Lattice effects on the physical properties of half-doped perovskite ruthenates

Jaskirat Brar\textsuperscript{1}, Saurabh Singh\textsuperscript{2,3,4}, Kentaro Kuga\textsuperscript{2,3}, Priyamedha Sharma\textsuperscript{1}, Bharath M\textsuperscript{1}, Tsunehiro Takeuchi\textsuperscript{2,3} and R Bindu\textsuperscript{1,4,5}

\textsuperscript{1} School of Physical Sciences, Indian Institute of Technology Mandi, Kamand, Himachal Pradesh 175005, India
\textsuperscript{2} Toyota Technological Institute, Nagoya, Aichi 468-8511, Japan
\textsuperscript{3} Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan

E-mail: bindu@iitmandi.ac.in

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Abstract

We investigate the unusual phase transitions in SrRuO\textsubscript{3} and Sr\textsubscript{0.5}Ca\textsubscript{0.5}Ru\textsubscript{1-x}Cr\textsubscript{x}O\textsubscript{3} (x = 0, 0.05 and 0.1) employing x-ray diffraction, resistivity, magnetic studies and x-ray photoemission spectroscopy. Our results show the compounds undergo a crossover from itinerant ferromagnetism to localized ferromagnetism. The combined studies suggest Ru and Cr be in the 4+ valence state. A Griffith phase and an enhancement in Curie temperature (T\textsubscript{c}) from 38K to 107K are observed with Cr doping. A shift in the chemical potential towards the valence band is observed with Cr doping. In the metallic samples, interestingly, a direct link between the resistivity and orthorhombic strain is observed. We also observe a connection between orthorhombic strain and T\textsubscript{c} in all the samples. Detailed studies in this direction will be helpful to choose suitable substrate materials for thin-film/device fabrication and hence manoeuvre its properties. In the non-metallic samples, the resistivity is mainly governed due to disorder, electron-electron correlation effects and a reduction in the number of electrons at the Fermi level. The value of the resistivity for the 5% Cr doped sample suggests semi-metallic behaviour.

Understanding its nature in detail using electron spectroscopic techniques could unravel the possibility of its utility in high-mobility transistors at room temperature and its combined property with ferromagnetism will be helpful in making spintronic devices.

Keywords: ruthenate, structure, bad metal

(Some figures may appear in colour only in the online journal)

1. Introduction

SrRuO\textsubscript{3} is an infinite layer material in the Ruddlesden Popper series \cite{1}. This compound is a Fermi liquid at low temperatures \cite{2}, ferromagnetic below 165 K \cite{3}, shows invar effect \cite{4} and is a bad metal \cite{5} at high temperatures. On Ca doping at the Sr site \cite{6}, throughout the series, the structure is orthorhombic but with increased distortion. The end compound, CaRuO\textsubscript{3} is a paramagnet and exhibits non-Fermi-liquid behaviour at low temperatures \cite{6}. The magnetic anisotropy is also unusually large in the end compounds \cite{3}. The end compounds, despite having structural similarity, have very different physical properties. Such behaviours are strongly related to the change in the Ru-O-Ru network and the orthorhombic distortion and hence to the ground state properties through the behaviour of states close to the Fermi level.

With increase in Ca doping in Sr\textsubscript{1-x}Ca\textsubscript{x}RuO\textsubscript{3}, a ferromagnetic to paramagnetic quantum phase transition is observed. Because of the random distribution of Sr and Ca ions, there occurs distribution in the exchange interaction and the ferromagnetic to paramagnetic transition is not an abrupt one
but an extended one, tailing over a broad range of Ca doping. In the case of Sr$_{1-x}$Ca$_x$RuO$_3$ epitaxial thin films, it has been observed that the tail extends beyond $y = 0.52$ with critical concentration to be $y_c = 0.38$, where the clean system is expected to undergo quantum phase transition \[ T_c \]. In most disordered systems, magnetic quantum phase transitions are found to be sharp. In the case of itinerant magnetic systems, because of the coupling of the magnetic fluctuations with the electronic excitations, the dynamics of the fluctuations get slowed down leading to non-homogeneous ferromagnetic order. Along with the magnetic phase transition, a crossover from the Fermi-liquid to non-Fermi-liquid behaviour is observed at around 70% of Ca doping [8].

Sr$_{0.5}$Ca$_{0.5}$RuO$_3$ sample falls in the tail region of the smeared transition and lies close to the transition region from Fermi-liquid to non-Fermi-liquid. One also expects for the random disorder between Sr and Ca ions to set in at 50% of Ca doping. These behaviours help in studying the precursor to the quantum phase transition. It is also important to note that the critical concentration of Ca at which the $T_c$ goes to zero also depends on the sample preparation, experimental protocol etc. [7]. These compounds are widely used in spintronics [9] to make superlattices of oxides and is also a good candidate for perpendicular magnetic anisotropy-based spintronic material. Recent studies [10] have reported SrRuO$_3$ as a useful candidate in the quantum electronics applications. In these compounds, reports show that structure plays an important role in driving the magnetic ground state [6, 11]. Interestingly, in these ruthenates, on Cr doping at Ru site, an increase in the $T_c$ has been observed [12, 13]. But by doping other 3d transition metals, a decrement in the $T_c$ occurs [12, 14]. Such behaviours are puzzling. The radial extent of 3d states in Cr ion is smaller than the 4d states in Ru ion and also with Ca doping the 4d states are expected to become localized. In such situation, a small change in the structural parameters in terms of the tilt or rotation of the Ru$_2$O$_5$ octahedra can bring about multiple phase transitions. Such localization effects are expected to make the role of electron-electron interaction, electron-phonon coupling, magnetic anisotropy and disorder to be significant.

