Studies on the weak itinerant ferromagnet SrRuO$_3$ under high pressure to 34 GPa

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Abstract

The dependence of the Curie temperature $T_{\text{Curie}}$ on nearly hydrostatic pressure has been determined to 17.2 GPa for the weak itinerant ferromagnetic SrRuO$_3$ in both polycrystalline and single-crystalline form. $T_{\text{Curie}}$ is found to decrease under pressure from 162 K to 42.7 K at 17.2 GPa in nearly linear fashion at the rate $dT_{\text{Curie}}/dP \simeq -6.8$ K/GPa. No superconductivity was found above 4 K in the pressure range 17 to 34 GPa. Room-temperature X-ray diffraction studies to 25.2 GPa reveal no structural phase transition but indicate that the average Ru-O-Ru bond angle $\beta$ passes through a minimum near 15 GPa. The bulk modulus and its pressure derivative were determined to be $B_0 = 192(3)$ GPa and $B'_0 = 5.0(3)$, respectively. Parallel ac susceptibility studies on polycrystalline CaRuO$_3$ at 6 and 8 GPa pressure found no evidence for either ferromagnetism or superconductivity above 4 K.
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1 Introduction

In all 4d elemental metals, including Ru, the degree of overlap between neighboring 4d orbitals is far too great to permit the formation of either local-moment or itinerant magnetism \[1\]. One can estimate, however, that if one were to increase the interatomic separations in Ru metal by 45% or more, the degree of 4d-orbital overlap would decrease sufficiently for Ru metal to exhibit itinerant magnetism \[1, 2\]. We note that in the itinerant ferromagnet SrRuO\(_3\), the only known ferromagnetic metal among the 4d oxides \[3\], the nearest-neighbor separation between Ru ions (\(\sim 3.92\ \text{Å}\)) is 48% greater than that in Ru metal (2.65 Å). The oxygen anions in SrRuO\(_3\) also play an important role in its magnetism, the Ru-O direct exchange interaction being estimated to be strongly ferromagnetic \[3\]. Ferromagnetism would appear to be less likely in CaRuO\(_3\) than in SrRuO\(_3\) since in the former oxide the Ru-Ru nearest-neighbor separation is less and the degree of structural disorder is greater; indeed, CaRuO\(_3\) exhibits no magnetic order but is paramagnetic with a negative Curie-Weiss temperature \(\Theta \approx -68\ \text{K}\) indicative of antiferromagnetic correlations \[4\]. Both theoretical and experimental studies have underscored the important role structural disorder plays in suppressing the magnetic ordering temperature in these ruthenates \[3, 4, 5\] and other atomically arranged perovskites \[6\].

Weak itinerant ferromagnets such as ZrZn\(_2\) \[7\], UGe\(_2\) \[8\], MnSi \[9\], and SrRuO\(_3\) \[10\] have enjoyed considerable interest for many years because of the possibility of unconventional superconductivity, non Fermi liquid behavior, and other exotic phenomena near quantum critical points. Relatively minor perturbations, such as those generated by high pressures, are able to transport the system from one ground state to another, including the destruction of the ferromagnetic state. That the magnetism is weakened under pressure follows from the above discussion since the degree of overlap between the magnetic orbitals increases under pressure. Wohlfarth \[11\] derived an expression valid for weak itinerant ferromagnets whereby the rate of decrease of the Curie temperature with pressure, \(dT_{\text{Curie}}/dP\), is inversely proportional to the value of \(T_{\text{Curie}}\) itself. It is notable that the weak itinerant ferromagnet Sc\(_3\)In does not fit into this scheme since its Curie temperature initially increases under pressure \[12\].

Several years ago Belitz et al. \[13\] argued on general grounds that in a weakly ferromagnetic system the nature of the ferromagnetic transition would be expected to change from second to first order at a tricritical point, i.e. under an external perturbation such as pressure, the order parameter (magnetization) and Curie temperature should disappear discontinuously above a critical pressure \(P_c\). Metamagnetic transitions are anticipated out of the paramagnetic state for pressures above \(P_c\) if strong magnetic fields are applied. Such first-order transitions under pressure with accompanying field-induced metamagnetism have been found in the weak itinerant ferromagnets ZrZn\(_2\) \[7\] and UGe\(_2\) \[8\]; in the latter compound the weak ferromagnetism even coexists with superconductivity. It is clearly of interest to investigate further systems in order to establish whether the behavior found for ZrZn\(_2\) and UGe\(_2\)
is only an anomaly or representative for weak itinerant ferromagnets in general.

