

# Pressure effects on magnetic and structural properties of pure and substituted SrRuO<sub>3</sub>

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An influence of hydrostatic pressure on phase transition temperature  $T_C$ , spontaneous magnetization  $M_0$ , coercive field  $H_C$ , and remanent magnetization  $M_R$ , has been investigated for the parent perovskite SrRuO<sub>3</sub> and substituted ruthenates with decreased (La<sub>0.2</sub>Sr<sub>0.8</sub>RuO<sub>3</sub>, SrRu<sub>0.9</sub>Mn<sub>0.1</sub>O<sub>3</sub>) and increased (SrRu<sub>0.9</sub>Cr<sub>0.1</sub>O<sub>3</sub>) Curie temperature. We have observed a decrease of  $T_C$  with pressure for all of the studied samples, however, the lowering of  $T_C$  with pressure ( $dT_C/dP$ ) is not correlated with the value of  $T_C$  at ambient pressure. The spontaneous magnetization and coercive field remain unchanged for most of the samples, except the La<sub>0.2</sub>Sr<sub>0.8</sub>RuO<sub>3</sub> sample, where spontaneous magnetization decreases with increasing pressure. For SrRuO<sub>3</sub>, structural study by neutron powder diffraction shows clear contraction of the Ru-O bond lengths under external pressure whereas bond angles and the orthorhombic distortion remain constant at 295 and 50 K. The weakening of the ferromagnetic interactions with increasing pressure is consistent with complex band structure effects through a combination of modulation of the hybridization caused by contraction of the Ru-O bonds and with the significant role of the direct Ru-Ru interactions.

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## I. INTRODUCTION

Strontium ruthenate SrRuO<sub>3</sub> is known as unique  $4d$  transition metal  $ABO_3$  perovskite that displays ferromagnetic properties. Ferromagnetism (FM) in SrRuO<sub>3</sub>, with  $T_C$  of about 160 K,<sup>1</sup> arises from a parallel alignment of magnetic moments of Ru<sup>4+</sup> electrons in the low-spin  $4d^4$  ( $t_{2g}^4$ ) electronic configuration.<sup>2,3</sup> Strong Ru <sub>$t_{2g}$</sub> -O<sub>2p</sub> hybridization leads to an itinerant character of FM, evidenced by metallic conductivity, reduced magnetic moment  $1.6\mu_B$ /Ru atom, and a lack of saturation of magnetization to the expected  $2\mu_B$ /Ru atom even in high dc field of 300 kOe.<sup>3,4</sup> Since ferromagnetic order arises in partially filled (2/3) band of Ru<sup>4+</sup>, electronic transport is affected by double-exchange rules of electron hopping between Ru sites. Substitutions by lanthanide ions or alkaline earth ions at the  $A$  site<sup>4-7</sup> and by the  $3d$  transition metal ions at the  $B$  site<sup>8</sup> in SrRuO<sub>3</sub> usually suppress magnetic and conducting properties. The La<sup>3+</sup> substitution for Sr<sup>2+</sup> results in pronounced suppression of FM; for example, the  $T_C$  decreases to 75 K for La<sub>0.2</sub>Sr<sub>0.8</sub>RuO<sub>3</sub> (Ref. 7) most likely caused by attenuation of the Ru <sub>$t_{2g}$</sub> -O<sub>2p</sub> hybridization and by a change of the Ru valence state. The substitution of Ru ion by Mn also rapidly suppresses FM ( $T_C = 121$  K for SrRu<sub>0.9</sub>Mn<sub>0.1</sub>O<sub>3</sub>) and leads to the spin glass behavior for SrRu<sub>0.61</sub>Mn<sub>0.39</sub>O<sub>3</sub> (Ref. 9). The Cr substitution leads to a unique enhancement of  $T_C$  up to 188 K (Ref. 8) for SrRu<sub>0.9</sub>Cr<sub>0.1</sub>O<sub>3</sub> due to the minority-band mediated double exchange (DE) interaction for the mixed valence ions Ru<sup>4+/5+</sup> and Cr<sup>4+/3+</sup> (Refs. 10-12).

The external pressure experiments are useful to modify the magnetism in these oxides by compressing the  $A$ -O and  $B$ -O bonds and/or by reducing the structural distortions, i.e., by increasing magnitude of the atomic wave functions overlap on the electronically relevant  $B$ -O network. As a result, an increase of the bandwidth  $W$ , described by empirical for-