In order to understand the effect of Cr doping on the magnetic and transport properties of the ruthenates, it is important to determine the valence state of Cr and Ru in these compounds. However, there are contradictory reports in the literature on the valence state of Cr and Ru in the Cr-doped SrRuO$_3$ and CaRuO$_3$. Pi et al [12] studied the effects of doping different 3d ions at the Ru site in SrRuO$_3$. They reported the enhancement of $T_c$ with 10% Cr doping and explained this on the basis of strong hybridization of Cr$^{3+}$ with Ru$^{4+}$. However, this conclusion has been drawn without any experimental verification. Another study, using NMR experiments [15] performed on SrRu$_{1-x}$Cr$_x$O$_3$ ($x = 0.05, 0.12$) have reported that Cr has 3+ valence state and Ru has both 4+ and 5+ valence states. Dabrowski et al [13] studied the crystal structure, magnetic and transport properties of SrRu$_{1-x}$Cr$_x$O$_3$ in the range $0 < x < 0.15$. The rise in $T_c$ has been proposed due to Ru$^{4+}/5+/6+ (d^{3}/3) - O^{2-} - Cr^{4+/3+} (d^{2}/3)$ minority band double-exchange interaction. Williams et al [16] studied the crystal structure and magnetism of SrRu$_{1-x}$Cr$_x$O$_3$ system in the entire composition range $(0 < x < 1)$. From the variation of unit cell volume with composition, they have concluded that Cr is in 3+ valence state in the entire range of study. Another study [17] on the Cr-doped SrRuO$_3$ and CaRuO$_3$ shows the valence state of Cr to be 4+ in these compounds, based on the crystal structure and magnetic measurements.

In this work, we have undertaken x-ray diffraction(XRD), magnetic, transport and x-ray photoemission studies to know the valence state of the Ru and Cr ion, the origin of the phase transition as a function of composition and temperature and the behaviour of $T_c$ in SrRuO$_3$ to Sr$_{0.95}$Ca$_{0.05}$Ru$_{1-x}$Cr$_x$O$_3$ ($x = 0, 0.05$ and 0.1). We have performed spin-polarized density functional theory (DFT) calculations on SrRuO$_3$ to identify the features in the valence band spectra. Our results show a transition from itinerant ferromagnetism to localized ferromagnetism with the change in composition. The Cr-doped samples show an increase in the $T_c$ and the doped compounds stabilize in the Griffith phase. The samples that exhibit metallicity show a direct connection between the resistivity and orthorhombic strain but for the rest of the samples, the transport is mainly governed by disorder and electron-electron correlation effects and a reduction in number of electrons at the Fermi level. Our results show that Ru and Cr stabilize in 4+ valence state. With respect to the undoped sample, the Cr doped compound shows a shift in the chemical potential towards the valence band. Understanding the non-metallic nature of the 5% Cr doped compounds may find its applicability in electronic and spintronic devices.

The observation of direct link between the resistivity and orthorhombic strain in the ab plane will help the scientific community in probing further the origin of the itinerant behaviour or the bad metallic behaviour in case of SrRuO$_3$ and Sr$_{0.5}$Ca$_{0.5}$RuO$_3$. To the best of our knowledge, no such reports are available in the literature. We also observe a connection between the orthorhombic strain and $T_c$. These results will also provide a clue to tuning the exchange interaction or the $T_c$, especially in case of thin films where strain can be controlled by proper selection of substrate materials, offering potential technological applications. These results also provide a test ground for studying Griffith phase in detail in the Cr doped compounds, in understanding the critical exponents and the coupling of magnetic fluctuations to the electronic excitations through spectroscopic studies. Temperature dependent high resolution photoemission studies will be helpful in unravelling the manifestation of such coupling by studying the states close to the Fermi level. At low doping of Cr in the half-doped perovskite ruthenates, one can also harvest the effects of subtle interplay between spin–orbit coupling and electron localization and hence onto the nature of the distortion of the Ru-O$_6$ octahedra.

2. Experimental

Polycrystalline samples SrRuO$_3$, Ca$_{0.5}$Sr$_{0.5}$RuO$_3$, Ca$_{0.5}$Sr$_{0.5}$Ru$_{0.95}$Cr$_{0.05}$O$_3$ and Ca$_{0.5}$Sr$_{0.5}$Ru$_{0.9}$Cr$_{0.1}$O$_3$ were prepared by the solid state reaction method by using...
SrCO$_3$(99.995%), CaCO$_3$(99.995%), RuO$_2$(99.9%) and Cr$_2$O$_3$(99.9%) raw materials supplied by Sigma Aldrich. RuO$_2$ was preheated at 400 °C for 8 h to remove any moisture. Stoichiometric amounts of raw materials were mixed and ground thoroughly for 4 h and calcined at 1000 °C for 24 h. The calcined samples were ground and pressed into pellets of 10 mm diameter and then sintered at 1250 °C for 72 h with two intermediate grindings. The heating and cooling rates were fixed at 5 °C min$^{-1}$ during the sintering process.

