

ac susceptibility studies of the weak itinerant ferromagnet SrRuO₃ under high pressure to 34 GPa

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The dependence of the Curie temperature T_{Curie} on nearly hydrostatic pressure has been determined to 17.2 GPa for the weak itinerant ferromagnet SrRuO₃ in both polycrystalline and single-crystalline forms. T_{Curie} is found to decrease under pressure from 162 to 42.7 K at 17.2 GPa in nearly linear fashion at the rate $dT_{Curie}/dP \approx -6.8$ K/GPa. No superconductivity was found above 4 K in the pressure range from 17 to 34 GPa. Room-temperature x-ray diffraction studies to 25.3 GPa reveal no structural phase transition but indicate that the average Ru-O-Ru bond angle β passes through a minimum near 15 GPa. The bulk modulus and its pressure derivative were determined to be $B_o = 192(3)$ GPa and $B'_o = 5.0(3)$, respectively. Parallel ac susceptibility studies on polycrystalline CaRuO₃ at 6 and 8 GPa pressure found no evidence for either ferromagnetism or superconductivity above 4 K.

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I. 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 SrRuO₃, the only known ferromagnetic metal among the 4d oxides,³ the nearest-neighbor separation between Ru ions (~ 3.92 Å) is 48% greater than that in Ru metal (2.65 Å). The oxygen anions in SrRuO₃ 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 CaRuO₃ than in SrRuO₃, since in the former oxide the Ru-Ru nearest-neighbor separation is less and the degree of structural disorder is greater; indeed, CaRuO₃ exhibits no magnetic order but is paramagnetic with a negative Curie-Weiss temperature $\Theta \approx -68$ 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 ruthenates³⁻⁵ and other atomically arranged perovskites.⁶

Weak itinerant ferromagnets such as ZrZn₂,⁷ UGe₂,⁸ MnSi,⁹ and SrRuO₃ (Ref. 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. Rela-

tively 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. Wohlfarth¹¹ derived an expression valid for weak itinerant ferromagnets whereby the rate of decrease of the Curie temperature with pressure, dT_{Curie}/dP , is inversely proportional to the value of T_{Curie} itself. It is notable that the weak itinerant ferromagnet Sc₃In 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 ZrZn₂ (Ref. 7) and UGe₂ (Ref. 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 ZrZn₂ and UGe₂ is only an anomaly or representative for weak itinerant ferromagnets in general.

More than a decade ago, we carried out ac susceptibility (χ_{ac}) studies in a diamond-anvil cell (DAC) on polycrystal-

line SrRuO₃ to nearly hydrostatic (dense helium) pressures as high as 6 GPa.¹⁰ The Curie temperature was found to decrease approximately linearly from 161 to 130 K at the rate $dT_{Curie}/dP \approx -5.7$ 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 SrRuO₃ thin films epitaxially grown on a SrTiO₃ substrate under high quasi-hydrostatic 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 $dT_{Curie}/dP \approx -5.9$ K/GPa close to our value for bulk SrRuO₃ above; however, $T_{Curie}(P)$ was reported to pass through a minimum near 15 GPa, increasing at higher pressures only slightly in the former experiment¹⁵ 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 SrRuO₃ 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 SrRuO₃ 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 β 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 β 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.

II. EXPERIMENT

The polycrystalline sample of SrRuO₃ used in the present experiments was prepared by solid state reaction of stoichiometric quantities of high purity (99.9% or better) SrCO₃ and RuO₂. The starting materials were weighed, mixed, and placed in an Al₂O₃ crucible. The specimen was reacted for 4 h 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.

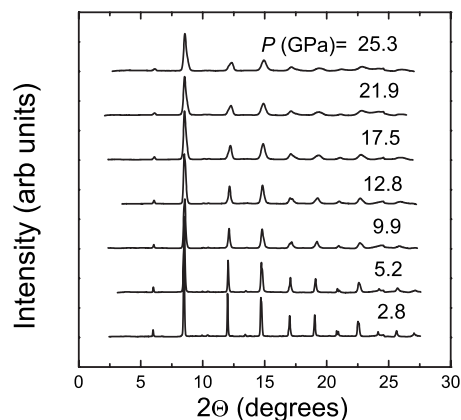


FIG. 1. X-ray diffraction pattern from a powdered polycrystalline SrRuO₃ sample at ambient temperature for various pressures from 2.8 to 25.3 GPa. Over this pressure range, the crystal structure remains orthorhombic.

