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# $^{99}$Ru Mössbauer effect study of off-stoichiometric $SrRu_{1-v}O_3$ synthesized with different Curie temperatures

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The $^{99}$Ru Mössbauer effect has been measured in the off-stoichiometric $SrRuO_3$ compounds that have been synthesized with lowered $T_C$ for compositions $SrRu_{1-v}O_3$ $(0.0 \leqslant v \leqslant 0.12)$. The $T_C$ of the compounds range from 162 K (pure $SrRuO_3$) to 45 K ($SrRu_{0.88}O_3$). The isomer shifts of these compounds measured above the $T_C$ for each compound reveal a small change in ion state of Ruthenium from 4+ toward 5+ as the $T_C$ decreases. However, the hyperfine magnetic fields remain at approximately 33 T at 4.2 K in depressed $T_C$ compounds and the absence of quadrupolar features in the spectra indicates that the $RuO_6$ octahedra remain undistorted in these samples. The rapid decrease in $T_C$ with the change in the charge distribution at the Ru site suggests that carrier concentration has a much stronger influence on $T_C$ than the rotation of the $RuO_6$ octahedra seen in the $Sr_{1-x}Ca_xRuO_3$ system.

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## INTRODUCTION

It has been known for many years that almost cubic $SrRuO_3$ is a ferromagnet with a $T_C = 163$ K.[1] It has a reported magnetic moment of between $0.8\mu_B$ and $1.6\mu_B$ depending on the study which is less than predicted by the $S=1$ state of the ruthenium (Ru) ion.[2] The ferromagnetism (FM) has been shown to be sensitive to the orthorhombic distortion of the perovskite structure which arises from rotations of $RuO_6$ octahedra. This has been demonstrated by studying the $Sr_{1-x}Ca_xRuO_3$ system in which Sr is replaced with isoelectronic Ca and causes $T_C$ to uniformly decrease to zero at $x=1$.[3] In comparison the compounds $Sr_x(Na_{0.5}La_{0.5})_{1-x}RuO_3$ (Ref. 4) exhibit local charge disorder which affects the Ru environment and leads to even faster suppression of the FM state than in $Sr_{1-x}Ca_xRuO_3$. The electronic structure of $SrRuO_3$ was calculated by Singh[5] using the linear augmented plane wave (LAPW) method. He found a piling up of the density of states near the Fermi level which points to a Stoner mechanism for the ferromagnetic transition. More recently, Mazin and Singh[6] have shown how the evolution of magnetic properties can be understood in terms of the interplay between band structure and lattice distortions not only in the $Sr_{1-x}Ca_xRuO_3$ system but in the much larger set of ruthenium oxide compounds.

$SrRuO_3$ is a member of the Ruddlesden-Popper (RP) series of compounds, $Sr_{n+1}Ru_nO_{3n+1}$, $n=0,1,2,\ldots$. Its structure is also similar to that of $Sr_2RuO_4$ which has the same structure as the original high-temperature cuprate superconductor $La_{2-x}Sr_xCuO_4$ and is an unconventional superconductor below 1.5 K.[7] Related ruthenate and ruthenocuprate oxides, which include compounds such as $Sr_2YRu_{1-x}Cu_xO_6$ (Ref. 8) and $GdSr_2Ru_{1-x}Cu_{2+x}O_8$ (Ref. 9), and cuprate oxides have in common rich phase diagrams containing different magnetic phases, anomalous metallic behavior,[10] and for some also superconductivity. The properties of the cuprates are thought to be driven by strong electronic correlations due in part to narrow 3*d* bands. By contrast, wider 4*d* bands associated with ruthenium might tend to reduce correlations. However, the properties of the ruthenate oxides have also been analyzed in terms of correlation effects. Anh *et al.*[11] measured the optical conductivity of $Ca_xSr_{1-x}RuO_3$ films and analyzed their data in terms of a metallic Mott-Hubbard system. Correlation effects have also been seen in photoemission and inverse photoemission measurements.[12] Anomalous metallic behavior has been identified in optical conductivity in $SrRuO_3$.[13] There is also a low-frequency peak at 35 meV above $T_C$ and non-Drude frequency dependence $\sigma(\omega) \propto \omega^{-1/2}$ instead of the quadratic dependence expected of a Fermi liquid. Schroeter and Doniach[14] identify this peak with pseudogap behavior similar to that in the cuprates and recently have proposed that this is due to fluctuations associated with an orbital antiferromagnetic phase which is cut off by the ferromagnetic transition. $SrRuO_3$ is also characterized as a "bad metal" in which the resistivity does not saturate when the Ioffe-Regel limit is reached,[15] as is the resistivity of many of the ruthenate oxides.[16] This behavior arises from the loss of weight in the quasiparticle pole due to strong scattering so that any single-particle approximation, such as electronic states described by the band structure, breaks down. There is still no consensus on the role of correlation effects in the ruthenate oxides.