Temperature-dependent XRD measurements were done using Rigaku Smartlab x-ray diffractometer for a temperature range of 300 K–10 K. Temperature-dependent dc susceptibility measurements for all the samples except Ca$_{0.5}$Sr$_{0.5}$Ru$_{0.95}$Cr$_{0.05}$O$_3$ were carried out using the Quantum Design SQUID magnetometer for a temperature range of 300 K–1.8 K. For the case of Ca$_{0.5}$Sr$_{0.5}$Ru$_{0.95}$Cr$_{0.05}$O$_3$, the measurements were done using the vibrating sample magnetometer. The field dependent magnetisation measurements up to 5 T were carried out using the Quantum Design SQUID magnetometer.

The temperature-dependent resistivity measurements were carried out using four probe method, commercial physical properties measurement system from Quantum design, USA.

The room temperature (RT) x-ray photoemission spectroscopy (XPS) were collected using a monochromatic AlK$_\alpha$ source and R3000 Scienta analyser having energy resolution of 400 meV. All the core levels were collected after surface cleaning the samples (pellet) in situ by scraping with a diamond file in the chamber with base pressure of $\sim$2 $\times$ 10$^{-10}$ mbar. In the forthcoming sections, we have labelled the samples SrRuO$_3$, Sr$_{1.5}$Ca$_{0.5}$RuO$_3$, Sr$_{0.5}$Ca$_{0.5}$Ru$_{0.95}$Cr$_{0.05}$O$_3$ and Sr$_{0.5}$Ca$_{0.5}$Ru$_{0.9}$Cr$_{0.1}$O$_3$ as sample 1, 2, 3 and 4, respectively.

3. Computational details

The spin-polarized density of states (DOSs) calculations were performed on SrRuO$_3$ using full potential linearized augmented plane wave method as implemented in the Elk code [18]. The PBEsol exchange-correlation functional [19] was used. The crystal structure parameters obtained after Rietveld refinement of the XRD patterns collected at RT were used for calculations. The muffin-tin radii for Sr, Ru and O atoms were considered to be 2.4, 2.0 and 1.6 Bohr, respectively. The difference in total energy required for the termination of the self-consistent loop was set to be less than 10$^{-4}$ Hartree/cell.

4. Results and discussions

Figure 1 shows the Rietveld refinement of the RT XRD patterns of samples 1–4. All the compounds stabilize in orthorhombic structure with $Pbnm$ space group. In this space group, the Wyckoff position of Sr is 4c (x, y, 1/4), Ru is 4a (0, 0, 0), O1 is 4c and O2 is 8d (x, y, z). The crystal structure is shown in figure 2. The RuO$_6$ octahedra show a tilt along the c axis and a rotation in the $ab$ plane in the case of all the compounds studied, figure 2. This is in line with the literature [20, 21]. The features corresponding to the tilting of RuO$_6$ octahedra [20, 22] were found in the XRD patterns. The lattice parameter values thus obtained for the parent compound SrRuO$_3$ are in line with the literature [20]. An unidentified impurity peak [6, 23] is observed only in the case of the parent compound ~34.4° marked as *, figure 1.

4.1. Magnetic studies

Figure 3(a) shows the dc susceptibility of all the samples collected during the field cooled (FC) and zero FC cycles (ZFC) with an applied magnetic field of 2000 Oe. The value of the $T_c$ was obtained from the minima in the temperature derivative of the susceptibility data of the ZFC cycle. It is important to note that the value of the $T_c$ as shown for the case of samples 3 and 4, do not change with the applied field, figures 3(a), (c) and (d). With the decrease in temperature, all the samples show a broad maximum. In the case of sample 1, during ZFC two features are observed, one ~144 K and a broad one ~25 K. It is well...
an increment in the Curie Weiss temperature suggesting the strengthening of the ferromagnetic interactions. The effective magnetic moment obtained from the Curie constant is observed to increase as one goes from sample 1 to sample 2 and later on it decreases, figure 3(f).

The FC and the ZFC curves exhibit bifurcation for all the samples. This suggests magnetic anisotropy exists in all the compounds. Magnetic anisotropy arises due to magnetic crystalline anisotropy, short-range magnetic correlations and/or spin–orbit coupling. In the case of sample 1, reports [25, 26] show magnetic anisotropy with an easy axis lying in the basal plane. The difference between the FC and ZFC magnetisation is represented as $M_{irr}$ is shown in figure 3(g). The $T_{irr}$ values were found from the $M_{irr}$ vs temperature curves. $T_{irr}$ marks the temperature at which the FC and ZFC curves start to bifurcate. It is observed that the values of $T_{irr}$ for samples 1, 2, 3 and 4 are around 155 K, 38 K, 87 K and 96 K, respectively.

In the case of sample 1, the $M_{irr}$ increases rapidly below $T_{irr}$ up to $\sim 110$ K, figure 3(g). The increment is smaller in the temperature range 110 K–18 K and below $\sim 18$ K, there is a sharp increase. From the behaviour of $M_{irr}$, we observe that the magnetic anisotropy decreases as one goes from sample 1 to sample 2. With Cr doping, i.e. as one goes from sample 3 to sample 4, the increase in the $M_{irr}$ suggests an increment in the magnetic anisotropy. It is found that the magnetic anisotropy for sample 3 and sample 4 is more than that of sample 1 at the lowest collected temperature, as compared to the behaviour above 26 and 32 K, respectively. In all the samples, with the decrease in temperature, we observe a continuous increment in the FC susceptibility, figure 3(a). This suggests large coercivity at low temperature. From this behaviour, coercivity at the lowest collected temperature can be written in the following order $\text{Sr}_0.5\text{Ca}_0.5\text{RuO}_3 < \text{SrRuO}_3 < \text{Sr}_0.3\text{Ca}_0.7\text{Ru}_{0.95}\text{Cr}_{0.05}\text{O}_3 < \text{Sr}_0.5\text{Ca}_0.5\text{Ru}_{0.9}\text{Cr}_{0.1}\text{O}_3$. This behaviour can be further substantiated for samples 2, 3 and 4 from the M vs H behaviour collected at 2 K, figure 3(h). The behaviour of the shapes of the FC and ZFC susceptibility curves and the M vs H curves suggest that magnetic anisotropy plays a significant role in these compounds. The effect of magnetic anisotropy is further evident from the decrement in the $M_{irr}$ with the increase in the applied field as seen in the case of samples 3 & 4, figures 3(inssets of (c) and (d)).

