Ferromagnetic CaRuO$_3$

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The non-magnetic and non-Fermi-liquid CaRuO$_3$ is the iso-structural analog of the ferromagnetic (FM) and Fermi-liquid SrRuO$_3$. We show that an FM order in the orthorhombic CaRuO$_3$ can be established by the means of tensile epitaxial strain. The structural and magnetic property correlations in the CaRuO$_3$ films formed on SrTiO$_3$ (100) substrate establish a scaling relation between the FM moment and the tensile strain. The strain dependent crossover from non-magnetic to FM CaRuO$_3$ was observed to be associated with switching of non-Fermi liquid to Fermi-liquid behavior. The intrinsic nature of this strain-induced FM order manifests in the Hall resistivity too; the anomalous Hall component realizes in FM tensile-strained CaRuO$_3$ films on SrTiO$_3$ (100) whereas the non-magnetic compressive-strained films on LaAlO$_3$ (100) exhibit only the ordinary Hall effect. These observations of an elusive FM order are consistent with the theoretical predictions of scaling of the tensile epitaxial strain and the magnetic order in tensile CaRuO$_3$. We further establish that the tensile strain is more efficient than the chemical route to induce FM order in CaRuO$_3$.

Among various 4d transition metal oxides, the metallic SrRuO$_3$ is the only system which exhibits a long-range ferromagnetic order with a Curie temperature of 165 K$^{1-3}$. Attributes of a large magnetic moment and the metallic behavior of SrRuO$_3$ make it as one of the most suitable materials as ferromagnetic metal electrodes in the spintronic devices based on spin-polarized tunnel junctions$^4$. Owing to various fundamental and technological interests in SrRuO$_3$, a variety of studies have been devoted on this compound in the recent past. However, the large magnetic coercivity of SrRuO$_3$ is a drawback in context of the use of its magnetic order in magnetic devices. In this regard, CaRuO$_3$ is a natural alternative choice as it is iso-structural and iso-electronic with SrRuO$_3$ and is metallic down to low temperatures$^5$. It also exhibits a wide variety of properties such as non-Fermi liquid behaviour$^6$, magnetic quantum criticality$^6$, pressure induced post-perovskite structure$^7$, etc. However, contrary to expectations the CaRuO$_3$ does not exhibit a long-range magnetic ordering. Though it is a known metallic paramagnet$^8$, some studies have indicated that it exhibit antiferromagnetic order with $T_N \sim 110$ K$^2$. Its magnetic state, therefore, is still debated and is far from established. One agreement that has been reached among various researchers is that the CaRuO$_3$ is on the verge of establishing magnetic correlations$^9,10$. In ABO$_3$ structure, the difference in ionic radius of A-site cations Sr$^{2+}$ ($\sim 1.31$ Å) and Ca$^{2+}$ ($\sim 1.12$ Å) is responsible for the difference in the ground state of SrRuO$_3$ and CaRuO$_3$$^{11,12}$. Owing to this reason, there is a definite interest in understanding and manipulating the magnetic ground state of CaRuO$_3$ by the means of chemical substitution, disorder and strain with an aim to obtain ferromagnetic order as in its counterpart SrRuO$_3$.

The CaRuO$_3$ is a metal with a GdFeO$_3$ type orthorhombic structure (a = 5.541 Å, b = 5.362 Å, and c = 7.686 Å, space group – Pnma). The central Ca atom is surrounded by corner sharing RuO$_6$ octahedra$^{14}$. The distortion of RuO$_6$ octahedra affects the Ru-O-Ru bond angles, which consequently affects the electronic and magnetic properties$^{11}$. As per the phase diagram of a class of perovskites, the CaRuO$_3$ lies in the close vicinity of quantum critical region which separates FM and Fermi-liquid systems from the antiferromagnetic and non-Fermi liquids.

