of the broad anomaly seen in the specific heat (80 K), the decrease in intensity of the principle magnetic reflections is accounted for by a flop of the Mn spins into the *ab* plane [region II in Fig. 3(b)]. We also detected a small moment attributed to induced ordering of the Pr^{3+} sublattice, which shows a characteristic concave temperature dependence. The induced magnetic structure consists of antiferromagnetic bilayers of Pr^{3+} moments with the moments also lying in the *ab* plane. This interplay between sublattices is similar to what was reported[19] in PrFeAsO, except it is more obviously manifested due to the larger moments.

Below the T-O structural phase transition, we detected several new magnetic reflections which also indexed on the orthorhombic cell. The magnetic order in the low-temperature phase is identical to that seen in region II, except the orthorhombic distortion allows us to distinguish the di-

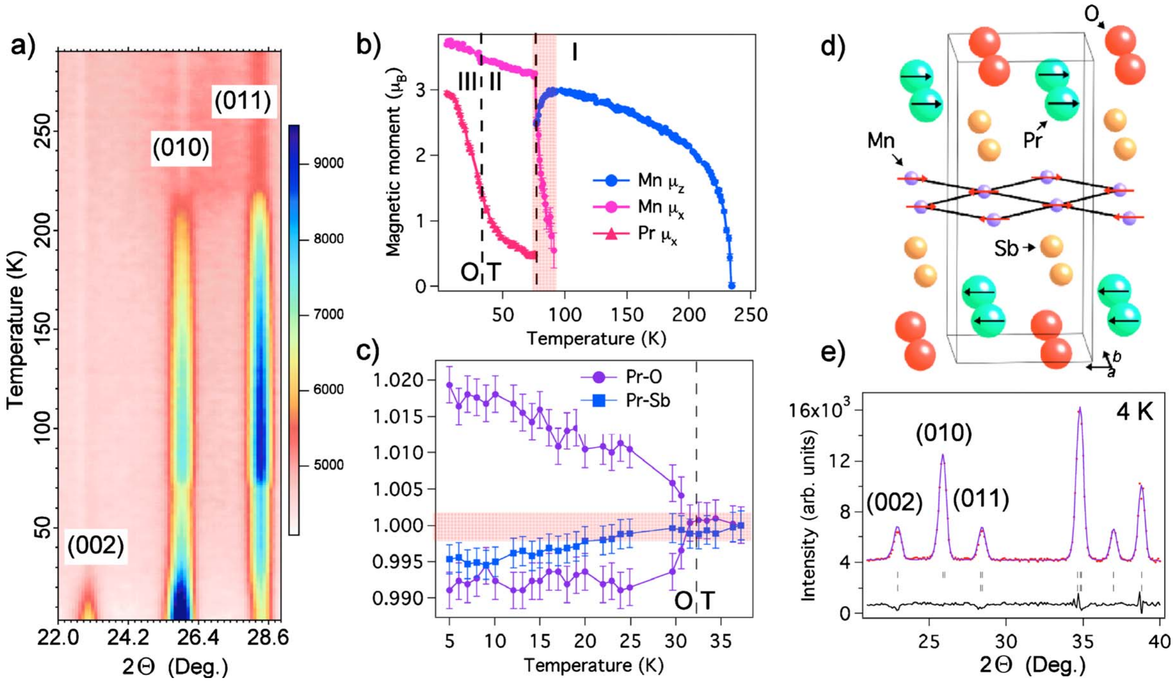

FIG. 3. (Color online) (a) Temperature dependence of principle magnetic reflections in PrMnSbO from neutron powder diffraction, labels refer to the orthorhombic cell; (b) refined magnetic moments through regimes referred to in the text as a function of temperature, the region over which the spin flop occurs is shaded; (c) relative changes in Pr-O and Pr-Sb bond distances below the T-O phase transition, the shaded area indicates the maximum changes in these distances found in PrFeAsO; (d) magnetic structure of PrMnSbO obtained at 4 K; (e) low-angle part of observed, calculated, and difference profiles for Rietveld fit to the neutron-diffraction profile of PrMnSbO at 4 K.

rection of the moments in the *ab* plane (along the long *a* axis). The saturated moments were 3.69(3) μ_B for Mn and 2.96(3) μ_B for Pr. The magnetic structure at 4 K is shown in Fig. 3(d) and the low-angle part of the Rietveld fit to the 4 K data is shown in Fig. 3(e).