The isothermal magnetization data for samples 2 to 4 was collected at 2 K. All the samples show hysteresis, figure 3(h) suggesting the samples to be in the ferromagnetic state. The magnetisation does not saturate even at 5 T. The value of saturation magnetization($M_s$) was obtained by plotting M vs H and extrapolating the x-axis to zero. The values of $M_s$ for different samples are shown in the inset of figure 3(g). For the case of sample 1, the value of $M_s$ was obtained from the literature [27]. It is observed that the value of $M_s$ increases as one goes from sample 2 to sample 4.

As shown in figure 3(e), the value of $\theta_{CW}$ is the same for sample 1 but different for other samples. Also, the inverse susceptibility curves for samples 2, 3 and 4 show a downturn above the ferromagnetic ordering temperature, figure 3(b) but a straight line is seen in the case of sample 1.

Figure 3. (a) FC and ZFC dc susceptibility of all compositions under study. (b) Inverse susceptibility as a function of temperature (Solid lines show the Curie–Weiss fitting). (c) and (d) show the dc susceptibility for samples 3 and 4, respectively at 200 Oe field strength. The insets show the $M_{irr}$ for 200 Oe and 2000 Oe field strength. (e) $T_c$ and $\theta_{CW}$ values for all samples. (f) $\mu_{eff}$ values for all samples. (g) $M_{irr}$ as a function of temperature for data collected at 2000 Oe (inset shows values of $M_{irr}$ at lowest temperature (empty squares) and saturation magnetization values (filled circles)). (h) M vs H curves for samples 2 (at 2K), 3 (at 5K) and 4 (at 2K).

known that this compound shows strong magneto-crystalline anisotropy with an easy axis lying in the $ab$ plane [17, 24]. These broad features observed in the dc susceptibility data are due to such anisotropy existing in this compound. This is also well depicted by the large bifurcation in the FC and ZFC data. Further, in the case of samples 3 and 4, we observe a broad maxima with the increment in the field from 200 to 2000 Oe, figures 3(a), (c) and (d).

In the high-temperature region, above $T_c$, the Curie–Weiss fit to the temperature-dependent inverse susceptibility data is shown in figure 3(b). The Curie Weiss temperature ($\theta_{CW}$) is found by extrapolating the intercept on the temperature axis and it is found to be positive. This suggests that the ferromagnetic exchange correlations exist in all the samples. The Curie Weiss temperature is found to decrease as one goes from sample 1 to sample 2. With Cr doping, we observe...
These observations hint at the possibility of local magnetic ordering in the doped samples. In samples 2 to 4, the Ca and Cr dopant ions are randomly substituted inside the polycrystalline sample which can create regions of local magnetic ordering in these systems above the respective Curie points. To investigate the origin of this behaviour we fitted the inverse susceptibility data with the modified Curie–Weiss equation \( \chi = C/(T - T_R) + 1/\chi_0 \) given as:

\[
\chi^{-1} \propto (T - T_R)^{1-\lambda}
\]

where \( \lambda \) is the Griffiths exponent and \( T_R \) is the temperature at which the system shows the transition from the Griffiths phase to the ferromagnetic phase \([29, 30]\). The exponent \( \lambda \) takes a value \( 0 < \lambda < 1 \) in the Griffiths phase region and is equal to zero in the paramagnetic phase. The best estimate of \( T_R \) is the Curie temperature \( \Theta_{CW} \) as equation (1) gives \( \lambda = 0 \) in the paramagnetic phase for \( T = \Theta_{CW} \) \([31]\).

Figure 4 shows the log of inverse susceptibility vs the log of \( (T/\Theta_{CW} - 1) \) for samples 2, 3 and 4. The temperature region showing linear behaviour (marked as Griffiths phase in the figure) is fitted with a straight line to extract the Griffiths exponent. \( \lambda \) takes the values 0.946, 0.955 and 0.831 for samples 2, 3 and 4, respectively. The positive values of \( \lambda \) confirm the presence of Griffiths phase in the doped samples. \( \lambda \) represents the strength of the Griffith phase \([32]\). The value of the Griffith exponent in the case of sample 3 is more as compared to sample 4. This means that the extent of deviation from the high temperature Curie–Weiss behaviour is more in the case of sample 3 as compared to sample 4. \( T_G \) is the temperature below which the local ordering starts in the sample. Values of \( T_G \) are estimated as the points where \( 1/\chi \) starts deviating from the straight line behaviour seen in the high-temperature region (paramagnetic regime), as shown in figure 4. Based on the values of \( T_G \) and \( \Theta_{CW} \), a magnetic phase diagram is made showing the extent of the Griffiths phase region for the doped samples, figure 4(d). As one goes from sample 2 to 4, the value of \( T_G \) is found to increase from 116 K to 195 K. The width of the temperature region of Griffiths phase is \( \sim 93 \) K for sample 2. It increases for samples 3 and 4 to \( \sim 102 \) K and \( \sim 101 \) K, respectively.