It is established that both CaRuO$_3$ and SrRuO$_3$ have strikingly similar electronic structure and correlations$^{11,12}$. So, the sole reason for difference in their magnetic and electrical properties lies in the structural distortion; it is the size effect which results in larger Ru-O-Ru bond angles for the SrRuO$_3$ (see figure 1). Several theoretical studies have suggested the metallic CaRuO$_3$ to be on the verge of establishing ferromagnetic phase transition$^{11,12}$. A magnetic order in CaRuO$_3$ is expected if the Ru-O-Ru bond angles and bond distances can be manipulated by two primary means, namely, chemical substitution at Ca and Ru sites or physical means of epitaxial and uniaxial strains in thin films. He and Cava reported that disorder created by substitution of non-magnetic Ti at Ru site in CaRuO$_3$ induces ferromagnetism in the system$^6$. Extensive studies on CaRu$_{1-x}$M$_x$O$_3$, where M (transition metal) is either a magnetic or non-magnetic ion, have shown doping induced discernible modifications of the magnetic and electronic phases$^{15,16}$. Amongst various ions, the Cr substitution for Ru has proved the most effective as it induces substantial ferromagnetism in CaRuO$_3$$^{17-20}$, albeit transition from metallic to insulating state.
understanding and manipulating the magnetic ground state of metallic CaRuO$_3$ is one of the key issues in perovskite ruthenate. All above-mentioned methods to induce FM order in CaRuO$_3$ involve chemical substitution which disrupts the Ru sub-lattice. Zayak et al theoretically showed that a magnetic order in chemically pure CaRuO$_3$ can be established by applying tensile strain and that the magnitude of the induced FM moments scales with the tensile strain. Compressive strain, on the other hand, does not modify the magnetic state. Experimental observations of any such effects in which FM moment is induced as a function of epitaxial strain in single layer phase-pure films are yet to be realized. In the present work, we have deposited the CaRuO$_3$ thin films on substrates with lattice constants inducing either the compressive strain or the tensile strain. In this letter, we show that the tensile strain induces a weak FM order in pure CaRuO$_3$ thin films and that the magnetic moment scales with the tensile strain, which is commensurate with the theoretical predictions. We further demonstrate that the tensile strained CaRuO$_3$ films possess larger magnetic moment compared to that of chemically modified CaRu$_{0.9}$Cr$_{0.1}$O$_3$ films.

The CaRuO$_3$ films of various thicknesses, in the range of 20–140 nm, were deposited using a 248 nm KrF excimer laser. The parameters for various depositions were: energy density between 1.7–3.3 J/cm$^2$, laser pulse frequency - 4 Hz, substrate temperature - 700°C, O$_2$ partial pressure - 40 Pa, O$_2$ annealing pressure of 1000–1800 Pa. The SrTiO$_3$ (100) [STO] substrate (lattice constant $a$ = 3.905 Å) with a mismatch of about 2% was chosen to obtain tensile strained CaRuO$_3$ (CRO) thin films. Though phase-pure oriented films were formed on BaTiO$_3$ (100) [a ~ 3.99 Å] and MgAl$_2$O$_4$ (100) [a ~ 4.04 Å] substrates, strained films could not be obtained as the lattice mismatch of these substrates with CRO is too large to be accommodated for stability of strained phase. Only films on STO substrate could be stabilized with a reasonable tensile strain. It is known that the CRO films on STO have a tendency for formation of pseudo-heterostructures. The problem with these films is that it is difficult to assign the origin of magnetic moment, if any, to any of the co-existing phases. Hence, it is required to segregate these epistaxial phases and investigate their magnetic properties. We started the usual deposition by varying the energy density and keeping other parameters fixed. The film obtained with energy density of 1.7 J/cm$^2$, say CRO-A, possessed two phases as evident from two closely spaced epitaxial reflections in 0-20 patterns (Fig. 1a). To get rid of one phase in this pseudo-heterostructure, the energy density was increased to 2.3 J/cm$^2$. Thus obtained film, say CRO-B, too possessed two epitaxial phases. Finally, films with single homogenous phase were obtained when laser energy density was fixed at 2.0 J/cm$^2$. With these optimized parameters, films with thickness of 130 nm and 30 nm, respectively, labeled as CRO-C and CRO-D were deposited. For CaRu$_{0.9}$Cr$_{0.1}$O$_3$, the 30 nm and 130 nm films (CRO10-A and CRO10-B, respectively) were deposited with optimized energy density of 2.0 J/cm$^2$.