Here we examine the reported effect of ruthenium vacancies caused by off-stoichiometry on ferromagnetism in $SrRuO_3$ using the $^{99}$Ru Mössbauer effect (ME). Previously, powdered pure $SrRuO_3$ has been studied as a function of temperature by the $^{99}$Ru ME (Ref. 17) and those measurements showed a pure hyperfine magnetic field of 33 T which

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vanishes at 162 K. The isomer shift indicated a 4+ state with no change of the $T_C$. Recently, it was shown that single-phase compounds of $\mathrm{SrRu}_{1-v}\mathrm{O}_3$ can be produced with depressed Curie temperatures ($T_C$) from 160 K (powder) by annealing under oxygen at high pressures as measured by magnetization.[18,19] Neutron diffraction measurements[19] show that the compounds are single phase and that Ru vacancies are present in the compounds. The vacancies are reported for the octahedral sites and are related to the change in the $T_C$. X-ray diffraction measurements[19] show that the samples ($v=0.0, 0.05, 0.08$) are single phase. We have measured the $^{99}$Ru Mössbauer effect in these compounds of nominal formula $\mathrm{SrRu}_{1-v}\mathrm{O}_3$ ($v=0.0, 0.05, 0.12$) above and below the Curie temperatures. Above $T_C$ the spectra are single lines whose isomer shifts increase with the $T_C$. The spectra for depressed $T_C$ compounds show line broadening which is indicative of either a small quadruple interaction and/or multiple sites for Ru. However, at 4.2 K the spectra of all the samples have nearly the same hyperfine magnetic field, approximately 33 T, with little or no distortion of $\mathrm{RuO}_6$ octahedra in spite of the much reduced value of $T_C$.

## EXPERIMENTAL RESULTS

Polycrystalline samples of the nominal formula $\mathrm{SrRu}_{1-v}\mathrm{O}_3$ were synthesized from a stoichiometric mixture of $\mathrm{SrCO}_3$ and $\mathrm{RuO}_2$ using a solid-state reaction method. After calcination in 21% $\mathrm{O}_2/\mathrm{Ar}$ at 950 °C the synthesis of stoichiometric $\mathrm{SrRuO}_3$ was performed in flowing argon gas at 1100 °C. The off-stoichiometric samples of $\mathrm{SrRu}_{1-v}\mathrm{O}_3$ ($0.0 \leq v \leq 0.12$) were synthesized (1065–1100 °C) in high pressure of 21% $\mathrm{O}_2/\mathrm{Ar}$ corresponding to 600 bars of partial pressure oxygen. X-ray analysis shows that the compounds are single phase for $v=0.0$, 0.05, and 0.08 but not for $v=0.12$ (see Fig. 1 for the XRD diffraction patters for $v=0$ and $v=0.08$ samples).[18,19] Magnetization and ac susceptibility measurements were carried out on a Quantum Design MPMS superconducting quantum interference device (SQUID) and Quantum Design PPMS susceptometer for temperatures between $4.5\ \mathrm{K} < T < 300\ \mathrm{K}$ and magnetic fields $-70\ \mathrm{kG} < H_v < 70\ \mathrm{kG}$. The results of magnetic measurements for several differently annealed ($v=0.12, 0.08, 0.05, 0.0$) compounds are shown in Figs. 2 and 3.