When the random disorder is created in a ferromagnetic material, regions of local magnetic ordering termed as rare regions \([33]\) exist inside the paramagnetic bulk above the Curie temperature. Then the total susceptibility of the system is the sum of the susceptibilities due to the rare regions and the paramagnetic bulk. If the local regions have ferromagnetic ordering, the total susceptibility of the sample will have a higher value as compared to the paramagnetic susceptibility. As a result, a downturn is seen in the \( 1/\chi \) vs \( T \) curve at the temperature where the rare regions start to order.

4.2. Transport studies

Figure 5(a) shows the temperature-dependent resistivity for samples 1 to 4. At RT the resistivity values go in the order, sample 2 < sample 1 < sample 3 < sample 4. Metal to non-metallic transition is observed as one goes from sample 1 to sample 4. At the lowest collected temperature, the behaviour of resistivity of samples 1 and 2 reverses and as we go from sample 2 to 4, it becomes non-metallic. In the temperature region of the study, samples 1 and 2 show metallic behaviour.
and there is a crossover in the resistivity values of samples 1 and 2 below \( \sim 120 \) K. A kink is observed \( \sim T_C \) for samples 1 and 2. Additionally, a slope change is observed at \( \sim 70 \) K in the case of sample 1. In the case of sample 3, a metal to non-metallic transition is observed at \( \sim 116 \) K with the decrease in temperature. Sample 4 shows non-metallic behaviour in the entire temperature range of the study. We now look closely into the resistivity behaviour of each sample. Because samples 3 and 4 lie in the transition region, one can expect the non-metallic behaviour more of disorder-induced rather than the Arrhenius type of behaviour and the disorder being induced due to non-metallic regions present in the metallic matrix.

In literature [34], the kink observed in resistivity around \( T_C \) in case of the sample 1 is attributed to the scattering associated with the short-range spin fluctuations around \( T_C \). This is as per Fisher–Langer theory [35]. Reports show that in the case of this compound, the resistivity increases up to 900 K, violating the Mott-Ioffe-Regel limit [5]. The behaviour of the resistivity data was understood using different models. In the case of samples 1 and 2, for \( T < 25 \) K, the resistivity data follows the Fermi liquid behaviour with the functional form:

\[
\rho = \rho_0 + AT^2
\]

where \( \rho_0 \) is the residual resistivity and \( A \) is the temperature coefficient. The values of coefficient \( A \) obtained from fitting are \( 4.43 \times 10^{-5} \) cm and \( 3.77 \times 10^{-8} \) cm, respectively, figures 5(b) and (c). These values are close to the values obtained in the case of strongly correlated systems [35].

Two different conduction mechanisms were found in case of sample 4 in two temperature regions. In the intermediate temperature region, the resistivity data is fit with Greaves’ Variable Range Hopping (VRH) mechanism [36], following equation (3):

\[
\rho(T) = AT^{1/2} \exp(T_G/T^{4/7})
\]

where \( T_G \) is the characteristic temperature of Greaves’ VRH and \( A \) is the pre-exponential factor. Mott suggested that disordered systems have random potentials in the bulk, because of which the electrons show VRH \( (ln \rho \sim T^{-1/4}) \) in the lower temperature regimes [37, 38]. At the higher temperature range, the thermal energy is sufficient to hop electrons between the nearest neighbour sites irrespective of the potentials and the system shows activated conduction \( (ln \rho \sim T) \). For the intermediate temperature range, where both optical and acoustic phonons are responsible for the hopping of electrons, Greaves’ VRH conduction mechanism is expected. The temperature range of the Greaves’ VRH mechanism is typically \( \theta_B/4 \leq T \leq \theta_B/2 \) where \( \theta_B \) is the Debye temperature of the sample [36, 39]. The straight line fit between \( ln(\rho) \) and \( T^{-1/4} \) (figure 5(d)) is found in the temperature range 145 K–268 K, giving the value of \( \theta_B \) in the range 536 K–580 K.

In the lower temperature range, 70 K–100 K, the resistivity data is found to exhibit the Mott VRH conduction mechanism following equation (4). Natural log of \( \rho \) shows straight-line behaviour when plotted against \( T^{-1/4} \), figure 5(e):

\[
\rho(T) = \rho_0 \exp(T_0/T)^{1/4}.
\]

4.3. Structural studies

To understand the link between crystal structure, transport properties and magnetism, we now analyse the temperature-dependent structural parameters. In figure 6 we show the temperature dependence of the lattice parameters for all the samples. There is a significant change in the lattice parameter values with temperature and composition. The temperature-dependent volume of the unit cell for all the samples is shown in figure 7. To understand this behaviour, fitting was carried out using the anharmonic Debye model [4, 40] which gives the lattice contribution to the unit cell volume following the equation:

\[
V = V(T = 0) + \frac{9\gamma N \kappa_B}{B} T \left( \frac{T}{\theta_D} \right) \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx
\]

where \( V(T = 0) \), \( \theta_D \), \( \gamma \) and \( B \) are the volume at 0 K, the Debye temperature, the Gr"uneisen parameter and bulk modulus, respectively. The fitting was done in the temperature range extending from \( T_C \) to 300 K for all the samples under study. The results of the fitting are given in table 1. For sample 1, the values of \( \theta_D \) and \( 9\gamma N \kappa_B/B \) obtained from fitting are in line with the earlier reports [4]. As one goes from sample 1 to sample 4...
Figure 7. Variation of unit cell volume with temperature for samples 1, 2, 3 and 4 is plotted in (a)–(d), respectively. Solid lines show the curves generated by the Debye model.