mula  $W = \cos \Theta / [B-O]^{3.5}$ , where  $\Theta = 1/2(\pi - \langle B-O-B \rangle)$  and  $\langle B-O-B \rangle$  is the  $B$ -O- $B$  bond angle, and  $[B-O]$  is the  $B$ -O bond length, should typically lead to an enhancement of the double-exchange interactions and to an increase of  $T_C$  under pressure.<sup>13</sup> However, for  $4d$  metals, the overlap between extended  $4d$  orbitals is sufficiently large to permit also direct Ru-Ru exchange interactions. For metallic Ru (the Ru-Ru distance  $[Ru-Ru] \sim 2.65$  Å), the overlap is too large to produce either local-moment or itinerant magnetism.<sup>14</sup> For SrRuO<sub>3</sub> (the Ru-Ru distance  $[Ru-Ru] \sim 3.923$  Å), the overlap may be suitably reduced to exhibit itinerant magnetism. Reduction of the Ru-Ru distance under pressure should lead in this case to suppression of magnetism and lowering of  $T_C$  with pressure with  $d \ln T_C/dP$  that is inversely proportional to  $T_C^2$  (Ref. 15). Neumeier *et al.*<sup>16</sup> found that  $T_C$  of SrRuO<sub>3</sub> decreases under hydrostatic pressure with the rate  $dT_C/dP = -0.57$  K/kbar and concluded that this value is in qualitative agreement with predictions of the Wohlfarth model.<sup>15</sup> According to this model,  $T_C$  of a homogeneous ferromagnet is expected to vary with pressure following the formula:

$$\frac{d \ln T_C}{dP} = -\frac{\alpha}{T_C^2} + \frac{5}{3}\kappa, \quad (1)$$

where  $\alpha$  is a slowly varying quantity<sup>15</sup> and  $\kappa$  denotes compressibility. For a weak itinerant ferromagnet, both  $\alpha$  and  $\kappa$  are positive and the first term on the right-hand side of Eq. (1) is bigger than the second one.<sup>15</sup> Hence,  $T_C$  decreases with pressure. The value of  $dT_C/dP$  found by Neumeier *et al.* for SrRuO<sub>3</sub> allowed them to conclude that this compound is weak itinerant ferromagnet.<sup>16</sup>

In this paper, we present the results of magnetic measurements performed under hydrostatic pressure for pure and substituted SrRuO<sub>3</sub> with decreased (La<sub>0.2</sub>Sr<sub>0.8</sub>RuO<sub>3</sub>, SrRu<sub>0.9</sub>Mn<sub>0.1</sub>O<sub>3</sub>) and increased (SrRu<sub>0.9</sub>Cr<sub>0.1</sub>O<sub>3</sub>) Curie tem-

perature, hence with weakened and enhanced exchange interactions. We found that  $T_C$  decreases with pressure in all the cases. Neutron diffraction experiments under pressure for parent compound  $\text{SrRuO}_3$  show uniform decrease of lattice parameters, cell volume  $V$ , and Ru-O bond lengths, whereas bond angles appear to remain constant near  $\sim 162^\circ$  and  $163^\circ$  at 50 and 295 K, respectively. These results point to complex band structure effects related to the modulation of the hybridization by contraction of the Ru-O bonds and possibly to the significant role of the direct Ru-Ru interactions that cause uniform suppression of magnetic interactions.

## II. EXPERIMENTAL DETAILS

The stoichiometric  $\text{SrRuO}_3$ ,  $\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$ , and the substituted  $\text{SrRu}_{1-x}\text{M}_x\text{O}_3$  samples, where  $M$  is Cr or Mn, have been prepared using the standard ceramic synthesis method.<sup>17,18</sup> Calcination of the starting mixtures was done for short periods of time at  $800^\circ\text{C}$  to avoid the conspicuous volatility of  $\text{RuO}_2$  at elevated temperatures. The intimately mixed powders were then pressed into pellets and fired in air at increasing temperatures with several intermediate grindings up to the following final synthesis conditions.  $\text{SrRu}_{1-x}\text{M}_x\text{O}_3$  samples were obtained in air at  $1100$  and  $1340^\circ\text{C}$  for  $x=0$  and for  $x=0.1$  with  $M=\text{Cr}$  and  $\text{Mn}$ , respectively. The  $\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$  sample was prepared in Ar at  $1200^\circ\text{C}$ . All samples were found to be single phase and the chemical compositions have been verified in careful EDXS and TGA measurements, and the x-ray and neutron powder diffractions.<sup>10</sup> All magnetic measurements were performed with a PAR 4500 vibrating sample magnetometer in the temperature range  $5\text{--}250\text{ K}$  in magnetic fields up to  $16\text{ kOe}$ . Temperature dependence of magnetization was measured applying zero-field-cooling (ZFC) and field-cooling (FC) procedure, whereas the  $M(H)$  dependence was measured after FC in maximum applied field of  $16\text{ kOe}$ . For these measurements a miniature container of CuBe (Ref. 19) with an inside diameter of  $1.42\text{ mm}$  was employed as a pressure cell. A mixture of mineral oil-kerosene was used as a pressure-transmitting medium. The pressure at low temperatures was determined by the pressure dependence of the superconducting transition temperature of pure tin placed near the sample. Additionally, the measurements of ac susceptibility at ambient pressure, for various frequencies were performed with the ACMS option of the Physical Property Measurement System of Quantum Design.