More than a decade ago we carried out ac susceptibility ($\chi_{ac}$) studies in a diamond-anvil cell (DAC) on polycrystalline SrRuO$_3$ to nearly hydrostatic (dense helium) pressures as high as 6 GPa [10]. The Curie temperature was found to decrease approximately linearly from 161 K to 130 K at the rate $dT_{Curie}/dP \simeq -5.7$ K/GPa, a value somewhat less in magnitude than that (-7.5 K/GPa) from ac susceptibility studies to 0.78 GPa by Shikano et al. [14]. In two further experiments Le Marrec et al. [15] and Demuer et al. [16] carried out electrical resistivity measurements on SrRuO$_3$ thin films epitaxially grown on a BaTiO$_3$ substrate under high quasihydrostatic pressure (solid steatite pressure medium) to 23 and 21 GPa, respectively. In both experiments $T_{Curie}$ was observed to decrease from 150 K at ambient pressure to approximately 75 K at 13 GPa, yielding a negative pressure derivative $dT_{Curie}/dP \simeq -5.9$ K/GPa close to our value for bulk SrRuO$_3$ above; however, for $T_{Curie}(P)$ was reported to pass through a minimum near 15 GPa, increasing at higher pressures only slightly in the former experiment [15] but strongly in the latter [16]. This abrupt change in slope $dT_{Curie}/dP$ near 15 GPa may signal a structural phase transition. However, the fact that the $T_{Curie}(P)$ dependences differ in the two thin-film experiments suggests that shear stresses might play an important role; such shear stresses could arise either from the solid steatite pressure medium or from the increasing lattice mismatch between thin-film sample and substrate under pressure. X-ray diffraction and magnetic susceptibility studies on bulk SrRuO$_3$ samples to very high nearly hydrostatic pressures would clearly be of value to help clarify these issues and establish the intrinsic pressure dependence $T_{Curie}(P)$.

In the present paper we extend the pressure range of our previous ac susceptibility measurements and include high-pressure structural studies as well. Over the pressure range to 17.2 GPa $T_{Curie}$ is found to decrease nearly linearly with nearly hydrostatic pressure at the rate -6.8 K/GPa with no indication of a slope change near 15 GPa. Furthermore, ambient-temperature X-ray diffraction studies to 25.3 GPa reveal that SrRuO$_3$ remains in the orthorhombic structure over the entire pressure range. Interestingly, the pressure dependences of the lattice parameters are quite complex but allow the estimate that the average Ru-O-Ru bond angle $\beta$ initially decreases under pressure but passes through a minimum near 15 GPa. A possible correlation between the pressure dependence of the Curie temperature $T_{Curie}$ and the bond angle $\beta$ is discussed. The present results make it imperative that the magnetic and superconducting properties of this interesting system be extended to even higher pressures and lower temperatures.

2 Experiment

The polycrystalline sample of SrRuO$_3$ used in the present experiments was prepared by solid state reaction of stoichiometric quantities of high purity (99.9% or better) SrCO$_3$ and RuO$_2$. The starting materials were weighed, mixed and placed in an
Al$_2$O$_3$ crucible. The specimen was reacted for 4 hours at 1100°C, ground with an agate mortar and pestle for 5 min and reacted in air for 6 h at 1250°C. Subsequently, the specimen was reground for 5 min and reacted at 1250°C for 14 h and cooled by shutting the furnace off. Powder X-ray diffraction proved the specimen to be single-phase with no observable secondary phases.

Single-crystals of SrRuO$_3$ were grown in Pt crucibles from off-stoichiometric quantities of RuO$_2$, SrCO$_3$, and SrCl$_2$ mixtures with SrCl$_2$ self flux. The mixtures were first heated to 1500°C, soaked for 25 hours, slowly cooled at 2-3°C/hour to 1350°C, and finally cooled to room temperature at 100°C/hour. The single crystals were characterized by single crystal X-ray diffraction and by scanning and transmission electron microscopies. All results indicate that the single crystals are of high quality.