The samples with different nominal deficiency of Ru ($0.0 \leq v \leq 0.12$) are stabilized by annealing at high pressure of oxygen. The perovskite phase of these samples with $v=0.12, 0.08, 0.05$ have maxima in their ac susceptibility at 45, 76, 94, and 92 K, respectively.[18,19] The samples have been subsequently reannealed at ambient pressure. Instead of the expected decomposition of then cation-deficient $AB\mathrm{O}_3$-type phase, the material remains single phase according to the power x-ray diffraction analysis (see Fig. 1). If partial decomposition occurs, one would assume that there is very slow kinetics or fine dispersion of the reaction products, which precludes observation of the emergent phases in the diffraction spectra. These are not observed for subsequently repeatedly grinded and annealed material. Simultaneously, however, the magnetic characteristics of these samples change. The Curie temperature recovers to its high-temperature value in the range of 155–162 K (see Fig. 2). Also, the magnetic moment measured in low temperature and at high magnetic field, Fig. 3, recovers to its value characteristic of stoichiometric $\mathrm{SrRuO}_3$ (inset to Fig. 3). The co-

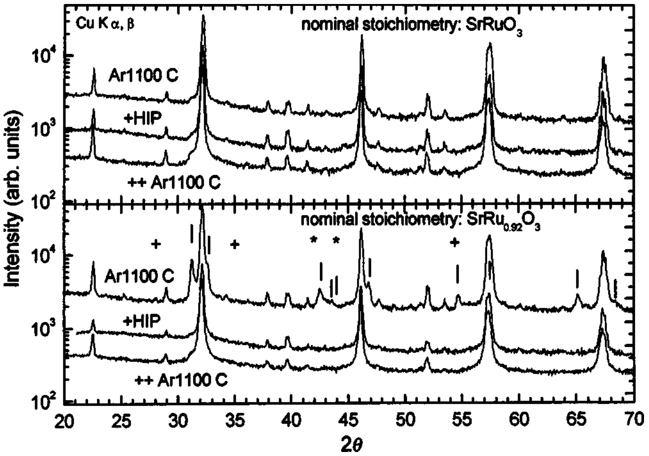

FIG. 1. Powder x-ray diffraction spectra as a function of angle for selected $\mathrm{SrRu}_{1-v}\mathrm{O}_3$ samples, $v$ (*nominal stoichiometry*)$=0$ (upper) and 0.08 (lower). Spectra represent samples after different annealing: *upper line*—initial synthesis in Ar 1100 °C; *middle line*—600 bars of $\mathrm{O}_2$ 1100 °C; *lower line*—after subsequent annealing in Ar at 1100 °C. In the lower spectra the main maxima of positions of impurity phases in the spectra are marked by short vertical lines for $\mathrm{Sr}_2\mathrm{RuO}_4$, stars (*) for Ru metal powder, and plus signs (+) for $\mathrm{RuO}_2$.

