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# Nuclear magnetic resonance study of the enhanced ferromagnetic ordering in polycrystalline $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$ ( $0 \leq x \leq 0.12$ )

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## Abstract

The ferromagnetic ordering temperature of  $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$  increases to 175 and 186 K for  $x = 0.05$  and  $0.12$ , respectively, from 162 K for  $\text{SrRuO}_3$  ( $x = 0$ ).  $^{53}\text{Cr}$  and  $^{99,101}\text{Ru}$  nuclear magnetic resonance reveals that Cr is in a ‘valence state’ of  $\text{Cr}^{3+}$  ( $t_{2g}^{3\uparrow}$ ), and Ru is in a mixed valence state, namely,  $\text{Ru}^{4+}$  ( $t_{2g}^{3\uparrow 1\downarrow}$ ) and  $\text{Ru}^{5+}$  ( $t_{2g}^{3\uparrow}$ ). A single Ru NMR signal corresponding to  $\text{Ru}^{(4+\delta)+}$  is observed, indicating that the spin-down electron in the Ru 4d shell is less localized in  $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \neq 0$ ). This result is consistent with a broadened Ru  $t_{2g}$  band and a possible  $\text{Ru}^{4+}(\text{d}^4) - \text{O}^{2-} - \text{Ru}^{5+}(\text{d}^3)$  as well as  $\text{Ru}^{4+}(\text{d}^4) - \text{O}^{2-} - \text{Cr}^{3+}(\text{d}^3)$  double-exchange interaction. This exchange interaction involves the  $\text{Cr}^{3+}$  in the ferromagnetic ordering and enhances the ordering temperature.

## 1. Introduction

$\text{SrRuO}_3$ , the only known 4d transition metal oxide which is ferromagnetic, has attracted much attention due to its rich electronic and magnetic properties [1, 2] and possible technological applications [3].  $\text{SrRuO}_3$  orders ferromagnetically below  $T_c \approx 160$  K and has an ordered moment as high as  $1.6 \mu_B/\text{Ru}$  [4]. Despite its robust ferromagnetism, the magnetic ordering temperature of  $\text{SrRuO}_3$  can be easily suppressed [3–10]. A moderate reduction of the ordering temperature ( $T_c = 140$  K) has been observed in thin films of  $\text{SrRuO}_3$  deposited on (100)  $\text{SrTiO}_3$  substrates [3]. This reduction is attributed to strain effects due to the lattice mismatch of 0.64%, which is consistent with the suppression of  $T_c$  under high pressure in bulk  $\text{SrRuO}_3$  [5]. Under high pressure,  $T_c$  is reduced at a rate of  $\partial T_c / \partial P = -5.7 \pm 0.2$  K GPa<sup>-1</sup> [5]. Annealing

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under a high-pressure (HiP) oxygen atmosphere introduces randomly distributed vacancies into the Ru sites while keeping the O content constant [6]. As a result,  $T_c$  drops drastically to 45 K with 9% Ru vacancies [6]. This suppression is attributed to an increased Ru formal valence. Substitution into Sr sites suppresses  $T_c$  as well. For example, isovalent Ca substitution for Sr suppresses  $T_c$  uniformly while maintaining the metallic conductivity [4, 7]; a small concentration of heterovalent Na ( $\leq 12\%$ ) which is substituted for Sr reduces  $T_c$  rapidly to 70 K and induces an insulating state [8]. In the former case, the suppression is attributed to an increased orthorhombic distortion and a larger deviation of the Ru–O–Ru bond angle from  $180^\circ$  [2], while in the latter case, the suppression is thought to be similar to the high-pressure effect [8].  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ , and  $Mn^{3+}$  doped into the Ru sites decrease  $T_c$  significantly, down to 105 K [9]. This suppression of  $T_c$  is thought to be due to the interaction between the doping cations and the Ru  $t_{2g}$  band, which results in a narrowed bandwidth [9]. Finally, a low- $T_c$  magnetically ordered phase of  $SrRuO_3$  has been reported which apparently depends on the synthesis temperatures [10].