The origin of the structural phase transition in PrMnSbO is clearly different from that found in the iron pnictides, which is driven by transition-metal magnetism. Furthermore, related materials such as NdCoAsO, which also show interplay between both magnetic sublattices, do not show any distortion from tetragonal symmetry.[13,14] The magnetic order in the orthorhombic phase is also not obviously symmetry breaking as it is similar to that found in region II. Finally, C-type magnetic order implies that $J_1 \gg J_2$ in the MnSb planes, i.e., magnetic frustration is negligible. What then is the origin of the structural phase transition? As Pr^{3+} has a $4f_2$ configuration, one possibility is multipolar order. This scenario would result in a subtle crystallographic distortion of the Pr site, which we detect with our diffraction measurements [Fig. 3(c)]. Below 35 K we find that the Pr-O distance splits into two and the Pr-Sb distance contracts. For comparative purposes we also plot the maximum variation found in these distances in PrFeAsO below T_N(Pr). These results are thus consistent with local *f*-electron degrees of freedom driving the structural transition. Ferromultipolar order with $k=(0,0,0)$, would be compatible with the observed magnetic structure, however our measurements do not directly probe this order parameter. Confirmatory investigations with resonant x-ray scattering are clearly justified.

Experimentally, the magnetism in PrMnSbO appears to involve large local moments, which barely couple to the con-

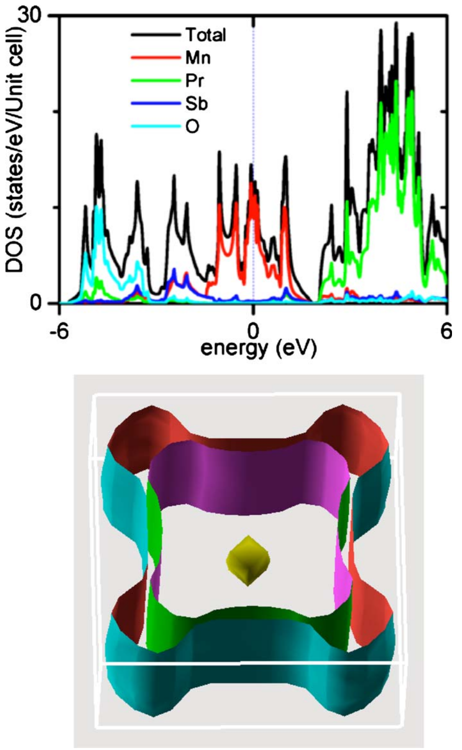

FIG. 4. (Color online) (Top) Total density of states for $P4/nmm$ PrMnSbO showing the large contribution of Mn $3d$ states to the DOS around E_F. (Bottom) Fermi surface of PrMnSbO in the first Brillouin zone, in contrast to the FeAs superconductors, no major nesting is observed.

duction electrons. To explore further the interplay between structure and magnetism in PrMnSbO, we performed density-functional calculations using the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) in the WIEN2K code[21] based on the room-temperature structure where the open-core approximation is employed for the Pr $4f$ states. Our major findings are shown in Fig. 4. Similarly to the iron pnictides, we find that the density of state (DOS) at the Fermi level is almost entirely made up of transition-metal d states. This is consistent with our proposal that local f-electron states drive the T-O transition and explains the lack of a resistive anomaly at 35 K. Among the Mn states, we find that the $d_{x^2-y^2}$ and d_{xz}/d_{yz} states are most prominent where the local coordinates are $x=a$, $y=b$, and $z=c$. The calculated Fermi surface of PrMnSbO is also shown in Fig. 4, which unlike the iron pnictides does not show prominent nesting. Instead we find a rather three-dimensional pocket at the zone center and warped sheets at the zone boundary. We also calculated the noninteracting susceptibility and did not detect strong peaks at $q=(\pi,\pi,0)$ or at $q=(0,0,0)$. These findings, together with the experimental observations above, show that the magnetism in PrMnSbO is a result of local exchange interactions rather than Fermi-surface nesting, despite the good electrical conductivity.

Furthermore, we performed both spin-polarized GGA (sp-GGA) and local spin-density approximation (LSDA) calculations based on the low-temperature orthorhombic structure. Without considering the magnetization on Pr, the C-type Mn magnetically ordered state is obtained with calculated magnetic moments of $\mu_z=3.59\ \mu_B$ (sp-GGA) and $3.46\ \mu_B$ (LSDA), which are comparable to experimental observation, indicating that spin fluctuations in PrMnSbO are not as strong as in iron pnictides. However, a metallic ground state is only realized if the moment size is constrained to $3\ \mu_B$. We additionally found that introducing AFM Pr order destabilizes the Mn order indicating strong coupling between sublattices as experimentally observed. However, further investigations have to be made to understand the microscopic origin of the spin-flop process and the origins of the structural distortion at 35 K.

In conclusion, we have reported a rare example of a structural distortion driven by magnetism in the ZrCuSiAs family of compounds outside the ferropnictides. This transition is not driven by Fermi-surface nesting and despite the large moments, magnetic frustration is apparently unimportant. Instead the distortion in PrMnSbO is driven by f-electron degrees of freedom. Future investigations using x-ray or neutron scattering will help to clarify this transition and determine any relation to those found in the iron pnictides.

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