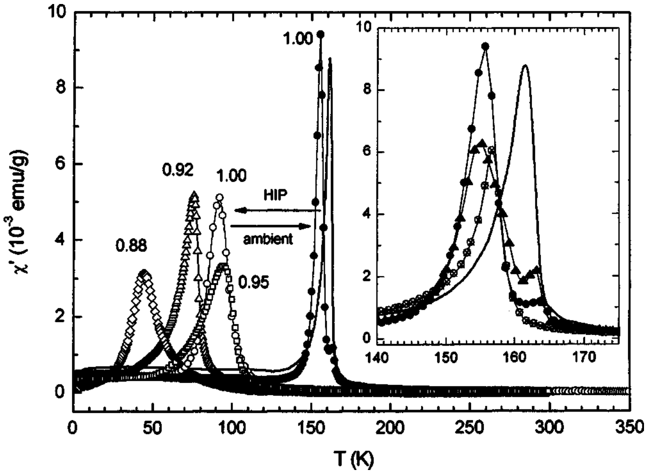

FIG. 2. Temperature dependencies for $\mathrm{SrRu}_{1-v}\mathrm{O}_3$ of the real component of the ac susceptibility ($H_{\mathrm{ac}}=1$ Oe, $f=200$ Hz) for $v$ (*nominal stoichiometry*)$=0.00$, 0.05, 0.08, and 0.12. Solid line (also inset) for stoichiometric sample of $\mathrm{SrRuO}_3$ (Ar, 1100 °C). Open circles, open squares, open triangles, and open diamonds: samples with $v$ (*nominal stoichiometry*)$=0.00$, 0.05, 0.08, and 0.12, respectively, synthesized in 600 bars of $\mathrm{O}_2$ in 1065–1100 °C; solid circles (also inset): sample $v=0.00$ after its subsequent annealing in Ar at 1100 °C. The inset compares the susceptibility at ferromagnetic transition upon its return to the 155–162 K temperature range: solid triangles—$v=0.08$, Ar 1100 °C; solid circles—$v=0.00$, Ar 1100 °C; crossed circles—$v=0.00$, 21% of $\mathrm{O}_2$ 1200 °C.

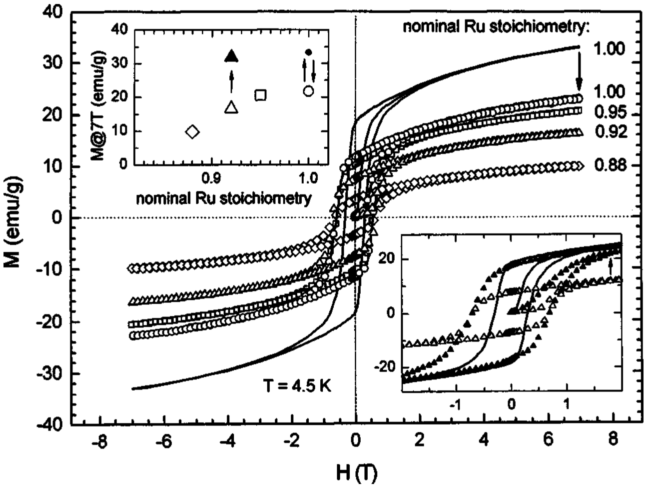

FIG. 3. Magnetic hysteresis loops of $SrRu_{1-v}O_3$ at 4.5 K. Solid line (also lower inset): $SrRuO_3$ synthesized in Ar in 1100 °C. Open circles, open squares, open triangles, and open diamonds: $v$ (*nominal stoichiometry*) $=0.00$, 0.05, 0.08, and 0.12, respectively, for samples synthesized in 600 bars of $O_2$ at 1065–1100 °C. Lower inset: sample $v=0.08$ (triangles) synthesized at high pressure of oxygen before and after its subsequent annealing in Ar at 1100 °C. Upper inset: magnetic moments at 7 T and 4.5 K for samples with different nominal Ru stoichiometry; the symbols correspond to the main graph.

ercive field, which should scale with pinning of magnetic domain walls, remains at its higher value gained in high-pressure annealing (inset to Fig. 3, also Ref. 18). In Ref. 20, where a lowered $T_C=150$ K was also reported for $SrRu_{0.95}O_3$, the possibility of the presence of defects induced at grain boundaries is suggested based on the observed difference in the resistivity of differently annealed samples. Unlike the polycrystalline material, the single crystals of $SrRuO_3$ annealed during the same high-pressure synthesis did not reveal lowering of $T_C$ and only a slight increase of the coercive field.[21] This indicates the importance of the effective surface of the material and the reaction kinetics in the chemical processes involved in synthesis of these compounds.

Further insight into effect of the recovery of ferromagnetism upon ambient pressure annealing is provided through the data in Figs. 1–3. For $SrRuO_3$ samples synthesized in Ar at 1100 °C (with preceeding calcination in 21% $O_2$ at 950 °C) the cutoff temperature of the maximum of ac susceptibility is 163 K (see Fig. 2). This value corresponds well to the $T_C$ reported for a single crystal of $SrRuO_3$,[3] and we assume it reflects the temperature of the ferromagnetic transition in the stoichiometric polycrystalline sample. The $T_C$ of several high-pressure synthesized samples, which subsequently were annealed at ambient pressure, returns to the somewhat lower value indicated by maximum of ac susceptibility centered in the range between 154 and 157 K (inset in Fig. 2). Only the reannealing in flowing Ar (i.e., at the conditions which stabilize the stoichiometric perovskite) partly reestablishes the phase with $T_C=163$ K—the inset in Fig. 2; see the second small maximum in ac susceptibility at a few kelvin higher than its main peak. We note that the disproportionation of $T_C$ in the range of 140–160 K was previously reported[22] for samples annealed in different ambient pressures. The $T_C$ discussed here in the off-stoichiometric polycrystalline materials was found to progressively shift toward its high-temperature value for annealing temperatures higher than 600 °C. The electronic structure calculations indicate that there is substantial magnetization density at the oxygen sites so that oxygen off-stoichiometry could modify the magnetism of $SrRuO_3$.[6]