High pressure X-ray diffraction experiments were performed in a DAC on polycrystalline SrRuO$_3$ using synchrotron X-rays ($\lambda = 0.41105$ Å) with beam size $20 \times 20$ μm$^2$ at the Advanced Photon Source HPCAT, Sector 16-IDB, Argonne National Labs. The powder sample was loaded together with a ruby chip and silicon fluid as pressure medium into a 135 μm diameter bore through a rhenium gasket [17]. The X-ray diffraction patterns (see Fig. 1) were collected using a MAR image plate camera with $100 \times 100$ μm$^2$ pixel dimension for 10-20 s. The images were integrated using FIT2D program [18] and structural refinements were carried out using JADE [19].

High-pressure ac magnetic susceptibility measurements $\chi_{ac}(T)$ were carried out using a DAC made of CuBe alloy [1] where two 1/6-carat type Ia diamond anvils with 0.5 mm diameter culets press onto a 3 mm diameter gold-plated rhenium gasket preindented from 250 μm to 80 μm thickness and containing a centered 235 μm diameter hole. After the sample (typical dimensions $80 \times 80 \times 30$ μm$^3$) and tiny ruby spheres [20] are placed in the hole, the DAC is assembled, cooled down to low temperatures and flooded with liquid helium pumped to 2 K. The opposing diamond anvils are then pressed into the gasket to trap and build up pressure in the liquid helium pressure medium surrounding the sample. As in the above X-ray studies, the standard ruby calibration [21] is used to determine the pressure to within ±0.2 GPa. The temperature was kept below 180 K during the entire experiment to reduce the chance that helium might enter the diamond anvils, possibly causing them to fail.

The ferromagnetic transition at $T_{Curie}$ is determined inductively using two balanced primary/secondary coil systems located immediately outside the metal gasket [22] and connected to a Stanford Research SR830 digital lock-in amplifier. The ac susceptibility studies were carried out using a 3 Oe r.m.s. magnetic field at 1023 Hz. Further experimental details of the diamond-anvil cell and ac susceptibility techniques are published elsewhere [1, 23].

The lock-in amplifier allows the measurement of not only the basic 1st harmonic of the ac susceptibility, $\chi_1$, but also the higher harmonics. Since in this experiment the signal from the ferromagnetic transition of SrRuO$_3$ in $\chi_1$ becomes very difficult to resolve for pressures above 10 GPa, we decided to also measure the 3rd harmonic $\chi_3$ which has a superior signal/noise ratio at the highest pressures. In contrast to
χ1(T), where the transition is only revealed after the subtraction of a relatively large temperature-dependent background, the background signal in χ3(T) has little temperature dependence. In Fig. 2 we compare at ambient pressure the real part of the 1st harmonic χ′1(T) to the imaginary part of the 3rd harmonic χ′′3(T) for a single-crystalline sample much larger (150 × 250 × 65 µm3) than that used in a typical high-pressure experiment in the DAC. It is seen that the temperature of the peak in χ′1(T), which we use to define the Curie temperature TCurie, corresponds well with the transition onset in χ′′3(T). As we will see, measuring the 3rd harmonic allows us to follow the ferromagnetic transition in SrRuO3 to higher pressures.

3 Results of Experiment

3.1 X-ray Diffraction Studies

At ambient pressure SrRuO3 is found to crystallize in the orthorhombic structure (Pbnm, 62) with lattice parameters a = 5.5754(7) Å, b = 5.5405(6) Å, c = 7.8546(8) Å, in good agreement with literature values [4, 24]. Fig. 1 shows the X-ray diffraction patterns at various pressures to 25.3 GPa. As pressure is increased, no new peaks are found indicating the sample retains the orthorhombic crystal structure. However, the peaks broaden due to increasing nonhydrostatic conditions in the solidified silicone pressure medium. The pressure dependences of the lattice parameters are given in Table I and are shown in Fig. 3 (upper). The smooth monotonic change in all lattice parameters under pressure to 25.3 GPa is consistent with the absence of even an isostructural phase transition over this pressure range. However, it is seen that there is a crossover of the b and c/√2 parameters near 15 GPa; this will be discussed in detail below.