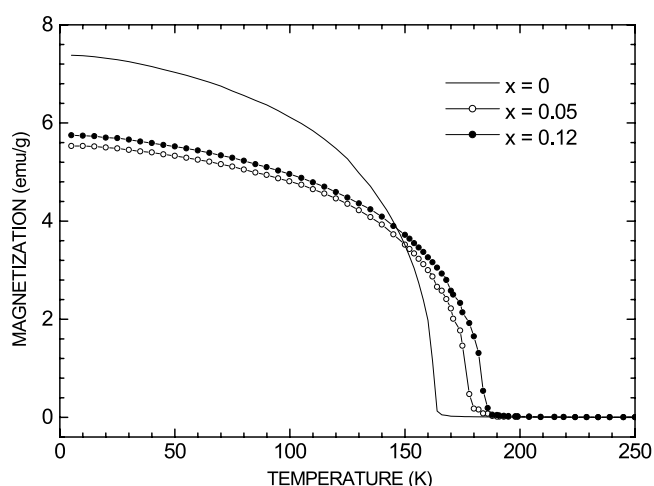
With all of the substitutions known so far,  $Cr^{3+}$ , when substituted for Ru, has been found to increase  $T_c$  up to 188 K and is the lone exception, making it very special [9]. A broadened Ru  $t_{2g}$  bandwidth has been suggested in this case [9]. In order to understand the microscopic origin of the enhancement of  $T_c$ , and how Cr is involved in the magnetic ordering, local studies using nuclear magnetic resonance (NMR), along with complementary magnetization measurements, have been carried out.

## 2. Experimental apparatus and procedure

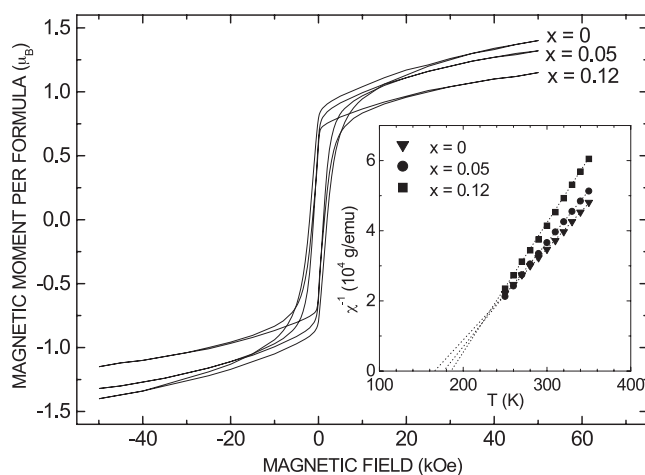
Polycrystalline samples of stoichiometric  $SrRuO_3$  and two Cr-substituted  $SrRu_{1-x}Cr_xO_3$  compounds with  $x = 0.05$  and  $0.12$  were synthesized from mixtures of  $SrCO_3$ ,  $RuO_2$  (prefired in air at  $600^\circ C$ ), and  $Cr_2O_3$ . Calcination of the starting mixtures was done for short periods of time at  $800^\circ C$  to avoid the conspicuous volatility of  $RuO_2$  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 sintering temperature of  $1100$  and  $1370^\circ C$  for  $x = 0$  and  $x \neq 0$  samples, respectively. A final annealing was performed in air at  $1100$  and  $1340^\circ C$  for the  $x = 0$  and  $x \neq 0$  samples, respectively. Three  $\approx 2$  g samples were obtained and examined by x-ray diffraction (XRD) on a Bruker powder diffractometer using  $Cu K\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). X-ray diffraction patterns were recorded within  $20^\circ \leq 2\theta \leq 80^\circ$  with a  $2\theta$  step of  $0.02^\circ$ . Within the sensitivity limit ( $\approx 5\%$ ), all three samples show a single phase with the  $GdFeO_3$ -like orthorhombic structure. Magnetization measurements were carried out on a Quantum Design MPMS SQUID magnetometer for temperatures  $5 \text{ K} \leq T \leq 350 \text{ K}$  and magnetic fields  $-50 \text{ kOe} \leq H \leq +50 \text{ kOe}$ . Zero-field spin-echo NMR was carried out on a conventional two-pulse spectrometer with phase sensitive detection. The NMR probe was located in a double dewar system with which temperatures down to  $1.3 \text{ K}$  were achieved by pumping on liquid helium. The NMR signals were optimized by adjusting the excitation power in a  $\pi/2-\tau-\pi$  pulse sequence. Once NMR signals were optimized, the same excitation conditions were maintained over the entire frequency range of measurement. Usable spectra were obtained by averaging the NMR signals 500–2000 times at various frequency intervals across the spectrum.