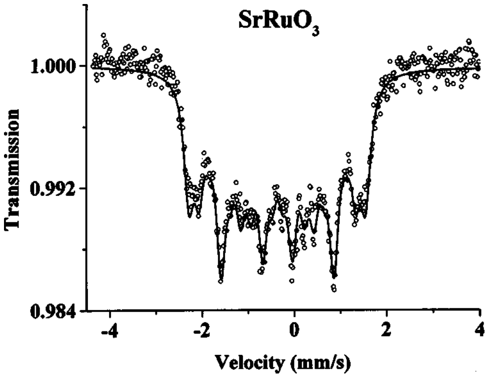

FIG. 4. Transmission versus velocity for a $^{99}$Rh(Ru) ME spectrum of a $SrRuO_3$ $T_C=162$ K sample measured at 4.2 K. The open circles represent the data and the black line represents the best fit to the 18-line spectra with the correct line intensities.

The $^{99}$Ru Mössbauer effect was performed by producing a source of $^{99}$Rh(Ru) by proton bombardment in a cyclotron on enriched targets and the experiments were performed in a transmission geometry as described elsewhere.[23] The calibration of the spectrum was determined by the inner four lines of a $^{57}$Co(Rh) source versus iron foil while the zero-velocity channel was determined by the $^{99}$Rh(Ru) versus Ru powder experiment. The aluminum absorber holders contained over 100 mg/cm$^2$ of natural Ru and were attached to a brass ring that was wrapped with heating wire. Both the source and absorber were kept at nearly the same temperature by the helium or nitrogen exchange gas in the cryostat. The temperature was maintained by Lakeshore temperature controller and diode to within 1 K.

First, we discuss the low-temperature measurement of stoichiometrically prepared $SrRuO_3$ prepared under normal solid-state conditions. The spectra in Fig. 4 shows the $^{99}$Ru ME of $SrRuO_3$ measured at 4.2 K. The line representing the fit to the data is a superposition of 18 lines derived from the hyperfine interaction based on the $E2$-$M1$ mixed-multipole $\gamma$-ray transitions occurring in the $^{99}$Ru nucleus.[24] The fit to the spectrum shows a full linewidth of 0.20 (0.01) mm/s for each line. This is an experimentally narrow linewidth which describes a single-phase sample with little or no disorder. The spectrum is fit with a hyperfine magnetic field of 33.6 (0.5) T, isomer shift of −0.37 (0.02) mm/s, and no electric-quadrupole interaction. The result is very similar to that published earlier for $SrRuO_3$.[16] Based on systematic studies of oxide compounds,[25] this isomer shift is consistent with a +4 charge state for the Ru ion.

In Fig. 5 we compare the spectrum of $SrRu_{0.95}O_3$ with that of $RuO_2$ at 4.2 K. We first point out that amplitude of