The equation of state for SrRuO3 is shown in Fig. 3 (lower) with the least-squares fit (solid line) obtained using the Birch-Murnaghan expression [25]

\[ P = \frac{3}{2} B_0 \left[ (V/V_0)^{-7/3} - (V/V_0)^{-5/3} \right] \times \left\{ 1 + \frac{3}{4} \left( B'_0 - 4 \right) \left[ (V/V_0)^{-2/3} - 1 \right] \right\}, \]

where \( B_0 = 192(3) \) GPa is the bulk modulus and \( B'_0 = 5.0(3) \) its pressure derivative. These values are similar to those found in Ca-based perovskites with Pbnm symmetry and similar ambient pressure volumes [26, 27, 28].

Again, we find no evidence for a structural phase transition near \( P \approx 15 \) GPa where abrupt changes in dTCurie/dP were seen for two different thin-film SrRuO3 samples [15, 16]. However, this pressure lies near that for the lattice parameter crossover seen in Fig. 3 (upper). As it is known that TCurie is reduced [4, 14, 24] as one moves farther away from cubic symmetry by substituting Ca for Sr, it is instructive to ask whether pressure might have a similar effect. Following the work of others [29, 30], if one assumes that the RuO6 coordination octahedra are not distorted
only rotate when pressure is applied (a reasonable assumption for the small rotations occurring in SrRuO$_3$), the angles of rotation around the characteristic directions of the ideal cubic perovskite structure can be calculated by simply using the orthorhombic lattice parameters. The validity of using this model in a semi-quantitative manner for determining the tilt angles has been shown by the good agreement between the angles estimated from the lattice parameters and directly from the atomic positions [31]. The Ru-O-Ru bond angles can be found simply from the angle of rotation $\Phi$ around the (111)$_p$ direction of the ideal cubic perovskite structure given by

$$\Phi = \cos^{-1}\left(\frac{\sqrt{2}b^2}{ac}\right).$$

(2)

The Ru-O-Ru bond angles $\beta_1$ and $\beta_2$ are then given by

$$\beta_1 = \cos^{-1}\left(\frac{2 - 5\cos^2\Phi}{2 + \cos^2\Phi}\right) \quad \text{and} \quad \beta_2 = \cos^{-1}\left(\frac{1 - 4\cos^2\Phi}{3}\right).$$

(3)

While the absolute values of the angles may not be in exact agreement, the relative change of the angles obtained using these formula agrees well with high resolution diffraction data. In fact, as one goes from SrRuO$_3$ to CaRuO$_3$, direct calculation of the average Ru-O-Ru bond angle $\beta$ decreases by $14.1^\circ$ [24], while the estimate from the lattice parameters is $15.4^\circ$. The inset in the bottom panel of Fig. 3 shows the pressure dependence of the average Ru-O-Ru bond angle calculated from the lattice parameters. Up to approximately 15 GPa we find that the value of the angle $\beta$ decreases in a nearly linear fashion ($d\beta/dP \approx -0.86$ deg/GPa) signifying that the perovskite structure is becoming more distorted. However, for pressures above 15 GPa the angle $\beta$ is seen to increase! We explore the significance of this finding below.

We have also found that these structural results are reproduced when Ar or a 4:1 methanol:ethanol mixture is used as the pressure transmitting media instead of silicon oil. This leads us to the conclusion that the results of our structural studies on bulk samples are not unduly sensitive to the pressure transmitting fluid used. This along with detailed structural information will be presented in a future report [32].

### 3.2 ac Susceptibility Studies

The first of the present experiments (run B) was carried out on a polycrystalline SrRuO$_3$ sample (dimensions $110 \times 130 \times 30 \ \mu m^3$) in a DAC under nearly hydrostatic pressures to 14.7 GPa. In Fig. 4 the results are compared to those from our earlier measurements to 6 GPa (run A) [10]; the agreement is reasonable, although the final two data points in the earlier study lie somewhat above the straight-line fit. From 0 to 14.7 GPa the height of the transition in the ac susceptibility decreased from
approximately 5 to 1.5 nV. One should not conclude from this that the value of the magnetic moment per ion necessarily decreases since the ac susceptibility measures only the initial response of the sample magnetization to an imposed magnetic field and thus also depends on extrinsic parameters such as the degree of domain wall pinning. A pressure-dependent reduction in the applied field by shielding currents in the Re gasket may also contribute to the signal reduction. The failure of the diamond anvils ended the experiment in run B.