**Results**

Figure 2 (a) shows the 0-20 x-ray diffraction (XRD) patterns of four representative CaRuO$_3$ thin films. The CRO-A and CRO-B films show two closely spaced peaks indicative of two co-existing structures. There is a clear splitting of both (100) and (200) peaks in CRO-A film (Fig. 2a), which arises from co-existing structural polymorphs, namely, fully and/or partial strained orthorhombic and cubic phases of the CRO film. On the other hand, the optimized films, namely, CRO-C and CRO-D showed only one epitaxial reflection suggesting only one structural form for these films. For analyzing the strain states in the films, the reciprocal space maps (RSMs) were acquired around asymmetric (301) peak. Figure 1c–e shows RSMs for CRO-A, CRO-C and CRO-D films around (301) peak. The salient features of these data are: i) similar to that of data in Fig. 2a, these RSM data show that the CRO-A shows dual peaks while the CRO-C and CRO-D films show only one epitaxial reflection suggesting only one structural form for these films. For analyzing the strain states in the films, the reciprocal space maps (RSMs) were acquired around asymmetric (301) peak. Figure 1c–e shows RSMs for CRO-A, CRO-C and CRO-D films around (301) peak. The salient features of these data are: i) similar to that of data in Fig. 2a, these RSM data show that the CRO-A shows dual peaks while the CRO-C and CRO-D films show only one epitaxial reflection suggesting only one structural form for these films. For analyzing the strain states in the films, the reciprocal space maps (RSMs) were acquired around asymmetric (301) peak. Figure 1c–e shows RSMs for CRO-A, CRO-C and CRO-D films around (301) peak. The salient features of these data are: i) similar to that of data in Fig. 2a, these RSM data show that the CRO-A shows dual peaks while the CRO-C and CRO-D films show only one epitaxial reflection suggesting only one structural form for these films. For analyzing the strain states in the films, the reciprocal space maps (RSMs) were acquired around asymmetric (301) peak. Figure 1c–e shows RSMs for CRO-A, CRO-C and CRO-D films around (301) peak. The salient features of these data are: i) similar to that of data in Fig. 2a, these RSM data show that the CRO-A shows dual peaks while the CRO-C and CRO-D films show only one epitaxial reflection suggesting only one structural form for these films. For analyzing the strain states in the films, the reciprocal space maps (RSMs) were acquired around asymmetric (301) peak. Figure 1c–e shows RSMs for CRO-A, CRO-C and CRO-D films around (301) peak. The salient features of these data are: i) similar to that of data in Fig. 2a, these RSM data show that the CRO-A shows dual peaks while the CRO-C and CRO-D films show only one epitaxial reflection suggesting only one structural form for these films. For analyzing the strain states in the films, the reciprocal space maps (RSMs) were acquired around asymmetric (301) peak. Figure 1c–e shows RSMs for CRO-A, CRO-C and CRO-D films around (301) peak. The salient features of these data are: i) similar to that of data in Fig. 2a, these RSM data show that the CRO-A shows dual peaks while the CRO-C and CRO-D films show only one epitaxial reflection suggesting only one structural form for these films. For analyzing the strain states in the films, the reciprocal space maps (RSMs) were acquired around asymmetric (301) peak. Figure 1c–e shows RSMs for CRO-A, CRO-C and CRO-D films around (301) peak. The salient features of these data are: i) similar to that of data in Fig. 2a, these RSM data show that the CRO-A shows dual peaks while the CRO-C and CRO-D films show only one epitaxial reflection suggesting only one structural form for these films.
like phase transition whereas CRO-A and CRO-B films do not show any indication of FM phase down to low temperatures. In the CRO-C film, the transition temperature is not well defined, but the bifurcation between ZFC and FC curves clearly points towards weak FM phase in this film. The CRO-D film, however, exhibits a pronounced magnetic transition with clearly discernible transition temperature in the vicinity of 100 K. Also, the FC magnetic moment of this film is about 3–4 times more than that of CRO-C film. This suggests that magnetic transition that tends to set in thicker CRO-C film manifests itself more clearly in more strained CRO-D film. To ascertain the hysteretic nature of the FM phase in these films, magnetization versus magnetic field isotherms for all the films were collected at 10 K (Fig. 3c). A linear variation of magnetization with magnetic field for CRO-A and CRO-B films unambiguously confirmed non-magnetic nature of these films. The CRO-C and CRO-D films, whereas, showed a FM like hysteresis which clearly corroborated with their temperature dependent magnetization data for existence of the FM order in these films. Furthermore, the saturation magnetic moment of these films increased with increasing tensile strain, larger for the CRO-D film compare to that for the CRO-C film. Overall, from both the temperature- and field-dependent magnetization data of these magnetic CaRuO$_3$ films, it may be inferred that the magnitude of magnetic moment scales with the tensile strain.