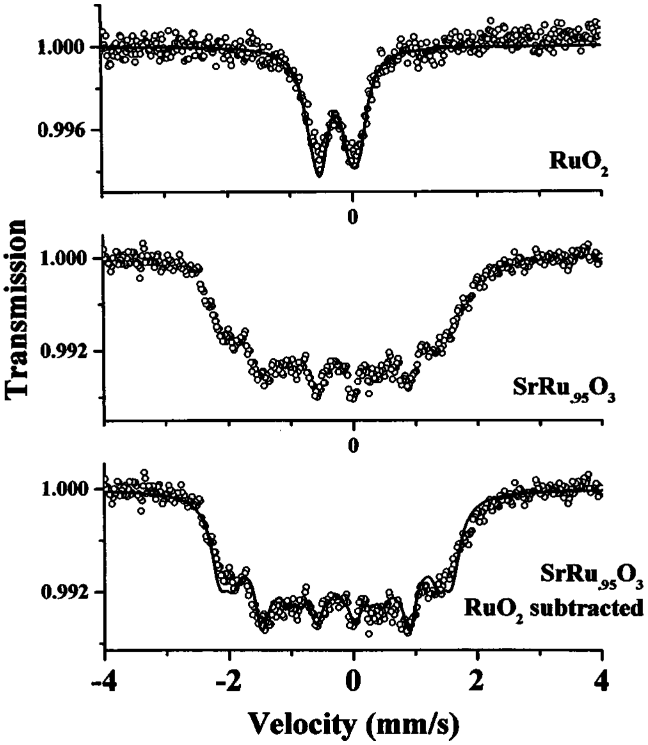

FIG. 5. Transmission versus velocity for a $^{99}$Rh(Ru) ME spectrum of $RuO_2$ and $SrRu_{0.95}O_3$, $T_C=90$ K measured at 4.2 K in the upper two spectra. The open circles represent the data and the black line represents the best fit to the data in $RuO_2$. The lower spectrum has $RuO_2$ subtracted from the data. The 18-line spectra with the correct line intensities is the black line fit to the data (circles).

the 8th (11th) (starting with the most negative velocity) line is larger than that of the 4th (15th) line in the 18 (Ref. 24) line spectrum. This is the reverse of what is seen in the pure magnetic spectrum in Fig. 4. The explanation for this can be seen by comparing the $SrRu_{0.95}O_3$ spectrum with that of $RuO_2$. The $RuO_2$ spectrum consists of two broad lines which arise from the electric fields gradients at the Ru site and whose positions are the same as the 8th and 11th lines in the $SrRu_{0.95}O_3$ spectrum. This suggests that there is a $RuO_2$ impurity phase in the sample. It should be noted that it is also possible that some $Sr_2RuO_4$ (Ref. 23) and pure Ru powder (see Fig. 6) might be present in the spectrum as shown in the x ray of the powders in Fig. 1. Each of these would fit into one of the lines of the subtracted part of the spectrum. Angular positions of the diffraction peaks of these phases are marked in the pattern in Fig. 1. The subtraction of a weighted $RuO_2$ spectrum from $SrRu_{0.95}O_3$ results in the third spectrum in Fig. 5. This last spectrum can be fit with a pure hyperfine magnetic field of essentially the same magnitude as in the normal synthesis $SrRuO_3$ sample with only a slightly increased quadrupolar component. Comparing the area under the weighted $RuO_2$ spectrum with that under the $SrRu_{0.95}O_3$ spectrum we can determine the amount of the impurity phase to be of order 5%. The $RuO_2$ phase was not detected in the neutron diffraction studies on these samples which suggests that the size of $RuO_2$ agglomerates should be less than 100 Å.

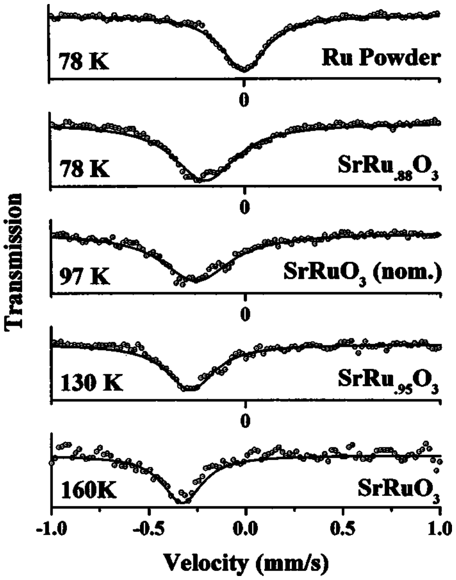

FIG. 6. Spectra which show the transmission versus velocity for a $^{99}$Rh(Ru) ME spectrum of $SrRu_{1-v}O_3$ measured at the indicated temperatures and values of $v$. Ru powder is included as a standard. The open circles represent the data and the black line represents the best fit to the single-line spectra. Nom. is the abbreviation of nominal. The spectra show that as the Ru content in the compound decreases toward $v=0.12$, the isomer shift decreases. Table I shows the results of the fitted parameters for the spectra.