Single crystals of SrRuO₃ were grown in Pt crucibles from off-stoichiometric quantities of RuO₂, SrCO₃, and SrCl₃ mixtures with SrCl₂ self-flux. The mixtures were first heated to 1500 °C, soaked for 25 h, slowly cooled at 2–3 °C/h to 1350 °C, and finally cooled to room temperature at 100 °C/h. 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 SrRuO₃ using synchrotron x rays ($\lambda=0.41105$ Å) with beam size 20×20 μm² at the Advanced Photon Source HPCAT, Sector 16-IDB, Argonne National Laboratory. 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 100×100 μm² pixel dimension for 10–20 s. The images were integrated using FIT2D program¹⁸ 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 to 80 μm thickness and containing a centered 235 μm diameter hole. After the sample (typical dimensions of $80 \times 80 \times 30$ μm³) and tiny ruby spheres²⁰ 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 calibration²¹ 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 and/or secondary coil sys-

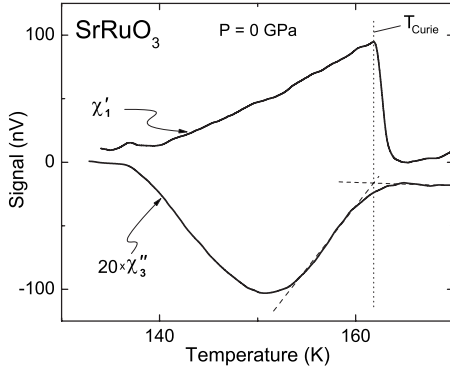


FIG. 2. Temperature dependence of the ac susceptibility $\chi(T)$ of single-crystalline SrRuO₃ at ambient pressure. χ'_1 gives the real part of the first harmonic and χ''_3 gives the imaginary part of the third harmonic in nV units; the scale of χ''_3 is expanded 20 times. The Curie temperature $T_{Curie} \approx 162$ K is defined by the peak in $\chi'_1(T)$ or, equivalently, by the onset in $\chi''_3(T)$, as shown in the figure.

tems located immediately outside the metal gasket²² and connected to a Stanford Research SR830 digital lock-in amplifier. The ac susceptibility studies were carried out using a 3 Oe rms 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 first harmonic of the ac susceptibility, χ_1 , but also of the higher harmonics. Since in this experiment the signal from the ferromagnetic transition of SrRuO₃ in χ_1 becomes very difficult to resolve for pressures above 10 GPa, we decided to also measure the third harmonic χ_3 , which has a superior signal/noise ratio at the highest pressures. In contrast to $\chi_1(T)$, where the transition is only revealed after the subtraction of a relatively large temperature-dependent background, the background signal in $\chi_3(T)$ has little temperature dependence. In Fig. 2, we compare at ambient pressure the real part of the first harmonic $\chi'_1(T)$ to the imaginary part of the third harmonic $\chi''_3(T)$ for a single-crystalline sample much larger ($150 \times 250 \times 65 \mu\text{m}^3$) than that used in a typical high-pressure experiment in the DAC. It is seen that the temperature of the peak in $\chi'_1(T)$, which we use to define the Curie temperature T_{Curie} , corresponds well with the transition onset in $\chi''_3(T)$. As we will see, measuring the third harmonic allows us to follow the ferromagnetic transition in SrRuO₃ to higher pressures.

III. RESULTS OF EXPERIMENT

A. 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, and $c=7.8546(8)$ Å, in good agreement with literature values.^{4,24} Figure 1 shows the x-ray diffraction patterns at various pressures to 25.3 GPa. As pressure is increased, no new peaks are found, indicating that the sample retains the orthorhombic crystal structure. However, the peaks broaden due to increasing nonhydro-

TABLE I. High pressure structural parameters for SrRuO₃. The lattice parameters are for the orthorhombic *Pbnm* (No. 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 ³)
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)

static conditions in the solidified silicon 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 $c/\sqrt{2}$ parameters near 15 GPa; this will be discussed in detail below. Note that in the present studies, the variation of the atomic positions within the unit cell, and thus the Ru-O bond lengths, could not be determined as a function of pressure.

The equation of state for SrRuO₃ is shown in Fig. 3 (lower), with the least-squares fit (solid line) obtained using the Birch-Murnaghan expression²⁵

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

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.^{26–28}

Again, we find no evidence for a structural phase transition near $P \approx 15$ GPa, where abrupt changes in dT_{Curie}/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 is known that T_{Curie} is reduced^{4,14,24} as one moves farther away from cubic symme-

