

**Prospects for quantum criticality in perovskite SrRhO<sub>3</sub>**

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Density-functional studies of the perovskite structure SrRhO<sub>3</sub> are reported using the full experimental orthorhombic crystal structure as well as a structure with relaxed atomic coordinates. A very soft ferromagnetic ground state is found as well as flat bands near the Fermi energy,  $E_F$ , that couple to the magnetism. As in the ruthenate magnets, a very large oxygen contribution to the magnetic moments is found. In light of experimental data for this compound, it is suggested that SrRhO<sub>3</sub> is near a quantum critical point, and that the properties are substantially affected by quantum critical fluctuations.

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Magnetism is much less common in  $4d$  and  $5d$  compounds than in  $3d$  and  $4f$  materials because the on-site Stoner and Coulomb parameters are lower, while the bandwidths tend to be larger, both because of the more extended nature of  $4d$  and  $5d$  orbitals relative to the  $3d$  case. However, when it does occur it may be more interesting than typical  $3d$  magnetism. In particular, the more extended active orbitals make it much more likely for itinerant electron physics to play an important role in such materials. This leads to interesting physics, such as strong coupling to lattice degrees of freedom and soft longitudinal magnetic degrees of freedom, especially on the borderline between ferromagnetism and paramagnetism. The discovery of unconventional triplet superconductivity in the layered perovskite Sr<sub>2</sub>RuO<sub>4</sub>, presumably mediated in some way by magnetic fluctuations,<sup>1-4</sup> has led to a renewed interest in such oxides, especially with perovskite-derived structures, and in particular their magnetic properties. Recently, unconventional superconductivity has been discovered in a number of compounds near quantum critical points when clean samples were studied at low temperature.<sup>5-8</sup> This leaves open the question of how close Sr<sub>2</sub>RuO<sub>4</sub> is to a critical point and what role if any this plays in its triplet superconductivity. Besides increasingly detailed characterization, one way to approach this question is by studying related perovskite metals near magnetism. Unfortunately, outside the ruthenates, magnetism is rather rare in  $4d$  and  $5d$  perovskite metals. The nearby Rh compounds are difficult to synthesize. Nonetheless, Sr<sub>2</sub>RhO<sub>4</sub> and, recently, SrRhO<sub>3</sub> have been synthesized and studied experimentally.<sup>9-12</sup> Although it is clearly demonstrated that Sr<sub>2</sub>RuO<sub>4</sub> does occur in the ideal  $I4/mmm$  structure, Sr<sub>2</sub>RhO<sub>4</sub> does not, but rather shows an orthorhombic distortion.<sup>10,13</sup>

SrRhO<sub>3</sub> is perhaps more interesting. Yamaura and Takayama-Muromachi synthesized the compound and reported an x-ray Rietveld refinement of the crystal structure, finding the usual distorted perovskite GdFeO<sub>3</sub>,  $Pnma$  (No. 62) structure, with a substantial rotation of the oxygen octahedra.<sup>12</sup> They found it to be a metal with no evidence for long-range magnetic ordering down to 1.8 K. Their investigations of transport, susceptibility, and specific heat in SrRhO<sub>3</sub> show remarkable properties. Starting with low-temperature properties of this metal, the electronic specific-heat coefficient  $\gamma$  is moderately large, but the  $T^2$  resistivity coefficient  $A$  and susceptibility  $\chi(0)$  are disproportionately

enhanced. The Wilson ratio was reported to be  $R_W=8.6$  and the Kadowaki-Woods ratio roughly 100 times the usual value. Although complicated by possible impurity contributions and the polycrystalline nature of the samples, the temperature dependence  $\chi(T)$  was found to be unusual with an upturn at low temperatures and could not be reasonably fit using standard forms consistent with the specific heat. Furthermore, the lattice specific heat indicated that SrRhO<sub>3</sub> was oddly soft, having a considerably lower Debye temperature than the corresponding ruthenate.

Here density-functional calculations are reported for SrRhO<sub>3</sub> using the full experimental crystal structure. A very soft ferromagnetic ground state is found as well as flat bands near the Fermi energy,  $E_F$ , that couple to the magnetism. As in the ruthenate magnets,<sup>3,14</sup> a very large oxygen contribution to the magnetic moments is found. In light of experimental data for this compound, it is suggested that SrRhO<sub>3</sub> is near a quantum critical point, and that the properties are substantially affected by quantum critical fluctuations.