Time-of-flight neutron powder diffraction data were collected on the Special Environment Powder Diffractometer<sup>20</sup> at the Argonne's Intense Pulsed Neutron Source. Diffraction data were acquired at  $295$  and  $50\text{ K}$  under the pressure of  $0\text{--}5.5\text{ kbar}$  using a closed-cycle helium refrigerator and a hydrostatic helium-gas pressure cell.<sup>21</sup> The data were measured at  $2\theta=90^\circ$  and analyzed by the Rietveld method with the General Structure Analysis System code (GSAS).<sup>22</sup> The Rietveld refinement included approximately  $1000$  Bragg reflections over the range of  $d$  spacing from  $0.5$  to  $5.0\text{ \AA}$ .

## III. RESULTS AND DISCUSSION

Four representative samples were chosen for magnetic measurements under pressure: the parent compound  $\text{SrRuO}_3$

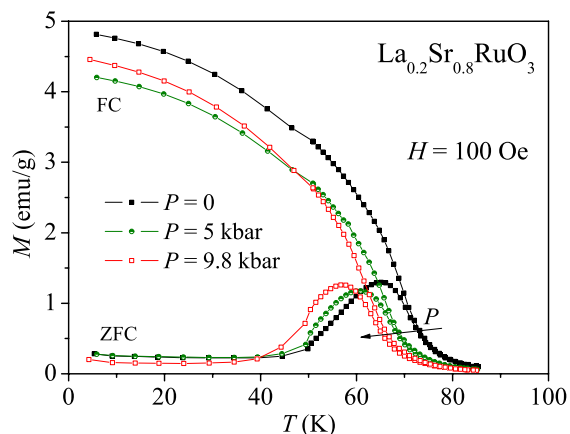


FIG. 1. (Color online) Temperature dependence of  $M_{\text{ZFC}}$  and  $M_{\text{FC}}$  for  $\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$  measured at  $100\text{ Oe}$ .

( $T_C=163.3\text{ K}$ ),  $\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$  ( $T_C=70.2\text{ K}$ ),  $\text{SrRu}_{0.9}\text{Cr}_{0.1}\text{O}_3$  ( $T_C=184.7\text{ K}$ ), and  $\text{SrRu}_{0.9}\text{Mn}_{0.1}\text{O}_3$  ( $T_C=117.0\text{ K}$ ), where  $T_C$ 's were determined from the magnetization  $M(T)$  curves as the temperature of the maximum slope of  $-dM/dT$ . For all the samples, both at ambient pressure and under hydrostatic pressure, marked divergence between  $M_{\text{ZFC}}$  and  $M_{\text{FC}}$  curves was noticed. In Fig. 1, as an example, temperature dependence of  $M_{\text{ZFC}}$  and  $M_{\text{FC}}$  is shown for  $\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$  measured in  $100\text{ Oe}$ .

The temperature dependence of both real and imaginary components of ac susceptibility for all of the studied samples was measured at four frequencies:  $10$ ,  $10^2$ ,  $10^3$ , and  $10^4\text{ Hz}$ ; a probing ac magnetic field of  $1\text{ Oe}$  was applied. In Fig. 2, an example of the temperature dependence of the real part  $\chi'$  and imaginary part  $\chi''$  of the ac susceptibility is shown for  $\text{SrRu}_{0.9}\text{Mn}_{0.1}\text{O}_3$ . The common features for all of the studied samples may be noticed: (i) peaks observed for both  $\chi'(T)$

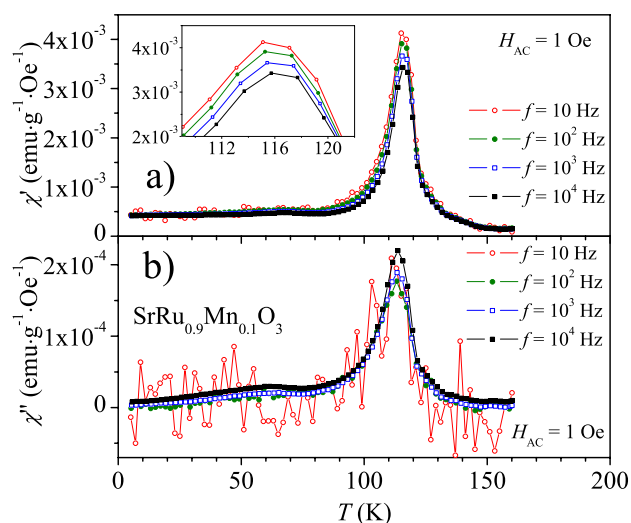


FIG. 2. (Color online) Temperature dependence of real (a) and imaginary (b) part of magnetic susceptibility for  $\text{SrRu}_{0.9}\text{Mn}_{0.1}\text{O}_3$  measured at ac magnetic field amplitude of  $1\text{ Oe}$ . Inset to panel (a) shows  $\chi'(T)$  in the vicinity of its maximum.