The efficiency of strain in inducing the magnetic moment in CaRuO$_3$ was evaluated by comparing the magnetic properties of the strained films and the Cr-modified films. The CaRu$_{1-x}$Cr$_x$O$_3$ ($x = 0–0.3$) series of bulk compounds shows a maximum of saturation magnetic moment ($M_S$) of $\approx 0.35 \mu_B/\text{f.u}$ for $x = 0.15$. The $M_S$ decreases sharply for $x > 0.15$ and for $x < 0.15$. In our studies we have deposited films of $x = 0.10$ for which the $M_S$ of the bulk compound is $\approx 0.15 \mu_B/\text{f.u}$. We investigated the structure and magnetization of two weakly FM CaRu$_{0.9}$Cr$_{0.1}$O$_3$ films, namely, a 30 nm film (CRO10-A) and a 130 nm film (CRO10-B). Figure 4 show the XRD and the magnetization data of these films. Similar to that in pure CRO films, the out-of-plane lattice constant decreases from 3.886(1) Å to 3.867(1) Å as the film thickness decreases from 130 nm for CRO10-B film to 30 nm for CRO10-A film. A consequent increase in the in-plane lattice parameters, as confirmed by RSM data (not shown here), suggests a larger tensile strain for 30 nm film. The ZFC-FC magnetization versus temperature data shows that both the films exhibit FM transition at around same temperature (Fig. 4b). The magnetization-field isotherms taken at 10 K clearly show that the saturation magnetization increases with the decreasing thickness of film, which implies that the FM moment increases as the tensile increases in Cr-doped films (Fig. 4c). There are two implications of these results, namely, i) the scaling of tensile strain and magnetization is similar to that observed for pure CRO films and ii) magnetic moment of pure strained CRO-D film is marginally large compared to that of Cr-doped strained CRO10-A film. This is surprising because Cr-doping alone has proved most efficient in inducing the FM order in CRO$^{17}$. In present case, the Cr-doped films were strained to same extent as the pure films. Despite this, larger moment in pure
films suggests that the tensile epitaxial strain is clearly more efficient than the chemical route to induce magnetic order in otherwise non-magnetic CaRuO$_3$.

At this point, it is imperative to discuss the Ca/Ru ratio in the CRO films under investigation. In an elaborate study, Rao et al. performed Rutherford Backscattering experiments on CRO/STO (100) thin films prepared under different conditions and showed that the stoichiometric films exhibit a bulk-like metallic behavior whereas the non-stoichiometric films exhibit semiconducting behavior. In present case, the temperature dependence of electrical resistivity for all films reveals that all the CaRuO$_3$ films exhibit metallic behavior (Fig. 5) while the Cr-doped films exhibit semiconducting behavior (see inset of Fig. 5). In both the cases, the resistive behavior is representative of their respective polycrystal bulk counterparts. This suggests a stoichiometric Ca/Ru ratio in the present CaRuO$_3$ films. Also it is known that the non-stoichiometric films possess lattice parameters quite different from that of the bulk then the stoichiometric films. We find that a unit cell volume ($\sim 231$ Å$^3$) of the present films is very close to that of the bulk ($\sim 228.5$ Å$^3$). On the other hand, the Ca-rich non-stoichiometric CRO/STO (100) films possess a significantly larger cell volume of $\sim 242$ Å$^3$. This clearly suggests that all the films used in the present work possess close to ideal Ca/Ru ratio.