The calculations were done within the local spin-density approximation (LSDA) using the general potential linearized augmented plane-wave (LAPW) method.<sup>15</sup> Well-converged basis sets consisting of approximately 630 LAPW functions per formula unit, plus additional local orbitals to treat the high-lying semicore states and relax linearization errors, were employed.<sup>16,17</sup> Core states were treated relativistically, while valence states were treated in a scalar relativistic approximation. The Brillouin-zone integrations during the self-consistent iterations were done using the special  $\mathbf{k}$ -points method. This was based on 144 special  $\mathbf{k}$ -points in the irreducible wedge for the 20-atom orthorhombic cell and 364 special  $\mathbf{k}$ -points in the irreducible wedge for the five-atom ideal perovskite cell. Convergence of the results with respect to zone sampling was checked by performing self-consistent calculations with various densities of  $\mathbf{k}$  points.

Within an ionic picture of octahedrally coordinated Rh<sup>4+</sup> ions, one expects a band structure showing crystal-field-split  $4d$  orbitals. The lower-lying  $t_{2g}$  manifold should contain five electrons (one hole) per Rh, while the higher-lying  $e_g$  manifold should be unoccupied. In fact, the band structure is not conveniently described in this way since the Rh  $4d$  and O  $2p$  states are very strongly hybridized. This is similar to what was found earlier for SrRuO<sub>3</sub>.<sup>18</sup> The band structure for ideal cubic perovskite SrRhO<sub>3</sub>, done at the same volume per Rh as

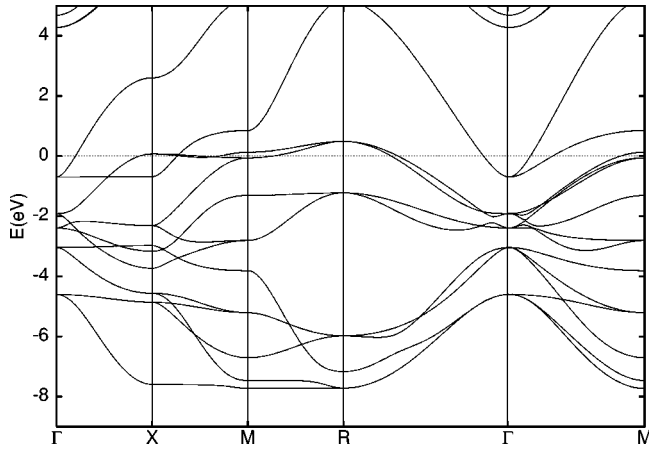


FIG. 1. Non-spin-polarized valence-band structure of  $\text{SrRhO}_3$  in the ideal cubic perovskite structure (see text).

the actual  $Pnma$  structure, is shown in Fig. 1. The corresponding electronic density of states (DOS) is given in the upper panel of Fig. 2. As may be seen, there are no clear gaps between the ionic levels. The valence-band structure may be described as follows: The bottom, starting at approximately  $-8$  eV (relative to  $E_F$ ) is mainly O  $p$  derived but has a bonding Rh  $e_g$ -O  $p_\sigma$  character. The corresponding antibonding  $e_g$  bands are above  $E_F$ . This is followed by a region of nonbonding O bands ( $-6$  eV to  $-2$  eV), then hybridized Rh  $t_{2g}$ -O  $p_\pi$  bands from approximately  $-2$  eV to just above  $E_F$ .

The bands around  $E_F$  then are Rh  $t_{2g}$  derived, but have significant O character as well. This is quite similar to  $\text{SrRuO}_3$ , though of course in  $\text{SrRhO}_3$   $E_F$  is closer to the  $t_{2g}$  maximum at the  $R$  point. What is different is a rather pronounced flatness of the band structure around  $E_F$  at the zone boundary, as is seen, for example, in the band-structure plot along the  $X$ - $M$  line. This gives rise to a pronounced peak in the DOS near  $E_F$ . The value of the DOS at the Fermi energy for this idealized cubic structure is  $N(E_F) = 7.8 \text{ eV}^{-1}$  on a per formula unit, both spins basis. This is sufficient to cause a Stoner instability. This is clearly seen from the fact that the fixed spin moment energy decreases with moment around the zero moment (paramagnetic) point. The calculated LSDA spin moment is  $1.27 \mu_B$  with an energy gain of 38 meV, both per formula unit. This implies an unambiguously ferromagnetic ground state for the ideal cubic perovskite structure.