Table 1. Parameters obtained from fitting of equation (5).

| Composition | $V(T = 0 \text{K})$ ($\text{Å}^3$) | $\theta_D$ (K) | $9\gamma Nk_B/B$ | $M_{sat}$ ($\mu_B$) |
|-------------|---------------------------------|----------------|------------------|---------------------|
| Sample 1    | 240.89                          | 522.29         | 0.01932          | 1.52$^a$            |
| Sample 2    | 234.02                          | 542.85         | 0.01661          | 0.50                |
| Sample 3    | 233.33                          | 555.03         | 0.01935          | 0.67                |
| Sample 4    | 232.77                          | 558.35         | 0.01968          | 0.75                |

$^a$The value is taken from [27].

The increment in the $\theta_D$ suggest an increment in the temperature required for phonon excitation which further reflects increment in the strength of the bonds. The value of $\theta_D$ obtained from fitting of the resistivity data (figure 5(d)) is in line with the value obtained from fitting of volume data for the case of sample 4.

The Debye curve, figure 7 generated in the entire temperature range was subtracted from the experimental data. Based on the temperature-dependent behaviour of volume, different regions can be set for each sample. We now present the results of the structural parameters for all the samples.

From figures 8(a)–(d), it is clear that the subtracted volume shows an increase in all the compounds around $T_c$. This is in line with the rise in the $\text{M}_{\text{irr}}$ vs Temperature curve figures 8(a$'$)–(d$'$). Sample 2 shows a hump around 150 K. This occurs due to the unusual behaviour of the b-parameter around this temperature. To explore the link between magnetic anisotropy and crystal structure for sample 2, dc susceptibility with different magnetic field will be helpful or performing such experiments on single crystals with the magnetic field parallel to and perpendicular to the c-axis will be helpful. These behaviours suggest a connection between ferromagnetism, magnetic anisotropy and the structural parameters.

In figures 9(a)–(d), the lattice parameters have been normalised with respect to RT. For the case of sample 1, it is interesting to note that a and c-parameters change by the same amount in all three regions, figure 9(a). In region I, the change in the b-parameter is slightly more as compared to the other two parameters and it deviates significantly in regions II and III. A weak hump is also observed around 50 K in the structural parameters. This is in line with other studies [4].

Unlike sample 1, the nature of the change and the percentage change in the lattice parameters in sample 2 is different, figure 9(b). In this compound, in region I, all the parameters decrease linearly. In region II, the b and c-parameters show a hump around 150 K. The a and c parameters deviate from each other and the change in the b-parameter is significantly different from the other two parameters. From this, it is clear that the change in the a and c parameters is markedly increased as compared to the b parameter. In all three lattice parameters, a small
peak is observed around $T_c$ and in region IV, all the parameters show an increment. Further, it is interesting to note that in the (b−a) vs temperature and (b−c) vs temperature plots, figure 10, a small peak is observed around $T_c$ and a kink around 125 K. The kink observed around 125 K in sample 2 is in line with the slope change observed in the resistivity data around this temperature, figure 5(a).

In figure 10, when we compare the graph obtained for samples 1 and 2, we observe that (b−c) and (c−a) values for sample 1 are larger than that of sample 2. While in the case of temperature dependent (b−a) plot, around 125 K, the (b−a) value of sample 1 is lower than that of sample 2. It is interesting to note that the resistivity of sample 1 also shows a similar crossover with the resistivity of sample 2 around 125 K, figure 5(a). This shows that orthorhombic strain governs the transport behaviour in a wide temperature range, even in the region where the resistivity is linear.

We now look into the behaviour of the normalised lattice parameters as a function of temperature for the case of sample 3. It is interesting to note that as one goes from sample 2 to sample 3, the width of region I extents from 65 K to 80 K, figure 9. The hump in the b-parameter that is observed in sample 2 has now reduced in sample 3 and as the sample enters region III, the b parameter shows a small peak around 30 K. The resistivity data also shows an increment in region III (below 60 K) and metal to non-metallic transition below 60 K as one goes from sample 1 to sample 3 sequentially (figure 5(a)). It is interesting to note that the value of the resistivity in the case of sample 3 lies in the resistivity range shown by semi-metals. However, low-temperature high resolution photoemission and angle-resolved photoemission on the single crystalline compound will be helpful to unravel the nature of this material. From these behaviours, it appears that the b-parameter plays a significant role in governing the resistivity. In the (b−c) vs temperature curve, below 150 K, the samples 2 and 3 values remain almost the same, figure 10. There is a significant difference in the temperature-dependent (c−a) and (b−a) behaviours for samples 2 and 3.

In figure 9(d), we show the temperature variation of the normalised lattice parameters of sample 4. All three lattice parameters are found to decrease in region I. In comparison to samples 2 and 3, the extent of region I has increased to 180 K. In region II, the lattice parameters a and c show a decrement while the b-parameter shows an increment. This is also accompanied by an increment in the resistivity data, figure 5(a). As the sample enters region III, around 40 K, a peak in the b-parameter (figure 9(d)) and an increment in the resistivity are observed. The difference in the lattice parameters namely, (b−c), (c−a) and (b−a) shows a decrement in its values in comparison to the rest of the samples, figure 10.