Run B was followed by run C on a polycrystalline sample (dimensions $68 \times 90 \times 25 \mu m^3$) to 9 GPa; as seen in Fig. 4, the results are in good agreement with those from run B. From 0 to 9 GPa the height of the transition decreased from 2.5 to 0.6 nV. At the next higher pressure (15 GPa) the transition had decreased sufficiently in size that it was not possible to unequivocally identify it.

The next high-pressure DAC experiment (run D) was carried out on a single-crystalline SrRuO$_3$ sample (dimensions $65 \times 90 \times 30 \mu m^3$) where both $\chi'_1(T)$ and $\chi''_3(T)$ were measured in an effort to track the ferromagnetic transition to higher pressures (Fig. 5). The transition height in $\chi'_1(T)$ is seen to decrease roughly by a factor of two from 0 to 9.9 GPa, but the transition also becomes broader, perhaps due to nonhydrostatic stresses even in the helium pressure medium; the area under the transition curve decreases by only $\sim 20\%$ over the pressure range to 9.9 GPa. At higher pressures the transition could not be identified in the 1st harmonic, so $\chi''_3(T)$ was measured (see the lower half of Fig. 5). Even though the transition in $\chi''_3(T)$ is relatively small, the absence of a strong temperature-dependent background signal allows one to track $T_{Curie}(P)$ to higher pressures. The dependence of $T_{Curie}$ on pressure is seen in Fig. 4 to be reversible and approximately linear to 17.2 GPa with slope $dT_{Curie}/dP \simeq -6.8$ K/GPa, $T_{Curie}$ decreasing from 162 K to 42.7 K, i.e. by nearly a factor of four. Unfortunately, at higher pressures (20.4 to 34 GPa) the ferromagnetic transition could no longer be resolved.

### 4 Conclusions

As mentioned in the Introduction, in a canonical weak itinerant ferromagnet the Curie temperature and saturation magnetization would be expected to decrease monotonically under pressure, falling to zero at a critical pressure $P_c$ [11]. That SrRuO$_3$ may exhibit more complex behavior is indicated by the fact that in thin-film studies [15, 16] the Curie temperature passes through a minimum near 15 GPa (Fig. 4), approximately the same pressure where we find the average Ru-O-Ru bond angle $\beta$ in a crystalline sample to pass through a minimum (Fig. 3). Indeed, in Sr$_{1-x}$Ca$_x$RuO$_3$ and related systems the value of $T_{Curie}$ appears to be inversely related to the degree of distortions away from the ideal cubic perovskite structure, i.e. the greater the distortions, the lesser the average bond angle $\beta$ and the lower the value of $T_{Curie}$ [3, 4, 5]. We can estimate the dependence of $T_{Curie}$ on $\beta$ by considering that upon increasing $x$ in Sr$_{1-x}$Ca$_x$RuO$_3$ from 0 to 1 the value of $T_{Curie}$ decreases from 162 K
to 0 K whereas the bond angle $\beta$ decreases by 15.4° [4], yielding $dT_{\text{Curie}}/d\beta \approx +10.5$ K/deg. We note that this value of $dT_{\text{Curie}}/d\beta$ is quite close to that derived from the values of $dT_{\text{Curie}}/dP$ and $d\beta/dP$ in the present high-pressure experiments from 0 to 15 GPa where $dT_{\text{Curie}}/d\beta = (dT_{\text{Curie}}/dP)/(d\beta/dP) \approx (-6.8 \text{ K/GPa})/(-0.86 \text{ deg/GPa}) = +7.9$ K/deg. The present experiments on the single-crystalline SrRuO$_3$ sample thus support the contention that $T_{\text{Curie}}$ is correlated with the degree of structural distortion as represented by the bond angle $\beta$, at least in the pressure range 0 - 15 GPa.

For pressures at 15 GPa and above, $\beta$ passes through a minimum and then increases quite rapidly, as seen in Fig. 3. The above correlation between $T_{\text{Curie}}$ and $\beta$ for bulk SrRuO$_3$ would then lead to the expectation that $T_{\text{Curie}}(P)$ should also pass through a minimum near 15 GPa and increase at higher pressures. Unfortunately, this possibility cannot be adequately checked in the present experiment since the anticipated minimum in $T_{\text{Curie}}(P)$ at 15 GPa lies close to the maximum pressure (17.2 GPa) for which the ferromagnetic transition can be resolved.