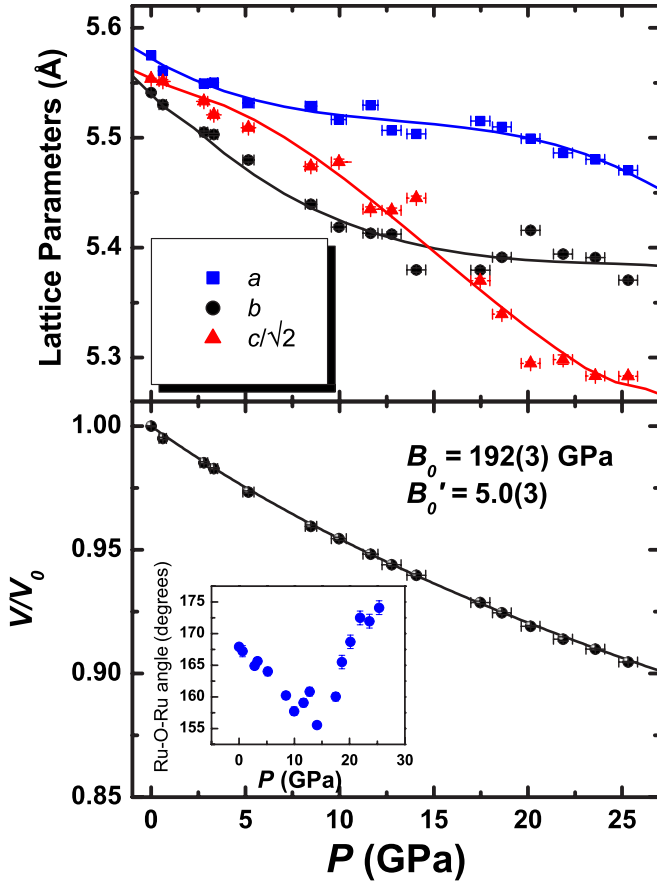


FIG. 3. (Color online) (Upper) Lattice parameters of orthorhombic SrRuO₃ versus pressure to 25.3 GPa at ambient temperature. Solid lines are guides for the eyes. (Lower) Equation of state from data in upper figure. Data fit using Eq. (1) (solid line) yields the bulk modulus $B_0=192(3)$ GPa and its pressure derivative $B'_0=5.0(3)$. Inset shows average Ru-O-Ru bond angle versus pressure (see text).

try 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 and only rotate when pressure is applied (a reasonable assumption for the small rotations occurring in SrRuO₃), 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 Φ around the $(111)_p$ direction of the ideal cubic perovskite structure given by

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

The Ru-O-Ru bond angles β_1 and β_2 are then given by

$$\beta_1 = \cos^{-1}\left(\frac{2 - 5 \cos^2 \Phi}{2 + \cos^2 \Phi}\right)$$

and

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

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 SrRuO₃ to CaRuO₃, direct calculation of the average Ru-O-Ru bond angle β decreases by 14.1°,²⁴ while the estimate from the lattice parameters is 15.4°. 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 β 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 β 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

B. ac susceptibility studies

The first of the present experiments (run B) was carried out on a polycrystalline SrRuO₃ sample (dimensions of $110 \times 130 \times 30 \mu\text{m}^3$) 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) Ref. 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 of $68 \times 90 \times 25 \mu\text{m}^3$) 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 SrRuO₃ sample (dimensions of $65 \times 90 \times 30 \mu\text{m}^3$), where both $\chi'_1(T)$ and $\chi''_3(T)$ were

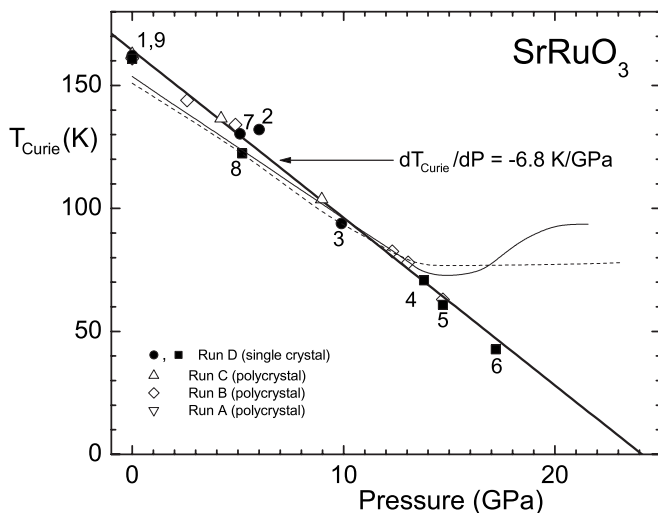


FIG. 4. Dependence of the Curie temperature T_{Curie} of $SrRuO_3$ on nearly hydrostatic pressure to 17.2 GPa. T_{Curie} is seen to decrease monotonically with pressure in reversible fashion. Thick solid straight line gives the fit to present data with slope $dT_{Curie}/dP \approx -6.8$ K/GPa. Numbers give order of present measurements (run D) on single crystal (\bullet from χ'_1 , \blacksquare from χ''_3); also shown are present results on polycrystals [\diamond , run B) and (\triangle 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.

