Mean-field behavior with Gaussian fluctuations at the ferromagnetic phase transition of SrRuO₃

D. Kim, B. L. Zink, and F. Hellman
Department of Physics, University of California, San Diego, La Jolla, California 92093
S. McCall, G. Cao, and J. E. Crow
National High Magnetic Field Laboratory, Tallahassee, Florida 32310

Specific heat, resistivity, and magnetization have been measured through the ferromagnetic critical point for single-crystal SrRuO₃. All data are well fitted to small reduced temperatures with mean-field critical exponents including Gaussian fluctuations. The specific heat and temperature derivative of resistivity scale with each other, confirming the Fisher-Langer relation. A long magnetic correlation length due to 4d-electron itinerancy is likely responsible for the mean-field behavior.

DOI: 10.1103/PhysRevB.67.100406 PACS number(s): 75.40.-s, 64.70.-p, 75.30.-m, 75.50.-y

Metallic oxides, including the ruthenates, show a wide variety of remarkable cooperative behavior attributed to narrow bands and correlated electron behavior. SrRuO₃ is a good example of this, with an extraordinarily high ferromagnetic ordering temperature T_c for a 4d metal, transport properties whose magnitude and strong temperature dependence suggest a breakdown of Fermi liquid theory (so-called "bad metal" behavior), enhanced low-temperature specific heat, and an anomalous vanishing of magnetism on substitution of isovalent Ca for Sr. 1-5 Despite the more extended nature of the 4d electrons, SrRuO₃ displays features similar to the high-T_c oxides and reflects anomalous behavior often associated with non-Fermi-liquid behavior. In contrast to many of the non-Fermi-liquid systems, however, SrRuO₃ is not near a quantum critical point. The anomalous transport behavior reported for SrRuO₃ may be related to strong local hybridization that drives the response at high temperatures but becomes less relevant at low temperatures where Fermi-liquid behavior is expected to be recovered.6

Magnetic properties show similar possibly related anomalies. Treated in a local moment picture, with crystal field splittings, the Ru⁴⁺ ions are expected to be in a low spin state S = 1, but there is considerable evidence that an itinerant band magnetism picture is a more appropriate description. High-temperature susceptibility measurements (T > T_c) give an effective moment p = 2.6μ_B per Ru ion, which agrees well with the local moment S = 1 per Ru⁴⁺ ion (2[S(S + 1)]°.5 = 2.83μ_B). 5,7,8 However, the low-temperature low-field magnetization p_s is 1.1μ_B, significantly lower than the 2μ_B expected from S = 1, and reaches only 1.6μ_B even at 30 K. 2,5,8 Neutron scattering confirms this low moment [m = 1.19±0.13 (statistical) ±0.15 (systematic)], and suggests that of order ½ of the moment is associated with the Ru site and ½ with the oxygen sites. 9 Band theory predicts 1.45–1.7μ_B due to splitting of t₂_g levels. 3,10,11 The ratio of p/p_s = 2.4 suggests an electronic state intermediate between the itinerant and localized limits. 12

Analysis of the paramagnetic/ferromagnetic phase transition might be expected to shed light on this issue of moment localization at T_c, but has been controversial. Critical analysis of magnetization exponents Β and γ by Klein and co-workers were interpreted as Ising-like, consistent with the anisotropy of thin-film SrRuO₃. Using Fisher-Langer theory to analyze their resistivity measurements, however, they found anomalous specific heat critical exponents α ≠ α', and suggested that this implies a breakdown of Fisher-Langer theory, evidence of the exotic nature of this material. 13,14 Their data were reanalyzed by Roussev and Millis as consistent with conventional theory, but the original authors rejected this reinterpretation. 15,16 There has been no report on the critical behavior of bulk samples, where T_c is 10–15 K higher, and the only direct specific heat measurements are on samples where inhomogeneity significantly broadened the transition. 3,17 In this paper, we report high-precision magnetization, resistivity, and specific heat measurements of single-crystal bulk SrRuO₃ through T_c.