## 3. Results and discussion

The temperature dependence of the DC magnetization presented in figure 1 clearly shows that the magnetic ordering temperatures of  $SrRu_{1-x}Cr_xO_3$  ( $x \neq 0$ ) are significantly increased



**Figure 1.** DC magnetization for  $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$  versus temperature in a field of 50 Oe upon cooling.  $T_c$  is increased to 175 and 186 K for samples with  $x = 0.05$  and  $0.12$ , respectively, from 162 K for  $\text{SrRuO}_3$ .



**Figure 2.** Full hysteresis loops for  $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$  obtained at 5 K. Samples with  $x \neq 0$  have smaller coercive fields than  $\text{SrRuO}_3$  and the ordered moments per formula at 50 kOe are monotonically suppressed with  $x$ . The inset shows best fits to the Curie–Weiss law in the paramagnetic state.

with respect to  $\text{SrRuO}_3$ . The values of  $T_c$  are determined to be 175 and 186 K for samples with  $x = 0.05$  and  $0.12$ , respectively, compared with 162 K for  $\text{SrRuO}_3$  (see table 1). These values are consistent with previous DC magnetization work [4, 9] as well as AC susceptibility measurements [11].

Table 1 summarizes all of the magnetic parameters obtained for  $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$  in this work. Ordered moments and coercive fields listed in columns three and four are derived from the complete hysteresis loops at 5 K (figure 2). A low temperature moment (component) value of  $1.40 \mu_B/\text{Ru}$  is achieved for  $\text{SrRuO}_3$  in the ferromagnetically-ordered state at the largest applied field of 50 kOe, which is in good agreement with previous work [4]. Saturation is not reached under these conditions (5 K and 50 kOe), consistent with the fact that  $\text{SrRuO}_3$

**Table 1.** Magnetic parameters for SrRu<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub>.

$x$	$T_c$ (K)	$\mu_z$ ( $\mu_B$ ) <sup>a</sup>	$H_c$ (Oe)	$\Theta$ (K)	$\mu_{\text{eff}}$ ( $\mu_B$ ) <sup>b</sup>
0	162	1.40	2000	164	2.72
0.05	175	1.32	1200	179	2.49
0.12	186	1.15	1300	187	2.21

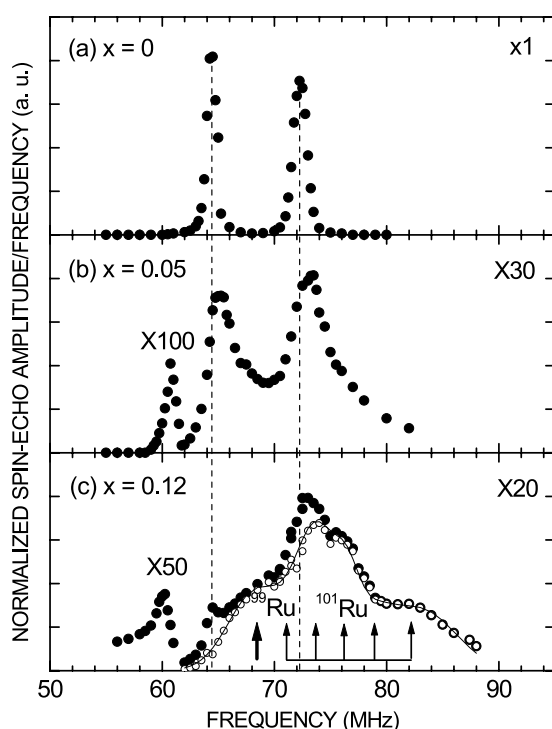
<sup>a</sup> Ordered moment per formula at  $T = 5$  K and  $H = 50$  kOe from hysteresis loops.