It is not unreasonable to assume that $T_{\text{Curie}}(P)$ may pass through a minimum at lower pressures in thin-film relative to bulk samples since the former are already in a strained state at ambient pressure which is consistent with their lower ambient pressure value of $T_{\text{Curie}}$. In the thin-film studies shear stresses may originate either from the solid pressure medium or from the increasing lattice mismatch between the thin-film SrRuO$_3$ sample and its CaTiO$_3$ substrate; the latter effect is expected since the bulk moduli $B_o$ of SrRuO$_3$ (192(3) GPa) and CaTiO$_3$ (176 GPa from Ref. [33]) differ by 9%. The fact that for both thin film samples a break in slope in $T_{\text{Curie}}(P)$ is observed near 15 GPa with quite different behavior at higher pressures can easily be explained by differing strain states in the two thin film samples. This would lead to different values of the Ru-O-Ru angles, and hence different $T_{\text{Curie}}$ values, as a function of pressure.

A search for superconductivity in single-crystalline SrRuO$_3$ with negative results was carried out by measuring $\chi'_1(T)$ or $\chi'_3(T)$ to temperatures as low as 4 K at the following pressures: 17.2, 20.4, 21.3, 22.5, 23.8, 25.8, and 34 GPa. Similar ac susceptibility studies on polycrystalline CaRuO$_3$ at 6 and 8 GPa found no evidence for either ferromagnetism or superconductivity above 4 K.

In summary, parallel ac susceptibility and X-ray diffraction studies have been carried out on poly- and single-crystalline samples of SrRuO$_3$ to 34 and 25.3 GPa, respectively. The structural studies yield the unexpected result that the lattice distortions increase with pressure to a maximum value near 15 GPa but then decrease (the bond angle $\beta$ passes through a minimum near 15 GPa). $T_{\text{Curie}}(P)$ is found to decrease nearly linearly to 17.2 GPa nearly hydrostatic pressure. Evidence is given for a possible correlation between $T_{\text{Curie}}(P)$ and $\beta(P)$ in the present experiments which would appear to imply that $T_{\text{Curie}}(P)$ should also pass through a minimum near 15 GPa, contrary to the expectations for a canonical weak itinerant ferromagnet where $T_{\text{Curie}}$ would fall monotonically to 0 K under pressure. Future experiments on bulk
SrRuO$_3$ to even higher pressures and lower temperatures are imperative to clarify the magnetic and superconducting properties of this interesting system.

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[2] In elemental solids the degree of overlap between neighboring partially filled orbitals determines whether or not the solid is magnetic. We define $\alpha \equiv r_a/r_m$, where $r_m$ is the radius of maximum charge density for the magnetic orbital and $r_a = V^{1/3}/a/2$ is half the average interatomic separation, $V$ being the available volume per atom. $\alpha$ is thus inversely related to the degree of orbital overlap. It has been shown that for $\alpha > \alpha_c = 3.2$ the degree of overlap is sufficiently small that the system is magnetic, but nonmagnetic for $\alpha < \alpha_c = 3.2$. Indeed, it is found that magnetism prevails in elemental solids from all rare-earth elements ($4f$), as well as from the heavy $3d$ transition-metal elements and heavy actinides ($5f$) where in all cases $\alpha > 3.2$. On the other hand, for all the $4d$ and $5d$ transition-metal elements $\alpha \approx 1.9$ to $2.4$ which is less than $\alpha_c = 3.2$. This critical value exceeds that for Ru metal ($\alpha \approx 2.2$) by 45%, so that the lack of magnetic behavior in Ru metal comes as no surprise.

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Table 1: High pressure structural parameters for SrRuO$_3$. The lattice parameters are for the orthorhombic Pbnm (#62) structure. The values in parentheses represent the estimated uncertainty in pressure and the error in least significant digits from the standard errors in unit cell refinements.