Experiments were performed with nominally prepared stoichiometric $SrRuO_3$ which was synthesized under high-pressure (HP) oxygen as shown in Fig. 1. The nominal preparation of $SrRuO_3$ yielded a $T_C$ of approximately 92 K after HP oxygen treatment as shown in Fig. 2. The $^{99}$Ru ME measurement of this nominally prepared sample under HP oxygen was equivalent to that of $v=0.05$ in Fig. 5 at 4.2 K which also indicated the presence of $RuO_2$ (or possibly the other secondary phases). The neutron diffraction experiments on this nominally stoichiometrically prepared sample at HP in oxygen showed the absence of Ru from the Ru octahedra. This is interpreted as meaning that there are Ru vacancies in these samples. A $^{99}$Ru ME measurement at 97 K showed a single broadened line as shown in Fig. 6. This nominally prepared sample was then annealed and it recovered to a $T_C$ of 155 K and produced equivalent ME spectra at the measurement temperatures of 4.2 and 160 K as the $SrRuO_3$ produced under normal solid-state synthesis (Ar 1100 °C) as shown in Figs. 4 and 6. It is plausible that the Ru from the impurity phase $RuO_2$ (and/or Ru from other impurities) went back into the vacant Ru octahedra upon annealing in argon gas and therefore helped raise the $T_C$.

Experiments were performed with $SrRu_{0.88}O_3$ at 4.2 and 78 K. The results for $SrRu_{0.88}O_3$ do not show any structure at 4.2 K but only a broadened line which could accommodate a 33-T magnetic hyperfine field. The measurement at 78 K shows a broadened single line. The x-ray and neutron experiments show this $SrRu_{0.88}O_3$ sample to have impurities.

The spectra shown in Fig. 6 represent the $^{99}$Ru ME of $SrRu_{1-v}O_3$ for various values of $v$ and temperatures above $T_C$. The spectra show a rapid evolution with changes in the Ru content.

Table I shows the results of fitting the data to Lorentzian single lines. These spectra are single line but the lines are

TABLE I. Samples, their Curie temperatures, their isomer shifts at elevated temperatures, and the full width at half maximum for the lines.

| Sample (synthesis stoichiometry) | $T_C$ (K) | Isomer shift (mm/s) | $\Gamma_{1/2}$ (mm/s) |
|---|---|---|---|
| Ru Powder | | 0 | 0.14 (.01) |
| $SrRu_{.88}O_3$ | 45 | −0.19 (.01) | 0.20 (.01) |
| $SrRuO_3$(nom.) | 92 | −0.25 (.01) | 0.22 (.01) |
| $SrRu_{.95}O_3$ | 94 | −0.28 (.01) | 0.15 (.01) |
| $SrRuO_3$(nom.) (annealed) | 155 | −0.31 (.01) | 0.13 (.01) |
| $SrRuO_3$ | 160 | −0.33 (.01) | 0.13 (.01) |

progressively more broadened as the $T_C$ is depressed from 160 K toward 45 K and the position of the line, the isomer shift, moves to higher velocities. Clear evidence of $RuO_2$ and other impurities is absent at these higher temperatures in the HP oxygen-annealed samples, consistent with their measured small amounts. But some of the broadening may be due to $RuO_2$ (and other stated impurities). The ME isomer shift in absorbers containing $^{99}$Ru shows no measurable thermal shift. This temperature independence for the isomer shift (in the temperature range measured for $SrRu_{1-v}O_3$) has been found experimentally in $Sr_2RuO_4$ (Ref. 23), $CaRuO_3$ (Ref. 17) and $La_4Ru_2O_{10}$ (Ref. 26), Ru powder (Ref. 26), $BaRuO_3$ (Ref. 26), and, of course, in $SrRuO_3$ (Ref. 17). There is no shift because the both the source and absorber are at the same temperature.[27] The variation of the isomer shift comes from the change in the density of electrons at the Ru site with an increasing number of Ru vacancies and is indicative of an evolution of the Ru charge state from +4 at $v=0$ towards +5 (Ref. 25).