Hall resistivity measurements represent a reliable method of determining the carrier concentration, the sign of the charge carriers in conducting systems and the magnetic ground state. The Hall resistivity ($\rho_{xy}$) in is commonly arises from the ordinary Hall effect (OHE) and the anomalous Hall effect (AHE), as given by the relation

$$\rho_{xy}(B) = R_0 B + R_s 4\pi M(B)$$

where B is the magnetic field. First and second terms on right-hand side originate from ordinary and anomalous Hall effects ($\rho_{OHE}$ and $\rho_{AHE}$), respectively. $R_s$ is coefficient of $\rho_{AHE}$ which depends on carrier concentration via relation $R_0 = 1/(nq)$ [n - carrier density, and q - carrier charge]. The $R_s$ is the coefficient of $\rho_{AHE}$ which arises from the sample magnetization. Also, the $\rho_{AHE}$ scales with the magnetic moment and has its origin in spin-orbit interactions. The variation of $\rho_{OHE}$ with magnetic field is linear as $B \ll H$. Any nonlinearity in $\rho_{xy}$ as a function of magnetic field is attributed to the emergence of AHE. The $\rho_{AHE}$ is directly proportional to sample magnetization. Hence, the nonlinear AHE contribution to the $\rho_{xy}$ originates from the
ferromagnetic order in the system. In the low-field regime, the con-
tribution of OHE is generally negligible compared to the AHE.
Hence, a non-zero value of $r_{\text{AHE}}$ in low field regime points towards
ferromagnetic order in the system $^{23,24}$. To verify the magnetic ground
state via anomalous Hall component in our samples, Hall measure-
ment were performed on two CaRuO$_3$ films, namely, a non-magnetic
compressive-strained film on LaAlO$_3$ (100) substrate [CRO/LAO]
and a magnetic tensile-strained film on SrTiO$_3$ (100) substrate
[CRO/STO]. As seen in Figure 6, the CRO/LAO film exhibits linear
variation of $r_{xy}$ with the applied field. Also, there is switching in sign
of charge carriers at about 50 K, however, albeit absence of any non-
linear component (Fig. 6a). This is in agreement with existing
report$^{25}$. In the magnetic CRO/STO film, however, there is a distinct-
ive non-linear behaviour in $r_{xy}$ which arises from AHE having its
origin in ferromagnetic ground state (Fig. 6b–c). Separation of OHE
and AHE from the $r_{xy}$ is done in the following way. The high-field
slope of $r_{xy}$ versus magnetic-field provides $R_0$ as the high-field mag-
ettization gets saturated ($dM/dH$, $0$) and this contribution of $r_{xy}$
depicts the behavioral trend of OHE. Furthermore, the sign of $R_0$
suggests the type of charge carriers, i.e., the holes or the electrons.
The anomalous component is determined by the extrapolation of
high-field linear $r_{xy}$ to $H = 0$. This extrapolated non-zero $r_{xy}$ at $H$
$= 0$ is the contribution from the AHE. We observed a distinct non-
linear behavior in $r_{xy}$ vs magnetic field below $T = 60$ K which mani-
fests as a discernible “kink” in the vicinity of $H = 2$ T (see inset
of Fig. 6c). This clearly signifies the induced FM order in CRO/STO
film below 60 K. Above this temperature, the $r_{xy}$ is linear and resem-
bles with that of CRO/LAO film. The value of $R_0$ obtained for CRO/
STO sample at 5 K is $4.76 \times 10^{-2} \Omega \cdot \text{cm/Oe}$ or equivalent to $4.7653$
$\times 10^{-13} \text{ cm}^3/\text{C}$. Using this data, a simple one-band model gives a
carrier concentration of $1.31 \times 10^{23}$ holes/cm$^3$. While the carrier
concentration derived for 200 K is $0.27 \times 10^{23}$ holes/cm$^3$. In case of
CRO/LAO, the carrier concentrations thus obtained is $0.32 \times$
$10^{23}$ holes/cm$^3$ at 200 K and $0.15 \times 10^{23}$ electrons/cm$^3$ at 5 K.
These values confirm the sign reversal of the carrier polarity for
CRO/LAO whereas no such sign reversal of charge carriers was
observed in CRO/STO. Overall, these Hall data provide an unam-
biguous proof to magnetization data depicting intrinsic ferromagnetic
order in tensile strained CRO/STO films and absence of the same in
compressive strained CRO/LAO film.