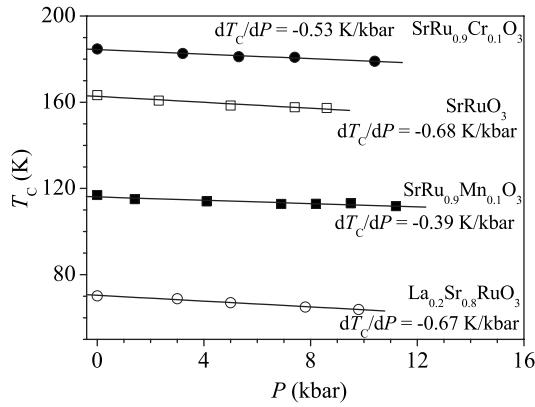


FIG. 3. Pressure dependence of Curie temperature for investigated samples. Values of the pressure coefficient  $dT_C/dP$  for each sample, determined by a linear fit, are indicated in the figure.

and  $\chi''(T)$  curves are narrow, maximum of both curves occurs at the temperature which is equal to  $T_C$  determined from dc magnetic measurements, (ii) maximum of both  $\chi'(T)$  and  $\chi''(T)$  curves does not depend on frequency, (iii) below  $T_C$  susceptibility is independent of temperature. Features (i) and (ii) indicate a presence of FM interactions, the feature (iii) points to itinerant character of FM. It should be stressed that for all of the studied samples no trace of spin glass behavior was noticed, as it was observed for higher level substituted sample  $\text{SrRu}_{0.61}\text{Mn}_{0.39}\text{O}_3$ .<sup>9</sup>

As one can see in Fig. 3, the ferromagnetic transition temperature  $T_C$  decreases with increasing pressure for all of the investigated samples independently on the substitution site and on the effect of the substitution on  $T_C$ . Furthermore, lowering of  $T_C$  with increasing pressure ( $dT_C/dP$ ) is not correlated with the value of  $T_C$  at ambient pressure since the highest (almost the same) values of  $dT_C/dP$  were reached for the samples with  $T_C=163.3$  and  $70.2$  K. According to the prediction of the Wohlfarth model [Eq. (1)] the magnitude of  $d \ln T_C/dP$  should be larger for the compounds with lower values of  $T_C$ . In fact, for the studied samples, the value of the coefficient  $d \ln T_C/dP$  is the highest for the  $\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$  sample with  $T_C=70.2$  K and the smallest for the  $\text{SrRu}_{0.9}\text{Cr}_{0.1}\text{O}_3$  with  $T_C=184.7$  K but the other two samples do not follow this trend.

For all studied samples FC hysteresis loops were measured at  $T=10$  K, both at ambient pressure and under hydrostatic pressure [see, for example, Fig. 4(a)]. All samples show clear spontaneous FM moment  $M_0$ , which was extracted by linear extrapolation of  $M(H)$  dependence from

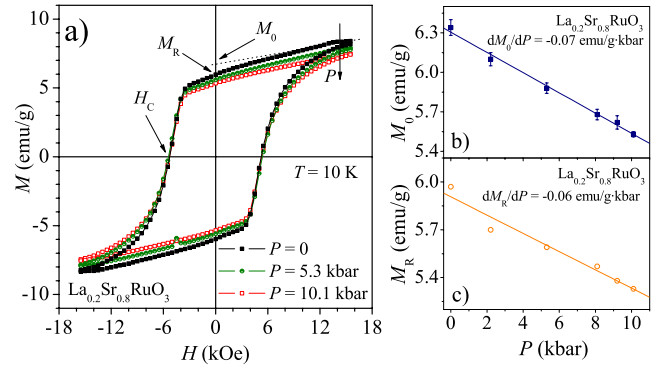


FIG. 4. (Color online) Magnetization hysteresis loops (a) and pressure dependences of spontaneous magnetization  $M_0$  (b) and remanent magnetization  $M_R$  (c) for  $\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$  at  $T=10$  K. Values of the pressure coefficients  $dM_0/dP$  and  $dM_R/dP$  are indicated in the figure.

high-field region to  $H=0$ . In Table I ambient pressure values of  $T_C$ , spontaneous magnetization  $M_0$ , coercive field  $H_C$ , remanent magnetization  $M_R$ , and dependence of these parameters on pressure are summarized. The strongest suppression of  $T_C$ ,  $M_0$ , and  $M_R$  is observed for the sample with Sr partially substituted by La. On the other hand, this sample shows considerably enhanced coercive field of  $\sim 5$  kOe—more than two times bigger than that observed for the  $\text{SrRuO}_3$  sample. Similarly enhanced coercive fields were previously observed for the Ru deficient samples of  $\text{SrRu}_{1-x}\text{O}_3$  (Ref. 23). This indicates that a disorder caused by substitution of  $\text{La}^{3+}$  for  $\text{Sr}^{2+}$  strongly enhances pinning of the magnetic domain walls. Partial substitution of Ru by Mn also leads to a suppression of ferromagnetic order—a decrease of  $T_C$ ,  $M_0$ , and  $M_R$  is clearly visible. In this case, only slight increase of  $H_C$  occurs—a disorder caused by Mn substitution is not very effective in terms of domain wall pinning. Partial substitution of Ru by Cr leads to an increase of  $T_C$ , however, this is not accompanied by an increase of spontaneous magnetization—both  $M_0$  and  $M_R$  decrease. Decrease of  $H_C$  may be related, at this low level of substitution, to removal of some amount of Ru vacancies present in  $\text{SrRuO}_3$  sample.<sup>24</sup> The existence of  $M_0 \neq 0$  confirms appearance of FM below  $T_C$ , reported earlier for these compounds.<sup>2,7,8</sup>

The  $M_0$  does not change under pressure for most of the samples, except for  $\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$ , where it decreases with increasing pressure—see Fig. 4(b). Comparison of the values presented in Table I indicates that there is no correlation between  $d \ln M_0/dP$  and  $d \ln T_C/dP$ . Such a correlation was predicted by Wohlfarth<sup>15</sup> and was expressed by the following formula:

TABLE I. Values of critical temperature  $T_C$  determined in 100 Oe, spontaneous magnetization  $M_0$ , coercive field  $H_C$ , remanent magnetization  $M_R$  determined at 10 K, and dependence of these parameters on pressure.