<sup>b</sup> Paramagnetic moment per formula from Curie–Weiss fits.

is an itinerant ferromagnet with large anisotropy [12]. A smaller ordered moment value of  $1.32 \mu_B/\text{formula}$  is obtained for the sample with  $x = 0.05$ , and this value is further reduced to  $1.15 \mu_B/\text{formula}$  with  $x = 0.12$ . The coercive field values for SrRu<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> ( $x \neq 0$ ), which are determined to be  $\approx 1200$  Oe, are smaller than that of SrRuO<sub>3</sub>, which is 2000 Oe. These results (both reduced ordered moments and reduced coercive fields) are not intuitively expected, since Cr<sup>3+</sup> (the Cr<sup>3+</sup> valence state is confirmed by <sup>53</sup>Cr NMR as is seen later), with spin  $S = 3/2$ , would have a larger ordered moment  $\langle S \rangle = 3 \mu_B/\text{Cr}$  than Ru<sup>4+</sup>, whose ordered moment would be  $2 \mu_B/\text{Ru}$  with the low spin configuration  $S = 1$ . Experimentally, a value of  $\langle S \rangle \approx 2.82 \pm 0.20 \mu_B/\text{Cr}^{3+}$  is deduced for CrCl<sub>3</sub> by neutron diffraction [13]. It must be noted that assigning of an integral valence in an itinerant system is not strictly valid, and in this work, any assignment of an integer to the valence states for Cr and Ru is taken in the same sense. As for the coercive field, disorder induced by doping is expected to enhance the pinning effect on the domain walls and, consequently, the coercive field would become larger [9, 14]. For example, high-pressure (HiP) oxygen annealing of SrRuO<sub>3</sub> introduces a small amount (a few per cent) of randomly distributed vacancies in the Ru network. As a result, the coercive field is increased to 4500 Oe [14]. These results, while somehow unexpected, do indicate a modified magnetism in SrRu<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub>, suggesting that the Cr dopants are participating in the magnetic ordering and not just acting as defects. Since the itinerant ferromagnetism in SrRuO<sub>3</sub> originates from the narrow Ru  $t_{2g}$  band and the bandwidth is crucial in determining the nature of the magnetism [4], any contribution to broaden the band is expected to enhance the ferromagnetism. Cr<sup>3+</sup>, due to its  $t_{2g}^3 e_g^0$  electronic configuration and close ionic size to Ru<sup>4+</sup> ( $0.615 \text{ \AA}$  versus  $0.62 \text{ \AA}$ ), favours hybridization with the Ru<sup>4+</sup>  $t_{2g}$  band, resulting in a broadened bandwidth [9]. As a result, the ferromagnetism in SrRu<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> is enhanced as is evidenced by the increased ordering temperature. Columns five and six list the parameters deduced from Curie–Weiss (CW) fits of the susceptibility over the temperature range  $250 \text{ K} \leq T \leq 350 \text{ K}$  (see the inset in figure 2). The Curie–Weiss law is given by