Single-crystal samples of SrRuO₃ with a resistivity ratio R(300 K)/R(2.2 K) ≈ 100–140 were prepared by a flux growth technique at 1500 °C. After slow cooling to 1350 °C, the samples were rapidly quenched through the cubic to tetragonal transition to orthorhombic transitions [between 800 and 975 °C (Ref. 18)] to room temperature, a technique used in YBa₂Cu₃O₆±δ to avoid twinning. Single-crystal x-ray analysis of five SrRuO₃ crystals from the same batch used in these experiments showed them to be untwinned. Further details of sample preparation and characterization are described in Ref. 5. In the present work, the magnetization M of a single crystal sample (0.5×0.5×0.5 mm³, 883 μg) as a function of applied field H_a and temperature T was measured in a superconducting quantum interference device (SQUID) magnetometer. M was measured with H applied along the easy axis, found by rotating the sample around all three directions to find the maximum magnetization at 1 T at 160 K, just below T_c. The anisotropy at 160 K is small compared to that at 5 K, 5 as expected; at 1 T, the easy axis M = 7.9 × 10⁻³ emu, intermediate axis M = 7.8 × 10⁻³ emu, and hard axis M = 7.0 × 10⁻³ emu. The hard axis was along the sample c axis, as previously seen. The demagnetization factor D = 0.49 was determined from the slope of the low-field M vs H_a data, yielding the internal field H = H_a - 4πDM; but the value of D has little effect on the analysis discussed below. The resistivity was measured with a standard four-probe ac bridge technique and the specific heat was measured with a low mass calorimeter using the relaxation
Near a second-order ferromagnetic phase transition, the specific heat $C_p$, spontaneous magnetization [$M_s = M(H=0)$], and initial magnetic susceptibility ($\chi = \partial M/\partial H|_{H=0}$) show power-law dependence on the reduced temperature, $t = (T - T_c)/T_c$ with critical exponents $\alpha$, $\beta$, and $\gamma$, respectively, and at $T_c$ $M(H) \propto H^{1/\delta}$.

$M(H)$ is shown in Fig. 1 as an $M$ vs $H/M$ Arrott plot for $T$ near $T_c$. The isothermal curves are very linear, suggesting mean-field behavior with $\beta = 0.5$ and $\gamma = 1$. To further refine these values, as discussed extensively in Refs. 8 and 19, we use an iterative modified Arrott plot scheme to obtain $T_c = 162.26$ K, $\beta = 0.50 \pm 0.03$ (from log $M_s$ vs log $t$) and $\gamma = 0.99 \pm 0.03$ (from log $1/\chi$ vs log$|t|$), as shown in the insets of Fig. 1. To obtain $\delta$, we plot $M$ vs $H$ for the two closest measured isotherms 162.2 and 162.4 K in Fig. 2; the inverse slope of log $M$ vs log $H$ (shown in the inset) gives $\delta = 3.21$ and 2.85, respectively. $\delta = 3.10 \pm 0.3$ was approximated by interpolation; this value is within error bars of the mean field value of $3$.

The specific heat $C_p$ of a $(0.1 \times 0.6 \times 0.6$ mm$^3$, 210 $\mu$g) bulk single-crystal sample of SrRuO$_3$ is shown in Fig. 3. The data were taken by a relaxation method, using sensitive SiN membrane-based microcalorimeters, as described in Ref. 19, and agree well with data shown in Refs. 3 and 17. The transition is, however, significantly sharper and clearly shows signs of fluctuations (upward curvature). The data were fitted in two ways: critical fluctuation analysis using a smooth background with a grid search method to minimize $\chi^2$, and a mean-field model with Gaussian fluctuations. The former method (described in Ref. 19) gave a good fit to the data, as shown in Fig. 4, with $\alpha = \alpha' = 0.084 \pm 0.04$ and amplitude ratio $A/A' = 0.63 \pm 0.2$, within error bars of Ising values $\alpha = \alpha' = 0.1$ and $A/A' = 0.524$, to low reduced temperatures (0.0002 above $T_c$ and 0.001 below $T_c$). Ising critical behavior is, however, inconsistent with the mean-field values found for the three magnetization exponents. We suggest instead that critical fluctuations should not be observed until extremely small reduced temperatures ($<10^{-4}$) are reached because of the itinerant nature of the magnetism and consequently long correlation length. We therefore fit the data to mean-field behavior, including the effect of three-
dimensional (3D) Gaussian fluctuations.\textsuperscript{20} Gaussian fluctuations are associated with the variance in $M = \langle \Delta M^2 \rangle = \langle M^2 \rangle - \langle M \rangle^2$; these occur on a short length scale and do not change the mean value $\langle M \rangle$. They have therefore no significant effect on magnetization, but give a contribution to $C_p$ with the same form as that for critical fluctuations but with a universal exponent $\alpha = \alpha' = 0.5$.