	$T_C$ (K)	$dT_C/dP$ ( $\frac{\text{K}}{\text{kbar}}$ )	$d \ln T_C/dP$ ( $\frac{\text{K}}{\text{kbar}}$ )	$M_0$ ( $\frac{\text{emu}}{\text{g}}$ )	$dM_0/dP$ ( $\frac{\text{emu}}{\text{g.kbar}}$ )	$d \ln M_0/dP$ ( $\frac{\text{emu}}{\text{g.kbar}}$ )	$H_C$ (kOe)	$dH_C/dP$ ( $\frac{\text{kOe}}{\text{kbar}}$ )	$M_R$ ( $\frac{\text{emu}}{\text{g}}$ )	$dM_R/dP$ ( $\frac{\text{emu}}{\text{g.kbar}}$ )
$\text{SrRuO}_3$	163.3	-0.68	-0.0042	20.3	$\approx 0$	$\approx 0$	2.1	0.03	18.0	$\approx 0$
$\text{SrRu}_{0.9}\text{Cr}_{0.1}\text{O}_3$	184.7	-0.53	-0.0029	15.2	$\approx 0$	$\approx 0$	1.7	$\approx 0$	13.3	$\approx 0$
$\text{SrRu}_{0.9}\text{Mn}_{0.1}\text{O}_3$	117.0	-0.39	-0.0033	16.0	$\approx 0$	$\approx 0$	2.3	$\approx 0$	15.0	$\approx 0$
$\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$	70.2	-0.67	-0.0095	6.3	-0.07	-0.011	5.3	$\approx 0$	6.0	-0.06

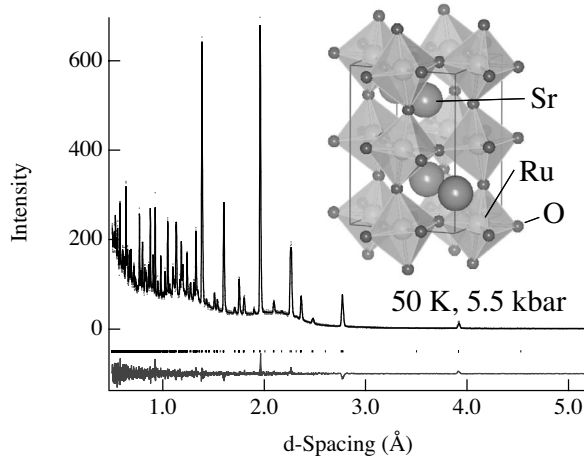


FIG. 5. Neutron diffraction pattern measured for SrRuO<sub>3</sub> at  $T=50$  K and  $P=5.5$  kbar. The Bragg positions of the reflections are indicated by vertical lines, below difference pattern between experimental and calculated line is shown.

$$\frac{d \ln M_0}{dP} = \frac{d \ln T_C}{dP} - \frac{5\kappa}{6} - \frac{1}{2} \frac{d \ln \left[ \frac{1}{2\chi_0 M_0^2} \right]}{dP}, \quad (2)$$

where  $\chi_0$  denotes ferromagnetic susceptibility at 0 K. The last two terms on the right-hand side of Eq. (2) are usually small for weak itinerant ferromagnets. The fact that behavior of coefficients  $d \ln T_C/dP$  and  $d \ln M_0/dP$  does not follow fully Wohlfarth's prediction could be understood taking into account that the formulas were derived assuming that the band structure remains unchanged under pressure and that the density of states  $N(E_F)$  scales smoothly with the bandwidth  $W$ . As it will be discussed below one should expect rather complex band structure effects under pressure in the studied compounds.

The observed changes of  $T_C$  and  $M_0$  can be approximated by the linear pressure dependence with fixed pressure coefficients of  $dT_C/dP$  and  $dM_0/dP$  for  $T_C$  and  $M_0$ , respectively. The coercive fields do not change with pressure, within an experimental error, except for SrRuO<sub>3</sub>, where it slightly increases with increasing pressure:  $dH_C/dP=0.03$  kOe/kbar. The changes of remanent magnetization with pressure were noticed only for La<sub>0.2</sub>Sr<sub>0.8</sub>RuO<sub>3</sub> sample, for which  $M_R$  decreases with increasing pressure with the rate  $dM_R/dP=-0.06$  emu/(g kbar).