Figure 6 | Magnetic field (H) dependent Hall resistivity $\rho_{xy}$ at different temperature for (a) CRO/LAO film (b) High temperature regime of CRO/STO film (c) Low temperature regime of CRO/STO film. Inset shows the non linear behavior of $\rho_{xy}$ for $T = 5$ K and 30 K in the vicinity of $H = 2$ T (d) Anomalous Hall resistivity $(4\pi R_0 M_s)$ as a function of magnetic field for CRO/STO film.

Figure 7 | Fitting of the resistivity data of CRO-B, CRO-C and CRO-D films to the empirical relation $\rho = \rho_0 + AT^\alpha$. 
Non-magnetic CaRuO$_3$ is a non-Fermi-liquid metal whereas its FM counterpart SrRuO$_3$ exhibits a Fermi-liquid behavior. The magnetic ground state of CaRuO$_3$ has been enigmatic for about past four decades. However, the present studies show that a FM order in this compound can be induced by manipulation of the structure. Now, to explore the consequent modifications in electronic properties of thus obtained FM CaRuO$_3$ films, the temperature (T) dependence of resistivity ($\rho$) data were fitted to the empirical relation $\rho = \rho_0 + AT^\alpha$ where exponent $\alpha \sim 1.5$ corresponds to non-Fermi liquid behavior and $\alpha \sim 2$ corresponds to the Fermi-liquid behavior [Figure 7]. We found a clear relation between FM order and Fermi-liquid behavior and the resistivity of non-magnetic CRO-B films with $\alpha \sim 1.23$ is suggestive of near non-Fermi liquid behavior, whereas that of the FM CRO-D films shows $\alpha \sim 2$ corresponding to the Fermi-liquid behavior. The resistivity of less ferromagnetic CRO-C films exhibits $\alpha \sim 1.76$. These analyses clearly show that there is a gradual transition from a non-Fermi liquid to a Fermi-liquid behavior as we traverse from a non-magnetic to a ferromagnetic CaRuO$_3$. In addition, there appears a clear similarity of the FM and Fermi-liquid behavior in CaRuO$_3$ (CRO-D film) with the corresponding properties of well known SrRuO$_3$.