Following the procedure outlined by Inderhees et al. for analysis of $\text{YBa}_2\text{Cu}_3\text{O}_7$, we fit $C_p(t) = (A_\chi/\alpha)|t|^{-\alpha} + C_{\text{MF}} + C_{\text{poly}}$ with $\alpha = 0.5$, + corresponds to $t > 0$, - corresponds to $t < 0$, and $C_{\text{poly}}$ is a polynomial fit to the background (taken from data far from the transition). The mean-field contribution $C_{\text{MF}} = -\frac{1}{2}Nk_B T_c \partial M^2/\partial T$, where $N$ is the number of magnetic electrons per mole of SrRuO$_3$ (a parameter fit by the $C_p$ data) and $M(t) = M(T)/M(0)$ is obtained by numerically solving the mean-field magnetization equation for $S = 1$.\textsuperscript{22} This yields $C_{\text{MF}}$ in units of $T/T_{\text{MF}}$, where $T_{\text{MF}} = T_c \exp(|t|^{1/\alpha})$. $T_c$ is removed because fluctuations suppress $T_c$ from its calculated mean-field value. Again following Ref. 21, $T_{\text{MF}} = 169.92$ K, higher than the real $T_c = 161.79$ K, is chosen such that the magnetic entropy $Nk_B \ln(3)$ is conserved (i.e., fluctuations suppress the entropy, conserve entropy). $C_{\text{MF}}$ below the real $T_c$ is then fitted with a fifth-order polynomial. Figure 3 shows the resulting $C_{\text{MF}}$ and $C_{\text{poly}}$.\textsuperscript{23} After subtracting $C_{\text{MF}}$ and $C_{\text{poly}}$, $C_p$ is fitted to Gaussian fluctuations with critical exponent $\alpha = 0.5$, giving $N = 0.6$ mol and $A/\alpha' = 0.68$. Data points very close to $T_c$ were removed from the fit due to presumed rounding. $N = 0.6$ per mole is less than 1, the expected number of $S = 1$ Ru ions per molecular unit if all effects of Ru ions are localized, but is consistent with the reduced low-temperature low-field magnetization $\rho = 1.1 \mu_B$, i.e., 0.6 per mole of $S = 1$ Ru ions = $0.6 \times 2 \mu_B = 1.2 \mu_B$. The amplitude ratio $A/\alpha' = n/2^{0.7}$ in a Gaussian fluctuation model where $n$ is the number of spin components and $d$ is the dimensionality.\textsuperscript{20} Our value of $A/\alpha' = 0.68$ is close to 0.71, the $n = 2$ value (fluctuations of $XY$-type spins), consistent with the anisotropy of bulk SrRuO$_3$ which is 5–10 T with easy axes in the (001) plane.\textsuperscript{5,24}

In order to understand the significant differences between our analysis of $C_p$ and that reported by Klein et al.,\textsuperscript{13} we also made high-precision resistivity measurements $\rho(T)$ on a bulk sample taken from the same processing batch. Fisher and Langer\textsuperscript{25} showed that short-range spin fluctuations near $T_c$ increase the carrier scattering rate and cause $d\rho/dT$ to scale with the same critical exponent $\alpha$ as the specific heat: $d\rho/dT \sim |t|^{-\alpha}$. Figure 5 shows the comparison among the directly measured $C_p$ with the polynomial background shown in Fig. 3 subtracted [i.e., $C_p(T) - C_{\text{poly}}$], $d\rho/dT$ on the bulk sample, and $d\rho/dT$ for the thin film sample digitized from the data shown in Ref. 13. The raw $C_p$ and $\rho$ data for the bulk samples showed a 0.26-K difference in $T_c$, likely associated with the different thermometers used in the two separate experimental apparatuses of these measurements (commercial thermometers do not have absolute calibrations better than 1%; this 1% absolute difference, however, should have no impact on the analysis, which requires accurate relative temperatures only). A temperature shift for $d\rho/dT$ of $-0.26$ K was made in Fig. 5 to account for this difference. The overlap between $C_S$ and $d\rho/dT$, as shown in Fig. 5 for the bulk samples, is a strong confirmation of the Fisher-Langer relation and the existence of fluctuations near $T_c$ to the best of our knowledge, this confirmation has not been previously seen in magnetic materials for which Gaussian fluctuations dominate (as opposed to materials such as Fe, Ni, or Cr where critical fluctuations dominate). The inset of Fig. 5 shows $d\rho/dT$ vs $T_c$ and demonstrates a remarkable proportionality. Figure 5 also shows the thin-film $d\rho/dT$ data from Ref. 13; data were shifted by $+9.1$ K, to account for the lower $T_c$ (150 K) of the films. This data show a peak at $T_c$, which is significantly broader than the bulk sample data, but matches well away from $T_c$. From these data, it appears that the analysis made in Ref. 13 is outside the critical regime, and may be negatively impacted by sample inhomogeneity or strains in the thin films grown on SrRuO$_3$.