TABLE II. Crystallographic data for SrRuO<sub>3</sub> sample at 50 K and 5.5 kbar. Space Group:  $Pbnm$ ,  $a=5.5554(3)$  Å,  $b=5.5193(2)$  Å,  $c=7.8276(5)$  Å,  $wRp=6.23\%$ ,  $R(F^2)=7.22\%$ . The atomic displacements are multiplied by 100.

Ion	$x$	$y$	$z$	$U_{\text{iso}}(U_{11})$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Sr	-0.0010(9)	0.0210(5)	0.25	0.36(4)					
Ru	0.5	0	0	0.27(4)					
O(1)	0.7227(5)	0.2785(5)	0.0288(4)	0.33(11)	0.32(11)	0.59(15)	0.03(12)	0.06(12)	-0.08(11)
O(2)	0.0542(9)	0.4941(8)	0.25	0.55(18)	0.27(21)	0.28(25)	0.01(15)	0	0

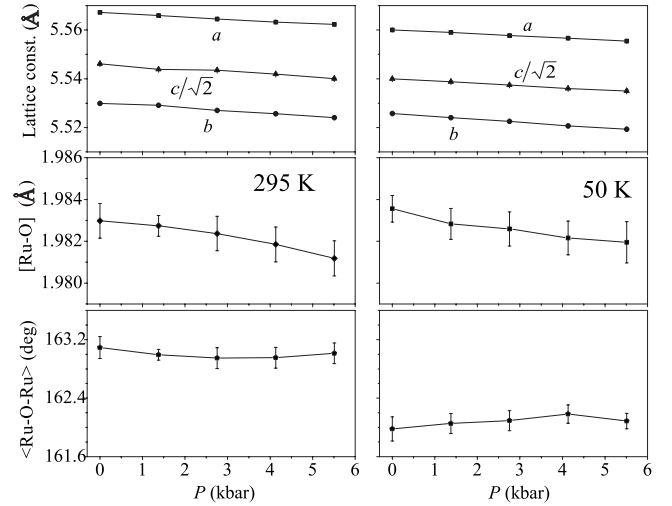


FIG. 6. The pressure dependence of lattice parameters, average Ru-O bond length and average Ru-O-Ru bond angle for SrRuO<sub>3</sub> at 295 and 50 K.

Neutron powder diffraction was performed as a function of pressure at room temperature (295 K) and at 50 K for the pure SrRuO<sub>3</sub> sample. Figure 5 shows exemplary Rietveld refinement profile. Crystallographic parameters, refinements data, atomic positions, and thermal parameters are given in Table II for the measurements taken at  $T=50$  K and  $P=5.5$  kbar. The crystal structure for all temperatures and pressures was refined using the orthorhombic space group  $Pbnm$  consistent with previous reports for stoichiometric SrRuO<sub>3</sub> samples obtained under similar synthesis conditions.<sup>17,25</sup> All of the refinements were of a similar quality. In the diffraction data, neither superstructure diffraction peaks nor unusual peak broadening were detected as a function of pressure. Figure 6 shows lattice parameters and internal structural parameters of the bond lengths Ru-O and bond angles Ru-O-Ru for the range of pressures 0–5.5 kbar. At both temperatures the lattice parameters as well as cell volume  $V$  show uniform decrease with the pressure. The isothermal bulk modulus  $K_T$  was found to be equal to 1800 and to 1900 kbar at 295 and 50 K, respectively. The bond lengths show clear decrease with pressure whereas bond angles appear to remain constant at  $\sim 162^\circ$  and  $163^\circ$  at 50 and 295 K, respectively. Contraction of the lattice parameters with pressure appears thus exclusively from a shrinkage of the [Ru-O] bonds, for example,  $(da/dP) \approx 2\sqrt{2}(d[\text{Ru-O}]/dP)$ . On the other hand, an invariance of the bond angles on pressure is



consistent with a constant tolerance factor  $t(P)=[\text{Sr-O}] \sim \sqrt{2}[\text{Ru-O}]$  (not shown), since these quantities are related,  $t \sim \cos 2\Theta$  (Refs. 17 and 26). It is also consistent with a uniform compression of the unit cell, i.e., within the temperature and pressure ranges of the measurements the structural distortions from the cubic symmetry remain constant. This constancy indicates that the compressibility of the Ru-O bonds is proportional to compressibility of the Sr-O bonds,  $[\text{Sr-O}] \sim \sqrt{2}[\text{Ru-O}]$  and the external pressure effect is quite different from the chemical pressure effect where only one of the bonds is changed through the chemical substitution.

Recently high pressure structural parameters were derived for  $\text{SrRuO}_3$  from low-resolution x-ray diffraction experiment to 250 kbar.<sup>27</sup> Since these x-ray measurements could not determine the atomic positions within the unit cell, the Ru-O-Ru bond angles were estimated from the lattice parameters dependence on pressure, and inferred to decrease initially at a rate of  $-0.086$  deg/kbar. This is not supported by our high-precision measurements for a lower range of pressures as discussed previously. We suspect that the origin of the disagreement comes from contraction of the Ru-O bond lengths under pressure at a rate similar to contraction of the Sr-O bonds. The Ru-O bond length contractions were not accounted for in Ref. 27. Inclusion of Ru-O bond length contraction is critical to interpretation of structural results and understanding of their effect on Curie temperature.

