Evidence of Variations of Magnetic Properties of Vanadium Doped CaRuO$_3$ using X-Ray Magnetic Circular Dichroism

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1. **INTRODUCTION:** The d-band metal oxides are renowned among materials due to the complexity of their phase diagram that exhibits a formidable array of close and almost overlapping transitions between metallic, insulating, magnetic, and even for superconducting phases [1]. After a long era of intensive study, a full theoretical understanding of such puzzled phase diagram still remains unsolved. In a typical scenario, one starts from an insulating, antiferromagnetically ordered state when the d-band is half-filled or nearly so. This is a classic example of a Mott insulator in which the single occupancy of each lattice site prevents free motion of the charge. Moving away from the half-filled situation (through chemical substitutions or doping, as for example) the charge eventually unfreezes, leading to a metallic phase with striking non-Fermi liquid properties and in some cases to a superconducting phase. In parallel to this, the nature of magnetic correlation changes dramatically from predominantly antiferromagnetic (superexchange-like) in the Mott-localized phase to predominantly ferromagnetic (Hund-like) in the delocalized metallic phase. Recent advances in the atomic-scale control of transition metal oxide interfaces offer new opportunities for the manipulation of strongly correlated electron systems with a growing awareness of the wealth of microscopic phenomena that need to be understood in order to arrive at a quantitative description of the electronic state at oxide interfaces. Magnetic fluctuations accompanying with insulator-to-metal transition and the associated quantum magnetic critical behaviour are often considered to be the underlying physics behind the unconventional superconductivity in magnetic materials of the strongly correlated electrons origin [2,3]. Despite the heavy interest in this topic, the situation is still not well understood.

Motivated by the above considerations, we have undertaken a careful experimental study of the interplay between the insulator to metal transition and magnetism in the perovskites Ca(Ru$_{1−0.05}$V$_{0.05}$)O$_3$. These compounds crystallize in an orthorhombic lattice configuration with end members, CaRuO$_3$ ($x=0$) and CaVO$_3$ ($x=1$), being an anomalous metal and a Mott insulator, respectively [1,4]. Although the static magnetic characteristics of CaRuO$_3$ is still a matter of debate—whether it is a paramagnet or on the verge of the ferromagnetic instability, strong magnetic fluctuations of ferromagnetic origin were detected in the NMR measurements [3]. Recent experimental studies suggest a coexistence of the quantum magnetic fluctuations and non-Fermi liquid behaviour for $T\leq25K$, albeit no magnetic order is detected to the lowest measurement temperature [1]. Y. Shirako et al reported that an inflection point near 270 K implies some transition, e.g. establishment of a long-range magnetic order below the temperature while the isothermal magnetization clearly indicates the absence of spontaneous magnetization over the temperature range which strongly suggest that CaRuO$_3$ possess antiferromagnetic interaction and its Néel temperature, $T_N$, is around 270 K [2].

2. **EXPERIMENT:** The high purity polycrystalline samples of Ca(Ru$_{1−0.08}$V$_{0.05}$)O$_3$ were synthesized by conventional solid-state reaction method using ultra-pure ingredients of V$_2$O$_5$, RuO$_2$ and CaCO$_3$. Starting materials were mixed in stoichiometric composition, with five percent extra RuO$_2$ to compensate for their rapid evaporation (in Ru-doped perovskites),
pelletized and sintered at 950°C for three days. The furnace cooled samples were grinded, pelletized and sintered at 1000°C for another three days. Resulting samples were characterized using Rigaku Smart Lab powder X-ray diffractometer, confirming the single phase of material. X-ray spectroscopy, scattering, and imaging experiments were performed at the variable-polarization soft x-ray beam-line BL-16A of the Photon Factory (KEK, Japan). Experimental geometry of soft x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) experiments are shown in Fig. 1 and 2. The sample was placed in the vacuum chamber with a pressure of 10⁻⁹ Torr equipped with a 5 T superconducting magnet. XAS and XMCD signals were measured at ±0.1T, ±1T and ±2T varying magnetic-fields (only the data of ±2T has been produced here) with right and left circularly polarized (RCP and LCP) x-rays having an energy resolution of 0.1 eV using the bulk-sensitive total fluorescence yield (TFY) method near Ru M₄,5 and V L₂,₃ absorption edges with right and left circularly polarized (RCP and LCP) x-rays.

3.RESULTS AND DISCUSSIONS: The XAS spectra obtained with applied magnetic fields of

![Fig 1(a) Normalised XAS spectra and Fig 1(b) Normalised XMCD spectra of Ru M₄,5 site. Fig 1(c) XMCD/XAS Intensity ratio w.r.t. applied magnetic-field ±0.1T, ±1.0T and ±2.0T.](image1)

![Fig 2(a) Normalised XAS spectra and Fig 2(b) Normalised XMCD spectra of V L₂,₃ site. Fig 2(c) XMCD/XAS Intensity ratio w.r.t. applied magnetic-field ±0.1T, ±1.0T and ±2.0T.](image2)
+2.0 and -2.0 T are denoted by $\mu^+$ and $\mu^-$ which represent left and right circularly polarized light, respectively as shown in Fig 1(a) and 2(a). The XMCD spectrum was recorded by taking a difference between the XAS spectra with negative and positive helicity of the circular polarized light. Ru and V both shows a tendency of multiplet structure at the $M_5$ and $M_4$, and $L_3$ and $L_2$ absorption edges, respectively. Well-resolved peaks at the absorption maxima at $E = 464.54$ eV and 468.64 eV at the $M_5$ and $M_4$ edges, respectively are clearly observable. This verifies that the fine structures of Ru $3d \rightarrow 4f$ transition should result from the localization of Ru $4f$ electrons rather than the oxidation of the material. V, on the other hand, have multiplet absorption peaks found at $L_3$ edges. The $L_3$ peak with absorption energy, $E = 518.61$ eV arrives with a satellite peak at 516.34 eV and a pre-peak region at 517.58 eV; whereas, $L_2$ shows a singlet peak at 525.68 eV. Such results implies that unlike Ru-site, V $2p \rightarrow 3d$ transition is non-localised and infuses oxidation of the material. XMCD signal measured in a magnetic field of $B = 2.0$ T (as produced here) for Ru $M_{4,5}$ and V $L_{2,3}$ is shown in Fig.1(b) and Fig.2(b), respectively. The XMCD feature of Ru $M_{4,5}$ and V $L_{2,3}$ is anti-parallel to each other which predicts that substitution of V in the place of Ru introduces an contrast effect in the mother-material CaRuO$_3$. The XMCD/XAS intensity ratio w.r.t. the variable magnetic field with $\pm 0.1$T, $\pm 1.0$T and $\pm 2.0$T are shown in Fig 1(c) for Ru-edges and in Fig 2(c) for V-edges. This result is quite relatable with the XMCD graphs. Fig 1(c) exhibits that the intensity ratio of XMCD/XAS is increasing with increasing magnetic-field; as same as Fig 2(c). This phenomenon suggests that after the doping of V at Ru-site, magnetic anisotropy gets increased which indicates an increase in ferromagnetism of the NPs. Although we do not have direct evidence of the ferromagnetic character of the fluctuation in x= 1 composition, it is justifiable to suggest that the data becomes negative, suggesting a tendency towards ferromagnetism arising a metallic feature of CaVO$_3$ at room temperature.

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References:


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