$$\chi(T) = \frac{N\mu_{\text{eff}}^2}{3k_B(T - \Theta)} + \chi_0, \quad (1)$$

where  $N$  is the concentration of the magnetic moments,  $\mu_{\text{eff}}$  is the effective paramagnetic moment (magnitude),  $k_B$  is the Boltzmann constant,  $\Theta$  is the CW temperature, and  $\chi_0$  is a temperature-independent term which reflects the core diamagnetism, Landau diamagnetism, and Pauli paramagnetism. The experimental data fit a single CW law although two types of moments exist for  $x \neq 0$ , and  $\Theta$  values of 164, 179 and 187 K are obtained for samples with  $x = 0, 0.05$  and  $0.12$ , respectively.  $\mu_{\text{eff}}$  is determined to be  $2.72 \mu_B/\text{Ru}$  for SrRuO<sub>3</sub>, consistent with a valence of Ru<sup>4+</sup> with  $S = 1$ . It is noteworthy that  $\mu_{\text{eff}}$  is monotonically reduced to  $2.49 \mu_B/\text{formula}$  and  $2.21 \mu_B/\text{formula}$  for samples with  $x = 0.05$  and  $0.12$ , respectively. These values are significantly smaller than the theoretical combination of Ru<sup>4+</sup> ( $2.83 \mu_B/\text{Ru}$  with  $S = 1$ ) and Cr<sup>3+</sup> ( $3.87 \mu_B/\text{Cr}$  with  $S = 3/2$ ). In a study of the Sr<sub>1-x</sub>Ca<sub>x</sub>RuO<sub>3</sub> system, the paramagnetic moments of Ru were reported to increase somewhat with  $x$ , while the Ru



**Figure 3.** Zero-field spin-echo NMR spectra for  $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$  at 1.3 K. (a)  $x = 0$ , the peaks at 64.4 and 72.2 MHz are due to  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  isotopes, respectively. (b)  $x = 0.05$ , the sharp peak centred at 60.8 MHz is attributed to  $^{53}\text{Cr}$  and the two peaks at 65.3 and 73.3 MHz are attributed to  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$ , respectively. (c)  $x = 0.12$ , the sharp peak centred at 60.3 MHz is attributed to  $^{53}\text{Cr}$ , and the broad spectrum ( $\bullet$ ) between 62 and 90 MHz is attributed to  $^{99,101}\text{Ru}$ . Open circles ( $\circ$ ) show the spectrum after subtraction of the intensity from the  $\text{SrRuO}_3$  impurity phase and the line is a fit to the data using Gaussian peaks indicated by the arrows (see text).

$t_{2g}$  bandwidth decreases with  $x$  [15]. Thus, the small paramagnetic moments obtained in  $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \neq 0$ ) may also hint at a broadened  $t_{2g}$  band due to the participation of the  $\text{Cr}^{3+}$  in the band formation.

Figure 3 shows the zero-field spin-echo NMR spectra obtained at 1.3 K for  $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$ . The NMR spin-echo signals for the two samples with  $x \neq 0$  are considerably weaker than that of  $\text{SrRuO}_3$ . In order to compare the spin-echo amplitudes directly, a factor (by which the amplitude has been multiplied) is provided in figure 3. The NMR spectrum for  $\text{SrRuO}_3$  (figure 3(a)) consists of two well-defined peaks at 64.4 and 72.2 MHz, assigned to the  $^{99}\text{Ru}$  (gyromagnetic ratio  $\gamma = 0.19645 \text{ MHz kOe}^{-1}$ , nuclear spin  $I = 5/2$ ) and  $^{101}\text{Ru}$  ( $\gamma = 0.22018 \text{ MHz kOe}^{-1}$ ,  $I = 5/2$ ) isotopes, respectively. These NMR peak frequencies correspond to a hyperfine field of  $-328 \text{ kOe}$  at the Ru nuclei, which is characteristic of the low-spin state of  $\text{Ru}^{4+}$  with  $S = 1$  [15]. The NMR spectra for the two samples with  $x \neq 0$  can be considered to fall within two frequency ranges. For the sample with  $x = 0.05$  (figure 3(b)), the sharp peak centred at 60.8 MHz is attributed to  $^{53}\text{Cr}$  and the two peaks located between 62 and 82 MHz are attributed to  $^{99,101}\text{Ru}$ . Similarly, for the sample with  $x = 0.12$  (figure 3(c)), the peak centred at 60.3 MHz is assigned to  $^{53}\text{Cr}$  and the broad spectrum with features located between 62 and 90 MHz is assigned to  $^{99,101}\text{Ru}$ .