The decrease of  $T_C$  with pressure for  $\text{SrRuO}_3$  was reported earlier and explained in terms of compressive strain acting on sample.<sup>16</sup> Our pressure coefficient  $dT_C/dP = -0.67$  K/kbar is in good agreement with that reported in Ref. 16 ( $-0.57$  K/kbar). Our structural and magnetic data indicate that the major result of application of external pressure is contraction of the Ru-O bonds that leads to decrease of  $T_C$ . While this is contrary to expectation of a rapid increase of the band width and concomitant enhancement of double-exchange FM interactions, it is consistent with suppression of magnetism due to direct exchange interactions through decrease of Ru-Ru distance at a rate of  $d[\text{Ru-Ru}]/dP \approx 0.0007$  Å/kbar. Detailed band structure calculations should be performed to elucidate observed behavior that is independent of the substitution made in  $\text{SrRuO}_3$  and  $T_C(P=0)$ . Below we make some speculations concerning magnetic behavior for specific compounds.

A considerable suppression of  $T_C$  in  $\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$ , when compared to  $\text{SrRuO}_3$  at ambient pressure, has been attributed to attenuation of Ru-O hybridization, caused by chemical pressure from La ion.<sup>7</sup> The external pressure creates further attenuation of Ru-O hybridization evidenced by negative pressure coefficient ( $-0.67$  K/kbar, Fig. 3), in such a way that some magnetic moments become less itinerant, and as a result, the  $\text{Ru}_{t_{2g}}\text{-O}_{2p}\text{-Ru}_{t_{2g}}$  antiferromagnetic (AFM) superexchange interactions are expected at the cost of FM ones.<sup>7</sup> This may lead to a decrease of  $M_0$  with pressure for this sample [Fig. 4(b)]. In the case of  $\text{SrRu}_{0.9}\text{Cr}_{0.1}\text{O}_3$  we observe a weakening of  $\text{Ru}_{t_{2g}}\text{-O}_{2p}\text{-Cr}_{t_{2g}}$  DE interactions evidenced by

decrease of  $T_C$  with increasing pressure ( $-0.53$  K/kbar, Fig. 3). The spin-down electron in  $\text{Ru}_{t_{2g}}$  band becomes more localized giving no contribution to AFM coupling of the Ru and Cr ions.<sup>10</sup> Therefore,  $M_0$  remains constant with increasing pressure. For  $\text{SrRu}_{0.9}\text{Mn}_{0.1}\text{O}_3$  the external pressure probably affects Ru-O hybridization in such a way that it decreases the itinerancy of the Ru 4d electrons and consequently weakens the FM coupling. It is evidenced by the decrease of  $T_C$  with increasing pressure ( $dT_C/dP = -0.39$  K/kbar, Fig. 3). The  $M_0$  remains constant with increasing pressure similarly to that of  $\text{SrRuO}_3$  and  $\text{SrRu}_{0.9}\text{Cr}_{0.1}\text{O}_3$ . Therefore, FM phase volume is not suppressed under pressure. The Mn substitution for Ru seems to be the single factor responsible for controlling the FM phase volume in  $\text{SrRu}_{0.9}\text{Mn}_{0.1}\text{O}_3$  (Ref. 9).

#### IV. CONCLUSIONS

An influence of hydrostatic pressure on phase transition temperature  $T_C$ , spontaneous magnetization  $M_0$ , coercive field  $H_C$ , and remanent magnetization  $M_R$ , of  $(\text{Sr},\text{La})(\text{Ru},\text{Cr},\text{Mn})\text{O}_3$  has been investigated. We have observed a decrease of  $T_C$  with pressure for all of the studied samples. The spontaneous magnetization  $M_0(P)$  and coercive field remain unchanged for most of the samples, except the  $\text{La}_{0.2}\text{Sr}_{0.8}\text{RuO}_3$  sample, where  $M_0$  decreases with pressure. Since within studied pressure range up to 11 kbar, the Ru-O-Ru bond angles remain unchanged and Ru-O bonds decrease, suppression of magnetism cannot be explained by decrease of DE interactions. The weakening of the FM interactions with increasing pressure is thus most probably related to complex band structure effects that include direct Ru-Ru interactions and the modulation of the hybridization caused by contraction of the Ru-O bonds. It should be pointed out also that it is possible to describe the overall suppression of  $T_C$  in these ruthenates within a simple Stoner model. The observed Ru-O bonds decrease increases the overlap between Ru and oxygen orbitals, increasing the effective bandwidth. The concomitant decrease in the density of states at Fermi level would lead than to a decrease of the Curie temperature. Studies of correlation of structural and magnetic properties at higher pressures are necessary to elucidate the dominant role of direct Ru-Ru and indirect Ru-O-Ru exchange interactions.