Discussion

There are several studies, mostly theoretical, on understanding the magnetic ground state of CaRuO$_3$ and SrRuO$_3$. It was predicted that a FM order might set in CaRuO$_3$ if by some appropriate means, chemical or physical, the tilt and rotation of RuO$_6$ octahedra is reduced and the Ru-O-Ru bond distances and angles increased to match with those of the SrRuO$_3$. A manifestation of the same was unambiguously realized by chemical means, i.e., via partial substitution of Ru both by magnetic ions as Cr or Fe and by non-magnetic ions as Ti. However, this technique has the drawback of transforming its metallic state to the semiconducting/insulating state. Zayak et al. carried out detailed calculations of the correlations of epitaxial strain and magnetic moment in CaRuO$_3$ and suggested that a FM CaRuO$_3$ may be formed by the means of inducing the tensile strain and in which the FM magnetic moment increases with the increasing tensile strain. Compressive strain, whereas, does not induce the same effect. An increase in in-plane Ru-O-Ru bond distances and a decrease in covalent character are two essential factors to induce magnetic order in CaRuO$_3$, which can be achieved by tensile strain. A tensile strain of 2% can induce a saturation magnetic moment of $\sim 0.5 \mu_B/f.u.$ In the present study, we find the experimental evidence to these theoretical predictions. We clearly see that a tensile strain of about 1% in CRO-C film induces a magnetic moment of $\sim 0.06 \mu_B/f.u.$ and an enhanced strain of about 1.5% in CRO-D films results in a magnetic moment $\sim 0.26 \mu_B/f.u.$ We could not form CaRuO$_3$ films with higher tensile strain on substrate such as BaTiO$_3$ (mismatch $\sim 4\%$) and MgAl$_2$O$_4$ (mismatch $\sim 6\%$). Indications of FM moment were found in pseudo-heterostructures of CaRuO$_3$. However, in such cases it is difficult to assign the occurrence of magnetic moment to a particular phase. A small magnetic moment in pseudo-heterostructures was attributed to the cubic phase which coexisted with relaxed and coherent orthorhombic phases. In comparison to this, the present studies show manifestation of an FM order with a clear magnetic transition in tensile strained orthorhombic CaRuO$_3$ single-phase films. On comparing the FM properties of CaRuO$_3$ films with those of the SrRuO$_3$, we noted that the magnetic moment of the former is lower than that of the latter. However, the most noteworthy feature is a magnetic coercivity of $\sim 200$–$300$ Oe of CaRuO$_3$ of CaRuO$_3$ films is considerably lower than coercivity in the vicinity of 10 kOe for SrRuO$_3$.

In summary, we have fabricated magnetic CaRuO$_3$ films with single structural form and with varying tensile strain. We explicitly showed that FM moment in CaRuO$_3$ can be induced by the means of tensile strain and that the magnitude of magnetic moment increases with the tensile strain. These observations are consistent with the theoretical predictions. We further show that tensile strain is more efficient that chemical route to induce magnetic order in CaRuO$_3$. These leaves an intriguing aspect open: is it possible to induce larger magnetic moment of up to 1 $\mu_B/f.u.$ in CaRuO$_3$ by adopting a combined approach of tensile epitaxial strain and optimal chemical substitutions? These studies also open up avenues to explore the utilization of tensile strained FM CaRuO$_3$ vis-à-vis the FM SrRuO$_3$ in spintronic and magnetic memory devices.

Methods

Sample preparation. Polycrystalline samples of CaRuO$_3$ and CaRu$_{0.9}$Cr$_{0.1}$O$_3$ were prepared by standard solid-state reaction route. The x-ray diffraction data confirmed the phase purity of both the samples. These samples were used for synthesis of thin films using pulsed laser deposition technique.

Sample characterization. The 0-20 diffraction patterns were collected by using PanAnalytical X-ray diffractometer. The 0-20 reciprocal space maps (RSM) using a four axis cradle mounted on same diffractometer were also obtained for detailed structural and strain analyses of the films. The thickness of the samples was deduced from the reflectivity measurements. The magnetization measurements were performed using superconducting quantum interference device magnetometer. The resistivity and Hall measurements were performed using the four-probe and Van der Pauw geometry in Quantum Design PPMS system. The Hall resistivity $\rho_H$ was measured as a function of the applied magnetic field (H = ± 9 T) at a constant temperature (5 K to 300 K).