Because of the  $^{53}\text{Cr}$  NMR peak frequencies, Cr is believed to be in a valence state of  $\text{Cr}^{3+}$ . In a series of chromium trihalides, where Cr is in the  $\text{Cr}^{3+}$  state [13], the  $^{53}\text{Cr}$  NMR

**Table 2.** NMR parameters for SrRu<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub>.

$x$	$H_{\text{hf}}^{\text{Cr}}$ (kOe)	$H_{\text{hf}}^{\text{Ru}}$ (kOe)	$^{101}\nu_{\text{Q}}^{\text{Ru}}$ (MHz)	$^{99}\nu_{\text{Q}}^{\text{Ru}}$ (MHz)
0	—	-328	0.44 <sup>a</sup>	0.077 <sup>a</sup>
0.05	-253	-333	1.6	0.28
0.12	-250	-348	4.7	0.81

<sup>a</sup> Data from [15].

peaks were found within 50–63 MHz [16]. With a reasonable assumption that the hyperfine coupling constant of Cr is independent of the valence state, frequency ranges of 67–84 and 33–42 MHz are estimated for  $^{53}\text{Cr}^{2+}$  and  $^{53}\text{Cr}^{4+}$ , respectively. A search for  $^{53}\text{Cr}^{4+}$  was made over the frequency range 27–50 MHz; however, no detectable signal was found. Given the facts that  $\text{Cr}^{3+}$  is the most stable valence state for chromium which forms stable salts with all the common anions and that  $\text{Cr}^{4+}$  is largely confined to peroxo- and fluoro-complexes [17], the peaks found at 60.8 MHz ( $x = 0.05$ ) and 60.3 MHz ( $x = 0.12$ ) can be taken as the evidence that Cr is in the  $\text{Cr}^{3+}$  state for SrRu<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub>. For  $^{53}\text{Cr}$ ,  $\gamma = 0.2406 \text{ MHz kOe}^{-1}$  and  $I = 3/2$ , which result in hyperfine fields ( $H_{\text{hf}}^{\text{Cr}}$ ) of -253 and -250 kOe for samples with  $x = 0.05$  and 0.12, respectively. The negative value indicates a dominant core-polarization contribution to  $H_{\text{hf}}^{\text{Cr}}$ , which is confirmed by the negative shift of the NMR frequency in an external magnetic field. Typically, in a ferromagnetically-ordered system, the zero-field NMR signals are strengthened due to an enhancement of the applied rf field ( $H_1$ ). This enhancement originates from the coherent motion of the ferromagnetic moments with  $H_1$  and makes the NMR signals observable with small amplitude of  $H_1$ . The appearance of the  $^{53}\text{Cr}$  NMR signal here is facilitated by the  $H_1$  enhancement, and thus provides evidence that Cr is involved in the ferromagnetic ordering for SrRu<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub>. Due to the small fraction of Cr in these samples as well as the low natural abundance for  $^{53}\text{Cr}$  (9.5%), the  $^{53}\text{Cr}$  NMR signals are weak compared with the  $^{99,101}\text{Ru}$  signals. In figure 3, the heights of the  $^{53}\text{Cr}$  peaks have been multiplied by different factors for clarity.

The  $^{99,101}\text{Ru}$  NMR peaks are progressively broadened with  $x$ , which is believed to be quadrupolar in origin as a consequence of the disorder introduced by Cr doping. The quadrupole effect, which originates from the interaction between the electric field gradient (EFG) and the nuclear quadrupole moment  $Q$ , is characterized by a quadrupole frequency  $\nu_{\text{Q}}$  given by