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- <sup>1</sup>A. Callaghan, C. W. Moeller, and R. Ward, *Inorg. Chem.* **5**, 1572 (1966).
- <sup>2</sup>L. Klein, J. S. Dodge, C. H. Ahn, J. W. Reiner, L. Mieville, T. H. Geballe, M. R. Beasley, and A. Kapitulnik, *J. Phys.: Condens. Matter* **8**, 10111 (1996).
- <sup>3</sup>I. I. Mazin and D. J. Singh, *Phys. Rev. B* **56**, 2556 (1997).
- <sup>4</sup>G. Cao, S. McCall, M. Shepard, J. E. Crow, and R. P. Guertin, *Phys. Rev. B* **56**, 321 (1997).
- <sup>5</sup>A. Kanbayasi, *J. Phys. Soc. Jpn.* **44**, 108 (1978).
- <sup>6</sup>M. F. D. Costa, R. Greatrex, and N. N. Greenwood, *J. Solid State Chem.* **20**, 381 (1977).
- <sup>7</sup>H. Nakatsugawa, E. Iguchi, and Y. Oohara, *J. Phys.: Condens. Matter* **14**, 415 (2002).
- <sup>8</sup>L. Pi, A. Maignan, R. Retoux, and B. Raveau, *J. Phys.: Condens. Matter* **14**, 7391 (2002).
- <sup>9</sup>G. Cao, S. Chikara, X. N. Lin, E. Elhami, V. Durairaj, and P. Schlottmann, *Phys. Rev. B* **71**, 035104 (2005).
- <sup>10</sup>B. Dabrowski, S. Kolesnik, O. Chmaissem, T. Maxwell, M. Avdeev, P. W. Barnes, and J. D. Jorgensen, *Phys. Rev. B* **72**, 054428 (2005).
- <sup>11</sup>Z. H. Han, J. I. Budnick, W. A. Hines, B. Dabrowski, S. Kolesnik, and T. Maxwell, *J. Phys.: Condens. Matter* **17**, 1193 (2005).
- <sup>12</sup>A. J. Williams, A. Gillies, J. P. Attfield, G. Heymann, H. Hupertz, M. J. Martinez-Lope, and J. A. Alonso, *Phys. Rev. B* **73**, 104409 (2006).
- <sup>13</sup>W. A. Harrison, *The Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980).
- <sup>14</sup>J. S. Schilling, *Mater. Res. Soc. Symp. Proc.* **22**, 79 (1984).
- <sup>15</sup>E. P. Wohlfarth, *Physics of Solids under High Pressure*, edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981).
- <sup>16</sup>J. J. Neumeier, A. L. Cornelius, and J. S. Schilling, *Physica B* **198**, 324 (1994).
- <sup>17</sup>B. Dabrowski, O. Chmaissem, P. W. Klamut, S. Kolesnik, M. Maxwell, J. Mais, Y. Ito, B. D. Armstrong, J. D. Jorgensen, and S. Short, *Phys. Rev. B* **70**, 014423 (2004).
- <sup>18</sup>B. Dabrowski, S. Kolesnik, O. Chmaissem, T. Maxwell, M. Avdeev, P. W. Barnes, and J. D. Jorgensen, *Phys. Rev. B* **72**, 054428 (2005).
- <sup>19</sup>M. Baran, V. Dyakonov, L. Gladczuk, G. Levchenko, S. Piechota, and H. Szymczak, *Physica C* **241**, 383 (1995).
- <sup>20</sup>J. D. Jorgensen, J. J. Faber, J. M. Carpenter, R. K. Crawford, J. R. Haumann, R. L. Hitterman, R. Kleb, G. E. Ostrowski, F. J. Rotella, and T. G. Worton, *J. Appl. Crystallogr.* **22**, 321 (1989).
- <sup>21</sup>J. D. Jorgensen, S. Pei, P. Lightfoot, D. G. Hinks, B. W. Veal, B. Dabrowski, A. P. Paulikas, and R. Kleb, *Physica C* **171**, 93 (1990).
- <sup>22</sup>A. C. Larson and R. B. von Dreele, *General Structure Analysis System*, University of California, 1985–1990.
- <sup>23</sup>B. Dabrowski, S. Kolesnik, O. Chmaissem, T. Maxwell, J. Mais, and J. D. Jorgensen, *Phys. Status Solidi B* **243**, 13 (2006).
- <sup>24</sup>B. Dabrowski, M. Avdeev, O. Chmaissem, S. Kolesnik, P. W. Klamut, M. Maxwell, and J. D. Jorgensen, *Phys. Rev. B* **71**, 104411 (2005).
- <sup>25</sup>C. W. Jones, P. D. Battle, P. Lightfoot, and W. T. A. Harrison, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **45**, 365 (1989).
- <sup>26</sup>B. Dabrowski, O. Chmaissem, J. Mais, and S. Kolesnik, *Acta Phys. Pol. A* **105**, 45 (2004).
- <sup>27</sup>J. J. Hamlin, S. Deemyad, J. S. Schilling, M. K. Jacobsen, R. S. Kumar, A. L. Cornelius, G. Cao, and J. J. Neumeier, *Phys. Rev. B* **76**, 014432 (2007).