The spin moment clearly shows the inadequacy of the ionic model. The maximum spin moment in a  $t_{2g}$  manifold with one hole is  $1 \mu_B$ ; the larger value here is the result of hybridization and the overlap of the nominally  $t_{2g}$  and  $e_g$  manifolds. The non-spin-polarized electronic structure for the experimental  $Pnma$  structure is qualitatively similar. The DOS is given in the lower panel of Fig. 2. Besides the expected broadening of sharp features due to orthorhombicity and narrowing of the main manifolds due to reduced hopping, one may note a gap (centered at  $\sim 1$  eV) between the top of the nominally  $t_{2g}$  manifold and the higher conduction bands.

Although the crystal structure is orthorhombic, the electronic structure near  $E_F$  is reasonably isotropic, e.g. showing

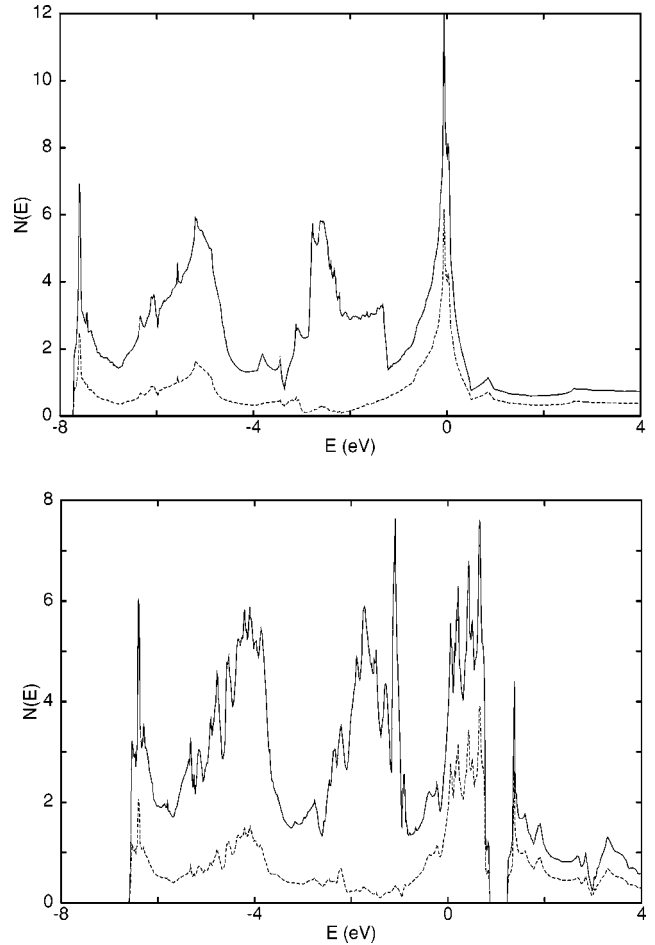


FIG. 2. Non-spin-polarized electronic density of states of  $\text{SrRhO}_3$  in the ideal cubic perovskite structure (top) and the experimental  $Pnma$  orthorhombic structure (bottom). The dotted lines are the Rh  $d$  contributions as defined by projection within the Rh LAPW sphere, radius 2.05 bohr.

only modest orthorhombicity in the Fermi velocities. The calculated values are  $\langle v_a^2 \rangle^{1/2} = 8.5 \times 10^6$ ,  $\langle v_b^2 \rangle^{1/2} = 9.0 \times 10^6$ , and  $\langle v_c^2 \rangle^{1/2} = 8.2 \times 10^6$  cm/s, with the  $a$ ,  $b$ , and  $c$  axes as given in Ref. 12. As in the ideal structure, there is a peak in the DOS around  $E_F$ , though it is broader. This resulting value,  $N(E_F) = 5.4 \text{ eV}^{-1}$  per formula unit, is 30% lower than for the ideal cubic structure, but is still high enough to lead to Stoner ferromagnetism within the LSDA, as is evident again from the fixed spin moment calculation.

The LSDA spin moment is  $0.9 \mu_B$  per formula unit, just slightly less than the maximum of  $1 \mu_B$  imposed by the gap at the top of the  $t_{2g}$  manifold. The corresponding energy gain with respect to the non-spin-polarized case is 11 meV per formula unit. It is remarkable that of this only  $0.51 \mu_B$ , i.e., less than 60%, is contained in the Rh LAPW sphere (radius 2.05 bohr), while each O sphere (radius 1.55 bohr), contains approximately  $0.1 \mu_B$ . Considering the compactness of the Rh atomic  $d$  orbitals as compared to the sphere radius, one may regard the interstitial contribution of  $\sim 0.1 \mu_B$  as mainly O derived as well, so that in this compound more than 40% of the spin moment is associated with O. This is an extraor-

dinarily high number, even larger than in the perovskite rhenates. According to the arguments of Ref. 14, this should bias the magnetism of this compound towards ferromagnetism.