The data shown in Figs. 1–5 thus present an extremely consistent picture of a transition dominated by mean-field behavior down to remarkably small reduced temperatures for a magnetic phase transition. Saturation magnetization $M_s$ and inverse susceptibility $1/\chi$ are well fitted with mean-field parameters $\beta = 0.5$ and $\gamma = 1$ over a wide temperature range. This result is quite different than that of the thin film found in Ref. 14, in which an Ising fluctuation model was suggested, but the present data are taken to significantly smaller reduced temperatures ($t = 0.002$ vs 0.01), and on samples of higher homogeneity (judging from the breadth of $T_c$ shown by the specific heat peak of Fig. 4 and the extremely large resistivity ratio of the single-crystal samples used in this study). The $M(H)$ exponent $\delta = 3$ is also consistent with mean-field behavior. The specific heat is shown to scale with $d\rho/dT$, indicative of fluctuation effects; these can be fitted within a mean-field model including the effects of Gaussian fluctuations. As discussed in Ref. 26, critical exponents associated with the average value of $M$, i.e., $\beta$, $\gamma$, and $\delta$, are not affected by Gaussian fluctuations, but $C_p$ and $d\rho/dT$ are affected not only by $\langle M \rangle$ but also by $\langle \Delta M^2 \rangle$.\textsuperscript{26}
Specific heat was here fitted with a mean-field local moment \( S = 1 \) model, plus Gaussian fluctuations. As discussed in the introduction, the magnetic properties of SrRuO\(_3\) show behavior between that of a local moment and itinerant model. It could, therefore, be of interest to determine \( C_p \) in a mean-field itinerant electron model, including effects of band structure. This was not attempted in the present work, and is not likely to significantly affect the critical analysis near \( T_c \) except to change the mean-field parameters \( N, \Delta C, \) and \( T_{MF} \). This statement is based on fits to \( C_p(T) \) with an \( S = \frac{1}{2} \) local moment mean-field model; because of the linearity of \( C_p \) near \( T_c \) in mean-field models, only the overall scaling factor \( N \) significantly changed.

Gaussian fluctuation analysis is valid in the same temperature range as mean-field theory and hence has the same Ginzburg criterion for validity: 

\[
t_G > (\frac{1}{2\pi^3})(k_B/\Delta C \xi_0^3)^2,\]

where \( \Delta C \) is the specific heat discontinuity and \( \xi_0 \) is the zero-temperature correlation length. True critical fluctuations are only significant for \( t < t_G \). Taking \( \Delta C = 9.4 \text{ J/mol K} \) from \( C_{MF} \) and using the smallest \( t = 0.0003 \) in our experiment yield a lower boundary for \( \xi_0 \) of 7 Å.

In conclusion, we have performed magnetization, resistivity, and specific heat measurements on single-crystal SrRuO\(_3\) to study the critical behavior of the ferromagnetic phase transition at \( T_c \sim 160 \text{ K} \). An Arrott plot method was used to obtain magnetization critical exponents \( \beta = 0.50 \pm 0.03, \gamma = 0.99 \pm 0.03, \) and \( \delta = 3.1 \pm 0.3 \), all within error bars of mean-field values down to reduced temperatures of 0.0003. The specific heat and the temperature derivative of the resistivity were shown to scale with each other and were well fitted using either critical fluctuation or mean-field including Gaussian fluctuations methods, but only the latter is consistent with the other mean-field critical exponents. The observation of mean-field behavior to 0.0003 yields a lower boundary of the correlation length \( \xi_0 > 7 \text{ Å} \). We argue that the itinerancy of the Ru electrons causes the long correlation length, which in turn causes mean-field behavior to persist to strikingly small reduced temperatures compared with the conventional 3d ferromagnetic metals, further evidence of the unique nature of this 4d ferromagnet.

D.K., B.L.Z., and F.H. thank the NSF for support (DMR 97-05300 and 02-00000); S.M., G.C., and J.E.C. acknowledge partial support from the National High Magnetic Field Laboratory through NSF Cooperative Agreement DMR-0084173 and support provided by the state of Florida.