$$\nu_{\text{Q}} = \frac{3e^2qQ}{2I(2I+1)}, \quad (2)$$

where  $eq$  is the EFG component  $V_{zz}$ , and  $I$  is the nuclear spin. An accurate determination of  $\nu_{\text{Q}}$  from the broadening, however, is not possible. In an earlier work on SrRuO<sub>3</sub>, quadrupole oscillations of the spin-echo amplitude were observed as a function of the separation  $\tau$  between the two rf pulses, and  $\nu_{\text{Q}}$  was accordingly determined as 0.077 and 0.44 MHz for  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$ , respectively. Since the broadening is directly proportional to  $\nu_{\text{Q}}$  according to first-order perturbation theory, values of  $\nu_{\text{Q}}$  are estimated for SrRu<sub>1-x</sub>Cr<sub>x</sub>O<sub>3</sub> with  $x \neq 0$  by comparing the FWHM width of the corresponding NMR peaks with that of SrRuO<sub>3</sub>. As is seen in table 2,  $\nu_{\text{Q}}$  increases rapidly with  $x$ . Consequently, the  $^{99,101}\text{Ru}$  peaks are no longer resolvable in the case of  $x = 0.12$ , and a broad spectrum is observed. Besides the broadening, the  $^{99,101}\text{Ru}$  NMR peaks shift to higher frequencies with Cr doping. This shift, which is attributed to an increase of the hyperfine field  $H_{\text{hf}}^{\text{Ru}}$  (magnitude) at the Ru nuclei, indicates a change of the Ru valence state compared to that for the undoped SrRuO<sub>3</sub>. Since Cr is doped in as  $\text{Cr}^{3+}$ , charge neutrality requires that an equal amount of Ru<sup>4+</sup> increases to Ru<sup>5+</sup> by losing its spin-down electron in the

4d shell. The existence of some  $\text{Ru}^{5+}$  has also been suggested for the  $\text{SrRu}_{1-v}\text{O}_3$  system, where  $v$  is the portion of vacancies in the Ru network introduced by either HiP oxygen annealing or a nonstoichiometric synthesis condition [6]. Also,  $\text{Ru}^{5+}$  is found to coexist with  $\text{Ru}^{4+}$  in the magnetic superconductor  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  [18]. In this work, a search for  $\text{Ru}^{5+}$  was made over the frequency range 110–145 MHz, which is a typical range for  $\text{Ru}^{5+}$  [18]; however, no detectable NMR signal was found. As mentioned above, by the charge neutrality requirement, 5% and 12% of  $\text{Ru}^{5+}$  would be introduced into the samples with  $x = 0.05$  and 0.12, respectively. By assuming that the enhancement factors for the  $\text{Ru}^{4+}$  and  $\text{Ru}^{5+}$  are essentially the same, and including the favourable factor of  $\approx 2$  for  $\text{Ru}^{5+}$  due to the higher frequency, an estimate for the  $\text{Ru}^{5+}$  NMR signal to noise can be made. Based on these considerations, the NMR spectrum for static  $\text{Ru}^{5+}$  would have approximately 11% and 27% of the intensity of  $\text{Ru}^{4+}$  for samples with  $x = 0.05$  and 0.12, respectively, which is easily within the sensitivity of the instrumentation. The absence of the  $\text{Ru}^{5+}$  NMR signal indicates that there exists essentially no static  $\text{Ru}^{5+}$  in the magnetically-ordered state on a timescale longer than  $10^{-8}$  s. Thus, it is likely that the spin-down electron in the Ru 4d shell is more itinerant in  $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \neq 0$ ) compared with  $\text{SrRuO}_3$  and, consequently, an average valence of  $\text{Ru}^{(4+\delta)+}$  results. This conclusion is consistent with the hypothesis that the Ru  $t_{2g}$  bandwidth is broadened with Cr doping [9] and creates the possibility of a  $\text{Ru}^{4+}(\text{d}^4)\text{-O}^{2-}\text{-Ru}^{5+}(\text{d}^3)$  double-exchange (DE) interaction. This DE interaction, which may involve  $\text{Cr}^{3+}$  in the magnetic ordering as well, since  $\text{Cr}^{3+}$  has a similar electronic structure ( $t_{2g}^{3\uparrow}$ ) to that of  $\text{Ru}^{5+}$  ( $t_{2g}^{5\uparrow}$ ), enhances the magnetic ordering and increases the ordering temperature. The slight difference in  $^{53}\text{Cr}$  NMR peak frequency for the two Cr-doped samples may be due to this DE exchange, with the spin-down electron having slightly larger probability on the Cr sites for the sample with  $x = 0.12$ . In a recent work on Mn-doped  $\text{SrRuO}_3$ , a similar DE interaction has been suggested [19].  $\delta$ , the average change in the Ru valence, is expected to be small due to the small fraction of  $\text{Ru}^{5+}$ , which is consistent with the small shift in the  $^{99,101}\text{Ru}$  NMR peak frequencies of  $\text{SrRu}_{1-x}\text{Cr}_x\text{O}_3$  ( $x \neq 0$ ) relative to that of  $\text{SrRuO}_3$ . From the  $^{99,101}\text{Ru}$  NMR peak frequencies,  $H_{\text{hf}}^{\text{Ru}} = -333$  kOe is determined for the sample with  $x = 0.05$ . The determination of  $H_{\text{hf}}^{\text{Ru}}$  in the case of  $x = 0.12$  is not so straightforward, since no distinct peaks are observed due to the much larger quadrupole effect. As is shown by solid circles in figure 3(c), besides the  $^{53}\text{Cr}$  sharp peak and the  $^{99,101}\text{Ru}$  main peak which are intrinsic to the  $x = 0.12$  phase, some intensity is also found between 62 and 73 MHz. This intensity is believed to originate from a trace amount of  $\text{SrRuO}_3$  second phase which is not detected by the XRD. A small peak at  $\approx 162$  K appears in the temperature derivative of the field-cooled magnetization,  $dM/dT$ , indicating the existence of  $\text{SrRuO}_3$  impurity. The occurrence of  $\text{SrRuO}_3$  second phase is almost inevitable in the preparation of polycrystalline samples involving Sr and Ru simultaneously [20]. It must be noted that the NMR signal from  $\text{SrRuO}_3$  is particularly strong due to a favourable enhancement factor, and that even a minute amount can contribute signal intensity [15]. Subtracting a weighted  $\text{SrRuO}_3$  spectrum (figure 3(a)) results in a corrected spectrum for the  $x = 0.12$  phase which is shown by open circles in figure 3(c). A fit is made to this spectrum and is shown by the curve in figure 3(c). In making this fit, a Gaussian peak centred at 68.3 MHz is used for  $^{99}\text{Ru}$  and a much broader peak centred at 76.5 MHz is used for  $^{101}\text{Ru}$ , which is the superposition of five peaks indicated by arrows. The reader is referred to Kumagai *et al* [18] for details of quadrupole splitting of the  $^{99,101}\text{Ru}$  NMR spectrum. From this fit, a value of  $H_{\text{hf}}^{\text{Ru}} = -348$  kOe is deduced for the sample with  $x = 0.12$ . Interestingly, if the angle between the Ru moment and the principal axis of the EFG tensor remains the same as that of  $\text{SrRuO}_3$ , a quadrupole frequency of 5.5 MHz is derived for  $^{101}\text{Ru}$  from this fit. As discussed above, a value of 4.7 MHz is derived by comparing the broadening of the NMR peaks with  $\text{SrRuO}_3$ . The difference is most likely due to the change in EFG as a result of the disorder introduced by Cr doping.



#### 4. Conclusions

In conclusion, the ferromagnetic ordering temperature is increased with Cr doping into the Ru sites in SrRuO<sub>3</sub>. The <sup>53</sup>Cr NMR results in a valence state of Cr<sup>3+</sup>. The <sup>99,101</sup>Ru NMR peaks are progressively broadened and shift to higher frequencies with Cr doping. The broadening is attributed to be quadrupolar in origin as a result of the disorder introduced by Cr doping. The shift in frequency indicates a change in the Ru valence state, i.e., part of the Ru<sup>4+</sup> is increased to Ru<sup>5+</sup>. However, only an average valence of Ru<sup>(4+δ)+</sup> is observed by NMR, which indicates that the spin-down electron in the Ru 4d shell is less localized. This result creates a possible Ru<sup>4+(d<sup>4</sup>)</sup>-O<sup>2-</sup>-Ru<sup>5+(d<sup>3</sup>)</sup> as well as Ru<sup>4+(d<sup>4</sup>)</sup>-O<sup>2-</sup>-Cr<sup>3+(d<sup>3</sup>)</sup> DE interaction which involves the Cr<sup>3+</sup> in the magnetic ordering and enhances the ordering temperature.

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