In order to check this ferromagnetic tendency, LSDA calculations were performed for a hypothetical  $G$ -type (rocksalt ordering) antiferromagnetic structure. Simple antiferromagnetic superexchange couplings, as in insulating perovskites such as  $\text{CaMnO}_3$ , lead to this type of ordering, in which all nearest neighbors are antiferromagnetically aligned. Furthermore, it is quite likely that if the material was antiferromagnetic but the  $G$ -type ordering was not the ground state, antiferromagnetic interactions strong enough to disrupt the ferromagnetic state would lead to a metastable low-energy  $G$ -type state. Calculations were done for both the relaxed LSDA structure (see below) and for the experimental structure. However, no stable  $G$ -type antiferromagnetic state was found. In both structures, applications of a staggered  $G$ -type antiferromagnetic “field” of 5 mRy to the Rh LAPW spheres resulted in induced moments within the Rh spheres of only  $0.15\mu_B/\text{Rh}$  (cf.  $0.43\mu_B/\text{Rh}$  in the equilibrium, unconstrained ferromagnetic ground state), indicating that the material is not close to this antiferromagnetic state. This underscores the itinerant nature of the ferromagnetism predicted within the LSDA.

Besides antiferromagnetism, another possible explanation for the experimental nonobservation of ferromagnetism despite its LSDA prediction is that the orbital and spin moments might nearly cancel. This is known to happen in certain actinide ( $5f$ ) systems, where the spin-orbit coupling is large on the scale of the hopping that leads to band formation. However, it seems quite unlikely to be the case in a well-hybridized  $4d$  oxide such as  $\text{SrRhO}_3$ .

In view of the differences between the calculations for the experimental structure and the idealized cubic structure, it is clear that there is non-negligible magnetoelastic coupling in this material. Unfortunately the calculated LSDA forces on the O atoms with the experimental structure were not very small. The largest force is  $0.028 \text{ Ry/bohr}$ —a number that is significantly larger than the expected accuracy of LSDA calculations. On the other hand, experimental crystal structure determinations are typically more reliable than theoretical determinations based on the LSDA. In oxides with heavy metal atoms, refinements by x-ray diffraction may yield inaccurate O positions because of the relatively weak scattering of x rays by light atoms. This is a point that was made early on in the context of perovskite structures by Jona and co-workers.<sup>19</sup> Considering the relative accuracies of LSDA calculations relative to x-ray structure refinement, the x-ray lattice parameters  $a$ ,  $b$ , and  $c$  are clearly much more reliable than could be determined in the LSDA. These, unlike the internal atomic coordinates, can be determined from the positions of the peaks in the x-ray scattering. The present local-density approximation (LDA) calculations of the equilibrium volume of  $\text{SrRhO}_3$  in the ideal cubic perovskite structure give an effective lattice parameter  $a = 3.89 \text{ \AA}$ , i.e., 1.1% smaller than the effective experimental pseudocubic lattice parameter (N·B· the octahedral rotations that characterize the  $\text{GdFeO}_3$  structure are volume lowering in perovskites

TABLE I. Calculated LSDA structural, electronic, and magnetic parameters for  $\text{SrRhO}_3$  for the idealized cubic structure (CUB), the experimental  $Pnma$  structure (EXP), and the partially relaxed structure (REL, see text). Velocities are in cm/s, while other quantities are per formula unit. The Fermi-surface-related quantities are for the non-spin-polarized case.  $m_{total}$  is the spin moment per formula unit,  $m_{\text{Rh}}$  is the part in the Rh LAPW sphere, and  $m_{\text{O}}$  is the part in the three O LAPW spheres.