## CONCLUSIONS

In the $Sr_{1-x}Ca_xRuO_3$ system $T_C$ decreases uniformly with $x$ between $x=0$ and 1. This decrease has been identified with an increasing rotation of the $RuO_6$ octahedra which changes the nature of states at the Fermi surface. On the other hand, $T_C$ drops much faster in $SrRu_{1-v}O_3$ without changing the magnitude of the hyperfine field. There is no evidence that there is any significant distortion of the $RuO_6$ octahedra in the Mössbauer spectra as $v$ increases. This result is in agreement with neutron scattering measurements on these materials.[19]

However, the Mössbauer spectra do show both a rapid change in the charge distribution at the Ru nucleus and a broadening of features in the spectra so that the spectrum is featureless by $v=0.12$ when $T_C=45$ K. The change in the charge state of the Ru atoms can be expected on charge counting grounds when Ru is removed from the octahedra. This suggests that the carrier density $n$ is decreasing. The broadening of the lines indicates a small distribution of hyperfine fields at the Ru sites. This could arise from fluctuations in electronic properties due to disorder from an inhomogeneous distribution of Ru vacancies and the presence of impurity phases in the samples..

We found that the average hyperfine field does not change with increasing number of Ru vacancies even though the value $T_C$ falls rapidly from 163 to 45 K. This has been seen also in a point contact Andreev reflection (PCAR) measurements[28] on $Sr_{0.8}Ti_{0.2}O_3$ and $SrRu_{0.92}O_3$. In these measurements it was shown that the transport spin polarization in $SrRuO_3$ does not change from 60% as ruthenium vacancies are introduced into this compound. The spin polarization at the nucleus produces the hyperfine magnetic field and so the PCAR measurements are consistent with the measurements presented here.

It is difficult to quantitatively account for the behavior of the hyperfine field and $T_C$ on the basis of the standard model for ferromagnetism. The standard model for itinerant ferromagnetism is the Stoner model[29] in which the magnetic ordering is driven by short-range interactions among electrons. This model has been extended by Hirsch to include orbital dependent short-range interactions.[30] At the Hartree-Fock level the dependences of magnetization at zero temperature, $M_s(0)$, and $T_C$ on carrier number $n$ are substantially independent of the density of states in the band.[31] $M_s(0)$ is proportional to $n$ and $T_C$ has a maximum at half-filling, $n=1$. This model was investigated further by Wahle *et al.*[32] who included the strong-coupling correlations which arise from the large value of the strength of the interaction among the electrons. They found that there is strong dependence on the form of the density of states, that the value of $T_C$ is strongly reduced from that found in the Hartree-Fock treatment, and that there is a maximum in $T_C$ at values of $n$ which depends on the strength of the interaction. This model does not describe the local moment character of the electronic degrees of freedom which survives above $T_C$ (Ref. 3) and cannot address the dependence of the hyperfine field which is determined by the polarization of the electron density at the Ru nucleus. The microscopic calculations of Mazin and Singh[5,6] are also unable to address the hyperfine field at the Ru site since they employ the LAPW method[33] in which the core electrons and the nuclear Coulomb potential are treated by a pseudopotential. As a result the polarization of the $s$-wave electrons due to magnetic ordering is not included explicitly in their calculations. However, the decrease of $T_C$ with $n$ is consistent with a Stoner-like shift in the Fermi level away from a maximum in the density of states of the Ru—O bands which is the origin of itinerant ferromagnetism in the Stoner model. The lack of dependence of $M_s(0)$ on Ru vacancies and $n$ suggests that the polarization of $s$ electrons is dominated by the localized $d$ electrons responsible for the local moment which survives above $T_C$ instead of the itinerant RuO band electrons, at least while the samples are ferromagnetically ordered and/or the RuO octahedral remain undistorted. Above $T_C$ the measured hyperfine field is zero because of the rapid fluctuations of the local moments. This issue can be resolved by detailed calculations of the hyperfine field in these compounds which, at present, may be intractable.

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