1. Randall, J. J. & Ward, R. The Preparation of Some Ternary Oxides of the Platinum Metals. J. Am. Chem. Soc. 81, 2629–2631 (1959).
2. Longo, J. M., Mccall, P. M. & Goodenough, J. B. Magnetic Properties of SrRuO$_3$ and CaRuO$_3$. J. Appl. Phys. 39, 1327–1328 (1968).
3. Cao, G., McCall, S., Shepard, M., Crow, J. E. & Guertin, R. P. Thermal, magnetic, and transport properties of single-crystal Sr$_1-x$Ca$_x$RuO$_3$ (0 $< x < 1.0$). Phys. Rev. B 56, 312–321 (1997).
4. Takahashi, K. S. et al. Inverse tunnel magnetoresistance in all-perovskite junctions of La$_2$Sr$_{2}$Mo$_3$O$_{12}$/SrRuO$_3$. Phys. Rev. B 67, 094413 (2003).
5. Klein, L., Antognazza, L., Geballe, T. H., Beasley, M. R. & Kapitulnik, A. Possible non-Fermi-liquid behavior of CaRuO$_3$. Phys. Rev. B 60, 1448–1451 (1999).
6. He, T. & Cava, R. J. Disorder-induced ferromagnetism in CaRuO$_3$. Phys. Rev. B 63, 172403 (2001).
7. Shirako, Y. et al. Magnetic properties of high-pressure phase of CaRuO$_3$ with post-perovskite structure. J. Phys.: Conf. Series 215, 012038 (2010).
8. Shepard, M., Cao, G. & McCall, S., Freibert, F. & Crow, J. E. Magnetic and transport properties of Na doped SrRuO$_3$ and CaRuO$_3$. J. Appl. Phys. 79, 4821–4823 (1996).
9. Cao, G., Freibert, F. & Crow, J. E. Itinerant-to-localized electron transition in perovskite Ca$_{1-x}$Rh$_x$O$_3$. J. Appl. Phys. 81, 3884–3886 (1997).
10. Mazin, I. I. & Singh, D. J. Electronic structure and magnetism in Ru-based ruthenates. Phys. Rev. B 67, 2556–2571 (1997).
11. Maiti, K. Role of covalency in the ground-state properties of perovskite ruthenates: A first-principles study using local spin density approximations. Phys. Rev. B 73, 235110 (2006).
12. Maiti, K., Singh, R. S. & Medicherla, V. R. R. Observation of particle hole asymmetry and phonon excitations in non-Fermi-liquid systems: A high resolution photoemission study of ruthenates. Europhys. Letts. 78, 17002 (2007).
13. Yoshimura, K. et al. O NMR Observation of Universal Behavior of Ferromagnetic Spin Fluctuations in the itinerant Magnetic System Sr$_1-x$Ca$_x$RuO$_3$. Phys. Rev. Lett. 83, 4597–4490 (1999).
14. Shepard, M., Cao, G. & McCall, S., Crow, J. E. Thermodynamic properties of perovskite $\text{Sr}_2\text{Ru}_2\text{O}_7$ (A = Ca, Sr, and Ba) single crystals. J. Appl. Phys. 81, 4978–4980 (1997).
15. Hardy, V., Raveau, B., Retoux, R., Barrier, N. & Maiguan, A. Nature of the ferromagnetism induced by nonmagnetic substitutions on the Ru site of CaRuO$_3$. Phys. Rev. B 73, 094418 (2006).
16. He, T. & Cava, R. J. The effect of Ru-site dopants on the magnetic properties of CaRuO$_3$. J. Phys.: Condens. Matter 13, 8347–8361 (2001).
17. Maiguan, A., Raveau, B., Hardy, V., Barrier, N. & Retoux, R. Ferromagnetism induced by chromium substitution in the CaRuO$_3$ perovskite. Phys. Rev. B 74, 024410 (2006).
18. Durairaj, V. et al. Highly anisotropic magnetism in Cr-doped perovskite ruthenates. Phys. Rev. B 73, 214414 (2006).
19. Ranjan, R. et al. Magneto-structural study of a Cr-doped CaRuO$_3$. J. Phys.: Condens. Matter 21, 326001 (2009).
20. Zayak, A. T., Huang, X., Neaton, J. B. & Rabe, K. M. Manipulating magnetic properties of SrRuO$_3$ and CaRuO$_3$ with epitaxial and uniaxial strains. Phys. Rev. B 77, 214410 (2008).
21. Rao, R. A. et al. Strain stabilized metal–insulator transition in epitaxial thin films of metallic oxide CaRuO$_3$. Appl. Phys. Lett. 70, 3035–3037 (1997).
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Author contributions
D.S.R. conceived the project and designed the experiments in discussions with R.S.S., S.T. and R.R. S.T. and R.R. performed the syntheses and magnetization measurements. S.T., R.R., P.P. and S.K. analyzed the data. S.T. and S.K. performed the hall measurements. D.S.R., S.T., R.S.S. and S.K. wrote the paper. All authors contributed through scientific discussions.

Additional information
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