	CUB	EXP	REL
$O1_x$		0.4990	0.477
$O1_z$		0.0587	0.074
$O2_x$		0.2825	0.290
$O2_y$		0.0366	0.038
$O2_z$		0.7088	0.710
$N(E_F)$ ( $\text{eV}^{-1}$ )	7.8	5.4	6.0
$\langle v_a^2 \rangle^{1/2}$ ( $10^6 \text{ cm/s}$ )	13.8	8.5	8.7
$\langle v_b^2 \rangle^{1/2}$ ( $10^6 \text{ cm/s}$ )	13.8	9.0	8.5
$\langle v_c^2 \rangle^{1/2}$ ( $10^6 \text{ cm/s}$ )	13.8	8.2	8.5
$m_{total}$ ( $\mu_B$ )	1.27	0.91	0.78
$m_{\text{Rh}}$ ( $\mu_B$ )	0.73	0.51	0.42
$m_{\text{O}}$ ( $\mu_B$ )	0.39	0.30	0.25

and therefore inclusion of these in the calculation, while more realistic, would slightly degrade agreement with experiment).

On the other hand, determination of atomic positions requires an analysis of the intensities of the x-ray pattern, usually done via a Rietveld method. For  $4d$  oxides, the relatively small atomic number of O relative to the metal atoms means that O contributes relatively little to the scattered intensity and this often makes accurate determinations of the O positions difficult. The Rh positions in the  $Pnma$  structure are fixed by symmetry, and are therefore the same in both methods. As mentioned, an LSDA determination of the O positions is expected to be more reliable in the present compound than the experimental result to date. This expectation is based on the calculated forces (if  $\text{SrRhO}_3$  behaves like other perovskite oxides, one may anticipate that LDA O coordinates would be accurate to  $0.1 \text{ \AA}$ , or better). On the other hand, it is likely that the experimental Sr positions are better than can be obtained in the LSDA. Accordingly, the O coordinates were relaxed using the LSDA forces, holding the Sr position and lattice parameters fixed at the experimental values. A similar approach was found useful for the structure of  $\text{PbZrO}_3$ , although in that case the structure was more complicated and a neutron refinement was known.<sup>19–21</sup> This point of view is supported *a posteriori* by the fact that, after relaxing the O positions in this way, an LSDA force of approximately  $0.007 \text{ Ry/bohr}$  remains on the Sr—below the LSDA reliability and also much smaller than the LSDA force on the Sr for the unrelaxed experimental structure. The resulting structure parameters are given in Table I, along with other information. Of particular note is the fact that the magnetic instability remains, with an equilibrium spin moment of approximately  $0.8\mu_B/\text{Rh}$ , although the magnetic energy is reduced to  $4 \text{ meV/Rh}$ . As a test, a calculation was done for the

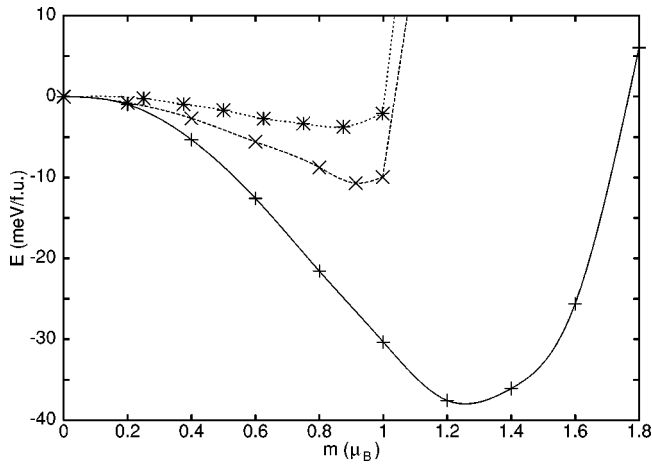


FIG. 3. LSDA fixed spin moment energy as a function of spin magnetization per formula unit for  $\text{SrRhO}_3$  using the ideal cubic perovskite structure (bottom curve), the experimental  $Pnma$  structure (middle curve), and the relaxed  $Pnma$  structure (top curve).

LSDA relaxed structure, including spin orbit in a second variational step, and keeping all other computational parameters the same. Although the equilibrium spin moment decreased by  $0.05\mu_B/\text{Rh}$  with the inclusion of spin orbit, the LSDA prediction of a ferromagnetic ground state remained.