| $P$ (GPa) | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å) |
|-----------|---------|---------|---------|---------|
| 0         | 5.5754(7) | 5.5405(6) | 7.8546(8) | 242.62(5) |
| 0.6(2)    | 5.561(1)  | 5.530(2)  | 7.851(2)  | 241.43(11) |
| 2.8(2)    | 5.549(1)  | 5.505(1)  | 7.825(2)  | 239.05(9)  |
| 3.3(2)    | 5.550(1)  | 5.503(1)  | 7.808(2)  | 238.46(9)  |
| 5.2(2)    | 5.531(1)  | 5.480(2)  | 7.791(2)  | 236.15(11) |
| 8.5(3)    | 5.529(2)  | 5.439(2)  | 7.741(3)  | 232.81(13) |
| 10.0(4)   | 5.517(2)  | 5.419(2)  | 7.747(4)  | 231.58(17) |
| 11.6(4)   | 5.530(2)  | 5.413(2)  | 7.686(3)  | 230.07(15) |
| 12.8(5)   | 5.507(2)  | 5.412(2)  | 7.685(3)  | 229.03(15) |
| 14.1(5)   | 5.503(2)  | 5.538(2)  | 7.700(3)  | 227.98(15) |
| 17.5(5)   | 5.515(2)  | 5.380(2)  | 7.594(3)  | 225.31(15) |
| 18.6(5)   | 5.510(3)  | 5.391(2)  | 7.551(3)  | 224.30(17) |
| 20.1(5)   | 5.499(1)  | 5.416(1)  | 7.488(2)  | 223.00(8)  |
| 21.9(5)   | 5.486(2)  | 5.394(2)  | 7.493(6)  | 221.73(21) |
| 23.6(5)   | 5.480(1)  | 5.391(1)  | 7.472(2)  | 220.74(8)  |
| 25.3(5)   | 5.470(1)  | 5.370(1)  | 7.471(1)  | 219.49(6)  |
Figure Captions

**Fig. 1.** X-ray diffraction pattern from a powdered polycrystalline SrRuO$_3$ sample at ambient temperature for various pressures from 2.8 to 25.3 GPa. Over this pressure range the crystal structure remains orthorhombic.

**Fig. 2.** Temperature dependence of the ac susceptibility $\chi(T)$ of single-crystalline SrRuO$_3$ at ambient pressure. $\chi'_1$ gives the real part of the 1st harmonic and $\chi''_3$ gives the imaginary part of the 3rd harmonic in nanovolt units; the scale of $\chi''_3$ is expanded 20$\times$. The Curie temperature $T_{Curie} \approx 162$ K is defined by the peak in $\chi'_1(T)$ or, equivalently, by the onset in $\chi''_3(T)$, as shown in the figure.

**Fig. 3.** (upper) Lattice parameters of orthorhombic SrRuO$_3$ versus pressure to 25.3 GPa at ambient temperature. Solid lines are guides to eye. (lower) Equation of state from data in upper figure. Data fit using Eq. 1 (solid line) yields the bulk modulus $B_o = 192(3)$ GPa and its pressure derivative $B'_o = 5.0(3)$. Inset shows average Ru-O-Ru bond angle versus pressure (see text).

**Fig. 4.** Dependence of the Curie temperature $T_{Curie}$ of SrRuO$_3$ on nearly hydrostatic pressure to 17.2 GPa. $T_{Curie}$ is seen to decrease monotonically with pressure in reversible fashion. Thick solid straight line gives fit to present data with slope $dT_{Curie}/dP \simeq -6.8$ K/GPa. Numbers give order of present measurements (run D) on single crystal (● from $\chi'_1$, ■ from $\chi''_3$); also shown are present results on polycrystals (◇ run B) and (△ run C) as well as previous results (▽ run A) from Ref. [10]. Thin solid and dashed lines give results from thin-film studies from Refs. [16] and [15], respectively.

**Fig. 5.** Temperature dependence of the ac susceptibility of single-crystalline SrRuO$_3$ at nearly hydrostatic pressures to 17.2 GPa (run D in text). Above and below the horizontal dotted line are shown, respectively, the measured ferromagnetic transitions in $\chi'_1(T)$ and $\chi''_3(T)$ from which $T_{Curie}$ is determined (see Fig. 2). The numbers give the order of measurements corresponding to the single-crystal data (●, ■) in Fig. 4.
$B_0 = 192(3)$ GPa
$B_0' = 5.0(3)$
The graph shows the relationship between pressure (GPa) and $T_{Curie}$ ($K$) for SrRuO$_3$. The slope $dT_{Curie}/dP = -6.8$ K/GPa is indicated. The data points represent different runs: Run D (single crystal), Run C (polycrystal), Run B (polycrystal), and Run A (polycrystal).