In figure 10(d) we observe that the behaviour of the $T_c$ and the orthorhombic strain obtained at the lowest collected temperature as a function of composition shows opposite behaviours. Hence depicting the direct link between the orthorhombic strain and $T_c$. Detailed band structure calculations will be helpful in understanding the occupancies of the electrons and deciphering the interactions that govern the properties of these compounds. This also could provide clues on the behaviour of $T_c$ and the origin of ferromagnetism with doping.

To understand the origin of the behaviour of the structural parameters, it is important to understand the valence state of Ru and Cr ions. In order to find out the valence state of Ru and Cr ions, the details of the ionic radii are studied. The ionic radii of Ru$^{4+}$ is 0.62 Å, Ru$^{5+}$ is 0.565 Å, Cr$^{3+}$ is 0.615 Å and Cr$^{4+}$ is 0.55 Å [13, 41]. Hence, if Ru$^{5+}$ and Cr$^{3+}$ exist in this compound, the lattice parameter is expected to increase based on the ionic model. But an opposing trend is observed experimentally, figure 6. Hence, the valence state of Ru is expected to be 4+ in all the samples and in samples 3 and 4, the valence state of Cr is 4+.

To investigate further into this, we look into the results of the magnetic studies. In the case of SrRuO$_3$, the electronic configuration of Ru$^{4+}$ is 4$d^4$ (with 2 unpaired electrons). Hence the magnetic moment ($\sqrt{\eta(n+2)}$) expected will be 2.84 $\mu_B$. The experimental magnetic moment value is similar to that of Ru$^{4+}$. Hence it is expected that Ru is in the 4+ valence state in SrRuO$_3$. In the case of the rest of the samples, had there been Ru$^{5+}$ and Cr$^{3+}$, the effective magnetic moment is expected to be more than that obtained for Ru$^{4+}$ and Cr$^{4+}$ ions but experimentally, the opposite was observed. Hence,
these results are in accordance with Ru and Cr being in the $4^+$ valence state. However, to find the valence state in these compounds XPS measurements were carried out for samples 1 and 4.

4.4. Electronic structure studies

In figure 11(a), we show the RT XPS valence band spectra collected for samples 1 and 4. It is important to note that the XPS represents the bulk electronic structure. The features in the valence band spectra are labelled as A, B, C and D. As we go from sample 1 to sample 4, the intensity at the Fermi level and feature A is found to decrease and an increase in the intensity of feature B is observed.

To identify the features in the valence band spectra, spin-polarized electronic structure calculations were carried out on SrRuO$_3$ compound under DFT, using the structural parameters obtained experimentally. Our calculation results show that the total DOSs (TDOSs) can be divided into 3 regions. Regions 1, 2 and 3 mark the energy range 1 to $-2$ eV, $-2$ to $-4.5$ eV and below $-4.5$ eV, respectively. In region 1, there is a significant contribution from Ru 4d states and less contribution from O 2p states. The region 2 is dominated by O 2p states and there is no significant contribution from Ru 4d states. The region 3 is dominated by O 2p states and there is a weak contribution from Ru 4d states. The contribution of Sr states is found to be insignificant in these regions.

In sample 1, the features A and B that cover the region 1, can be attributed to the dominant contribution from Ru 4d states in comparison to O 2p states. We know that for the Al Kα source, the photoionization cross section for Cr 3d states is one order of magnitude smaller than that for the Ru 4d states and also the number of electrons in the d states are expected to decrease with Cr doping. In such situation one expects decrement in the overall intensity in the region where d-states contribute. But experimentally, we observe, a reduction in the intensity at the Fermi level and feature A and an increment in the intensity of feature B. Such behaviour suggests spectral weight transfer of the intensity from feature A and at the Fermi level to feature B. With Ca and Cr doping, a disorder is expected to be induced that affects the network of Ru-O-Ru bonds. Further the radial extent of Cr 3d states is expected to lead to a reduction in the bandwidth and an increment in the electron-electron correlation strength. So the spectral weight transfer of the intensity from feature A to B and a small shift in these features towards higher binding energy suggest a decrement in the delocalization of the electrons in the d states and increment in its localization due to Cr doping and hence the states that contribute close to the Fermi level are expected to shift to the higher binding energy. The decrement in the number of electrons due to the doping effects could also lead to a decrement in the intensity at the Fermi level. Such behaviour has also been observed in literature and the features A and B have been attributed to coherent and incoherent features, respectively [6]. The coherent feature corresponds to the delocalized states and the incoherent feature to the localization due to electron-electron correlation effects. On connecting these results with the transport properties of samples 1 and 4, we understand that the metal to non-metal transition observed with an increase in doping is associated with disorder, electron-electron correlation and reduction in the number of electrons at the Fermi level.