The fixed spin moment energy as a function of the spin moment per formula unit is shown in Fig. 3 for the ideal cubic perovskite structure, and the experimental and LSDA relaxed  $Pnma$  structures. These calculations were done using the standard fixed spin moment technique in which the total energy and constraining field are calculated as a function of the constrained ferromagnetic moment.<sup>22</sup> The sharp increase in the energy at  $1\mu_B$  for the  $Pnma$  structures is due to the gap in the band structure above  $E_F$ . This yields a fixed spin moment energy versus magnetization that is reminiscent of  $\text{NaCo}_2\text{O}_4$ , where the energy also decreases with moment up to a gap and then increases strongly, and where the LSDA also predicts a ferromagnetic ground state, while experiment finds a strongly renormalized paramagnetic metal.<sup>23,24</sup>

Returning to the ruthenates, where, as mentioned, triplet superconductivity occurs,  $\text{Sr}_2\text{RuO}_4$  is a paramagnetic metal, whose basic ground-state properties are apparently well described by density-functional calculations,<sup>25–27</sup> although the strength of certain incommensurate antiferromagnetic fluctuations are possibly overestimated.<sup>28</sup> At the other end point of the Ruddlesden-Popper series,  $\text{SrRuO}_3$  is a robustly ferromagnetic metal<sup>9,29</sup> whose ground state is apparently also well described in density-functional calculations.<sup>14,18</sup> The intermediate bilayer compound  $\text{Sr}_3\text{Ru}_2\text{O}_7$  is a strongly enhanced paramagnetic metal,<sup>30</sup> which shows a metamagnetic quantum critical point under applied fields.<sup>31</sup> Density-functional calculations<sup>32,33</sup> incorrectly predict that this compound is ferromagnetic with a sizable moment of  $0.8\mu_B/\text{Ru}$  and substantial magnetoelastic coupling.<sup>33</sup> This overestimate of the moment in density-functional calculations is characteristic of a material subject to large quantum critical fluctuations, and is

found in other compounds known experimentally to be near quantum critical points.<sup>34,35</sup>

Density-functional theory is, in principle, an exact ground-state theory. It should, therefore, correctly describe the spin density of magnetic systems. However, common approximations to the exact density-functional theory, such as the local spin-density approximation (LSDA) and generalized gradient approximation (GGA), neglect Hubbard correlations beyond the mean-field level, with the well-known result that the magnetic tendency of strongly Hubbard correlated systems is often underestimated. Overestimates of magnetic tendencies, especially in the LSDA, are very much less common. Another type of correlation that is missed in these approximations is quantum spin fluctuations. This is because the LSDA and GGA are parametrized based on electron gases with densities typical for atoms and solids. However, the uniform electron gas is very far from magnetism in this density range. In solids near quantum critical points, the result is an overestimate of the magnetic moments and tendency toward magnetism (i.e., misplacement of the position of the critical point) due to neglect of the quantum critical fluctuations.<sup>36,37</sup> While a very large number of compounds displaying failures of the LSDA due to neglect of Hubbard correlations exists, only a very few cases showing LSDA failures due to neglect of quantum critical fluctuations are known.

To summarize, the present LSDA calculations show that  $\text{SrRhO}_3$  has a very soft ferromagnetic ground state. Assuming that the LSDA relaxed crystal structure is close to the true structure, as seems likely, the energy of the ground state is only 4-meV below the non-spin-polarized case. This longitudinally soft ferromagnetic state is a consequence of the lattice distortion from the ideal cubic structure. If  $\text{SrRhO}_3$  did occur in the ideal perovskite structure it would be a robustly ferromagnetic metal such as  $\text{SrRuO}_3$ . Furthermore, as may be seen from the low Fermi velocities and heavy bands, ferromagnetic fluctuations will strongly affect transport properties. This is very much like what was found for  $\text{Sr}_3\text{Ru}_2\text{O}_7$ , although in that material the LSDA magnetic energy was found to be larger on a per transition metal basis.<sup>33</sup> Thus non-Fermi-liquid behavior in transport properties should be observable in  $\text{SrRhO}_3$  in the range where quantum magnetic fluctuations are active. The question then is the size of that region. According to recent semiquantitative theories,<sup>36,37</sup> the key parameters are the softness of the LSDA ferromagnetic state against longitudinal fluctuations (characterized by the fixed spin moment curve) and the region of the Brillouin zone where the soft magnetic fluctuations can occur. Making this quantitative requires knowledge of an unknown cutoff, that roughly divides the soft quantum fluctuations, not included in the LSDA, from harder fluctuations that are included in the LSDA. However, it appears that  $\text{SrRhO}_3$  does satisfy the conditions for having significant quantum critical fluctuations, and comparing the LSDA ferromagnetic ground state with the experimental result, it would seem that these must be present. Considering the heaviness of the band structure, these should be observable in transport. As such it would be very interesting to make detailed measurements of



the transport and thermodynamic properties of SrRhO<sub>3</sub> under applied fields looking for metamagnetic behavior and non-Fermi-liquid scalings.

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