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 2 from 0 to 9.9 GPa, but the transition also becomes broader, perhaps due to non-hydrostatic stresses even in the helium pressure medium; the

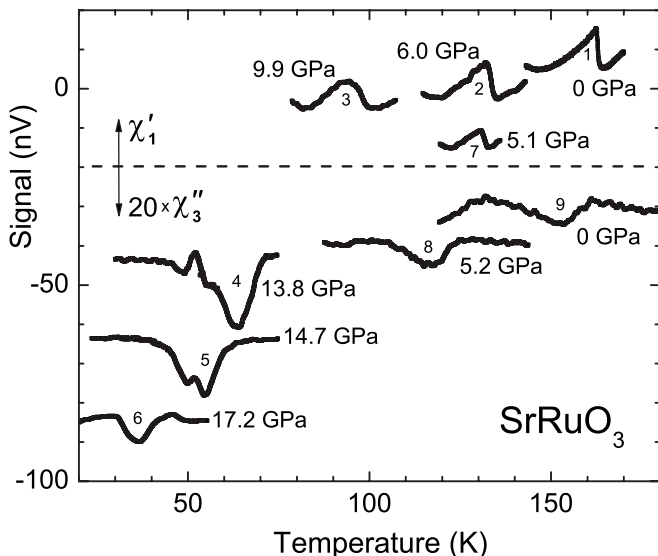


FIG. 5. Temperature dependence of the ac susceptibility of single-crystalline $SrRuO_3$ at nearly hydrostatic pressures to 17.2 GPa (run D in text). Above and below the horizontal dotted line are shown, respectively, the measured ferromagnetic transitions in $\chi'_1(T)$ and $\chi''_3(T)$ from which T_{Curie} is determined (see Fig. 2). The numbers give the order of measurements corresponding to the single-crystal data (\bullet , \blacksquare) in Fig. 4.

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 first 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 $dT_{Curie}/dP \approx -6.8$ K/GPa, T_{Curie} decreasing from 162 to 42.7 K, i.e., by nearly a factor of 4. Unfortunately, at higher pressures (20.4–34 GPa), the ferromagnetic transition could no longer be resolved.

IV. 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 β in a crystalline sample to pass through a minimum (Fig. 3). Indeed, in $Sr_{1-x}Ca_xRuO_3$ 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 β and the lower the value of T_{Curie} .³⁻⁵ We can estimate the dependence of T_{Curie} on β by considering that upon increasing x in $Sr_{1-x}Ca_xRuO_3$ from 0 to 1, the value of T_{Curie} decreases from 162 to 0 K, whereas the bond angle β decreases by 15.4° ,⁴ yielding $dT_{Curie}/d\beta \approx +10.5$ K/deg. We note that this value of $dT_{Curie}/d\beta$ is quite close to that derived from the values of dT_{Curie}/dP and $d\beta/dP$ in the present high-pressure experiments from 0 to 15 GPa, where $dT_{Curie}/d\beta = (dT_{Curie}/dP)/(d\beta/dP) \approx (-6.8 \text{ K/GPa})/(-0.86 \text{ deg/GPa}) = +7.9$ K/deg. The present experiments on the single-crystalline $SrRuO_3$ sample thus support the contention that T_{Curie} is correlated with the degree of structural distortion as represented by the bond angle β , at least in the pressure range 0–15 GPa.

For pressures at 15 GPa and above, β passes through a minimum and then increases quite rapidly, as seen in Fig. 3. The above correlation between T_{Curie} and β for bulk $SrRuO_3$ would then lead to the expectation that $T_{Curie}(P)$ 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 $T_{Curie}(P)$ 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 $T_{Curie}(P)$ 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_{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 SrRuO₃ sample and its SrTiO₃ substrate; the latter effect is expected since the bulk moduli B_o of SrRuO₃ [192(3) GPa] and SrTiO₃ (176 GPa from Ref. 33) differ by 9%. The fact that for both thin-film samples a break in slope in $T_{Curie}(P)$ 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_{Curie} values, as a function of pressure.

A search for superconductivity in single-crystalline SrRuO₃ 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 CaRuO₃ at 6 and 8 GPa found no evidence for either ferromagnetism or superconductivity above 4 K. In both materials, a superconducting volume fraction of 10%–20% would have been detected.

In summary, parallel ac susceptibility and x-ray diffraction studies have been carried out on poly- and single-crystalline samples of SrRuO₃ 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 β passes through a minimum near 15 GPa). $T_{Curie}(P)$ is found to decrease nearly linearly to 17.2 GPa nearly hydrostatic pressure. Evidence is given for a possible correlation between $T_{Curie}(P)$ and $\beta(P)$ in the present experiments, which would appear to imply that $T_{Curie}(P)$ should also pass through a minimum near 15 GPa, contrary to the expectations for a canonical weak itinerant ferromagnet where T_{Curie} would fall monotonically to 0 K under pressure. Future experiments on bulk SrRuO₃ to even higher pressures and lower temperatures are imperative to clarify the magnetic and superconducting properties of this interesting system.

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