To understand the transport behaviour from the core level spectra and also the valence state of the Ru ions, core level studies were carried out. All the core level spectra were normalised to the area under the curve after background subtraction.
Figure 12 shows the RT core level spectra collected for samples 1 and 4. In the case of the O 1s spectra, both the samples display two features labelled as peak A and B around 529 and 531 eV, respectively. The feature A is intense as compared to the feature B. In most of the perovskite compounds, the feature A has been attributed to the signal from the oxygen ions intrinsic to the sample while the weak feature B has been attributed to the signal from the surface oxygen and/or adsorbed impurities present in the sample. In the present compounds, the surface cleaning of the samples was done by scraping until the intensity of feature B is minimum with respect to feature A. We observe that the intensity ratio of feature A to feature B is less as compared to that observed in other transition metal oxides [42–44]. This suggests the signals from feature B are intrinsic to the sample. Similar behaviour has been reported in literature [6, 45] and has been attributed to the signals arising primarily due to lattice effects. The different oxygen sites namely apical and the basal oxygen ions in the RuO$_6$ octahedra give rise to different Madelung potentials. Considering the fact that the features A and B arise due to lattice effects, we now attribute the features A and B to the signal arising from O1 and O2 sites, respectively. As one goes from sample 1 to 4, the decrement in the separation between the features A and B suggest the decrement in the separation between the average Ru/Cr-O(1) and Ru/Cr-O(2) bonds lengths, thereby leading to the decrement in Madelung potential between both the oxygen sites. In the case of sample 1, it is 0.0146 Å and for the case of sample 4, it is 0.0059 Å. To understand the behaviour of this Ru 3d spectra, each of the peaks labelled as A and B’ (for Ru 3d$_{3/2}$) and A’ and B’ (for Ru 3d$_{5/2}$). The features A and B correspond to well-screened and poorly-screened final states, respectively. The well-screened feature arises due to the screening of the Ru 3d core hole by the electrons of the ligand through charge transfer. The poorly-screened feature arises when there is no such screening of the core hole. Our results show that the ratio of the area under the curve of peak A to peak B decreases as one goes from sample 1 to 4. It is also observed that the spectrum of sample 4 is shifted to higher binding energy as compared to sample 1. The behaviour of the ratio of the area under the curve of peaks A to B suggests that as the sample enters the non-metallic state, the screening of the core hole due to charge transfer is reduced thus leading to the increment in the area under the curve of the peak B as compared to peak A. The opposite behaviour observed in the shift in the peak position of O1s and Ru 3d states suggest that as the sample enters the insulating state, there is a reduced transfer of electrons from O 2p to Ru 3d states. These behaviours are in line with the structural results where we have observed decrement in the av. Ru-O bond lengths and av. Ru-O-Ru bond angle from sample 1 to sample 4. Considering the fact that the fit matches the experimental spectra in both samples, we attribute the valence state of Ru to be in the 4+ state for both the samples.

The comparison of the Sr 3d core levels of samples 1 and 4 is shown in figure 12(c). Our results show that the intensity of the Sr 3d core level in the case of sample 4 is less as compared to sample 1. This is because of the reduced percentage of Sr in the compound due to Ca doping. To simulate the experimental spectra, for each spin-orbit split peaks, two sets of peaks were generated that constitute the well-screened and poorly-screened final states [6, 46]. The features A and B correspond to the well-screened and poorly-screened channels, respectively of Sr 3d$_{3/2}$ spin-orbit split peak. Similarly, A’ and B’ correspond to that for Sr 3d$_{5/2}$ peak. As one goes from sample 1 to sample 4, the area under the curve of the peak A to B is found to reduce. Such reduction suggests the reduction in the hybridization of the Sr 3d and O 2p states due to the distortion in lattice introduced due to doping. We also observe that the av. Sr-O bond length decreases as one goes from sample 1 to 4. Hence it is expected that the peak position of the Sr 3d core level in the case of sample 4 to be shifted towards higher binding energy while in our case opposite behaviour is observed. So, the observed shift towards lower binding energy can be explained due to the chemical potential shift towards the valence band. This is expected when there is an effective decrement in the number of electrons due to Cr doping.

5. Summary

We investigate the structural, transport, magnetic and electronic properties of SrRuO$_3$, Sr$_{0.5}$Ca$_{0.5}$Ru$_{1−x}$Cr$_x$O$_3$ (x = 0, 0.05 and 0.1) labelled as sample 1 to 4. All the compounds (a) stabilize in orthorhombic structure with Pbnm space group, (b) exhibit a transition from paramagnetic to ferromagnetic state and (c) the magnetization does not saturate even at 5 T. Our combined core level and magnetic studies suggest that Ru and Cr are in 4+ valence state and the chemical potential is found to shift towards the valence band due to Cr doping. At RT, as one goes from sample 1 to sample 4, metal to non-metal behaviour is observed. The samples 3 and 4 lies in the transition region from metal to non-metallic. At low temperatures, the sample 4 obeys the Mott VRH type conduction mechanism and in the intermediate temperature range, it obeys Greaves’ VRH conduction mechanism, thereby suggesting disorder. In addition, the opposite behaviour of the effective paramagnetic magnetic moment and the moment obtained from M vs H as a function of composition; bifurcation of the ZFC and FC magnetic susceptibility data and its decrease with an increase in the applied magnetic field suggest strong magnetic anisotropy existing in the compounds under study.

The temperature-dependent resistivity of samples 1 and 2 reveal its direct link with the orthorhombic strain. A microscopic understanding of the nature of such strain is vital in unravelling the interactions at play. In the case of sample 4, even though the orthorhombic strain is reduced in comparison to the sample 1, a decrement in the metalllicity is observed. This can be understood based on the role played by electron-electron correlation effects and reduction in the number of electrons. These effects lead to the reduction in the
DOSs at the Fermi level which is revealed in the valence band studies. The disorder is also expected to localize the electrons at the Fermi level.

We also observe a direct link between the low-temperature orthorhombic strain, magnetic anisotropy and the $T_c$ values with composition. The non-metallic nature observed in the Cr-doped samples also demands careful studies for its utility in electronic and spintronic devices.

Data availability statement

The data cannot be made publicly available upon publication because they are not available in a format that is sufficiently accessible or reusable by other researchers. The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Saurabh Singh https://orcid.org/0000-0003-2209-5269
R Bindu https://orcid.org/0000-0002-6284-0561

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