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A-site substitution of $SrRuO_3$ using La, K and Pb

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Abstract
We have investigated $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$ and $Sr_{1-x}Pb_xRuO_3$, which have a larger average size of the A-site cations. They manifest a gradual loss of ferromagnetism in a similar way as their counterparts with smaller A-site cations. There is also evidence for a magnetism-suppressing disorder effect similar to that observed in $Sr_{1-x}La_{x/2}Na_{x/2}RuO_3$. Therefore, the Stoner ferromagnetism in $SrRuO_3$ is rather unique and cannot be easily tuned by lattice distortion to yield a higher Curie temperature.

1. Introduction

Metallic strontium ruthenate $SrRuO_3$ (SRO) has attracted much interest because of its unusually high Curie temperature ($T_c = 160$ K) which is unique among 4d and 5d transition metal oxides [1]. The ferromagnetism (FM) in this ABO_3 perovskite is of the Stoner type, arising from a high density of states (DOS) at the Fermi level (E_f) due to a nearby van Hove singularity [2]. A-site substituted $Sr_{1-x}Ca_xRuO_3$ is also metallic but it suffers a substantial lattice contraction and a gradual loss of FM [3, 4]. This has been attributed to the lowering of the DOS at E_f due to structural distortion [2]. Based on this result, Mazin and Singh speculated that the A-site substitution by an oversized cation might cause an enhancement of FM [2]. However, such an experiment has not been reported since Ba^{2+}, being the only non-radioactive alkali-earth cation larger than Sr^{2+}, yields a hexagonal, face-sharing $BaRuO_3$ compound that is structurally distinct from SRO perovskite. Meanwhile, nearly all alloying attempts to fine tune the DOS by modifying lattice distortions severely suppress the FM [4–11], whereas mixed A-site substitution (such as in $Sr_{1-x}La_{x/2}Na_{x/2}RuO_3$ which has a smaller average size of the A-site cations) appears to cause a disorder effect further suppressing FM [4]. Here we report that $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$, despite its larger average size of the A-site cations, still manifests a reduction of the FM. By comparing the magnetic properties of $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$ and similarly (A-site) oversized $Sr_{1-x}Pb_xRuO_3$ we also found evidence for a disorder effect similar to the one observed in $Sr_{1-x}La_{x/2}Na_{x/2}RuO_3$.

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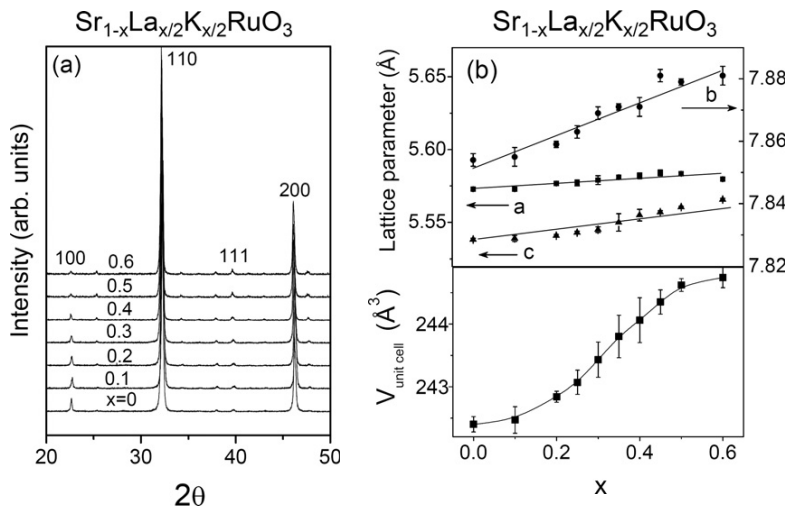

Figure 1. (a) X-ray diffraction patterns of $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$ indexed using the pseudocubic cell of perovskite; (b) orthorhombic cell parameters and cell volume as a function of x.

2. Experimental details

Polycrystalline ceramic samples of the composition $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$, with x up to 0.6, were prepared with starting materials of $SrCO_3$ (99.99%, Alfa Aesar, Ward Hill, MA), K_2CO_3 (99.9%, J T Baker Inc., Phillipsburg, NJ), La_2O_3 (99.99%, Alfa Aesar, Ward Hill, MA) and RuO_2 (99.95%, Alfa Aesar, Ward Hill, MA). For comparison, samples of $Sr_{0.9}Pb_{0.1}RuO_3$ were also prepared using PbO (99.9%, Aldrich, Milwaukee, WI). The starting powders were dissolved in dilute nitric acid and made to gel with poly(ethylene glycol) (MW = 2000, Aldrich, Milwaukee, WI) addition and slow heating. After further thermal decomposition in several stages, a powder product of oxide precursors was obtained. Phase-pure perovskite was formed by calcination at 800 °C and final sintering of pellets was performed at 1200 °C using an SRO powder pack to minimize Ru loss. In the case of Pb-containing samples, a powder pack of mixed SRO and $PbZrO_3$ was also used to minimize Pb loss.

Phase purity was monitored with x-ray powder diffraction (XRD) using Cu Kα radiation, with Si powder added as an internal standard. Only single-phase perovskite samples according to XRD were used for further studies. (Beyond $x = 0.6$, $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$ samples contained mixed phases and were discarded.) Magnetization (M), AC susceptibility (χ) and (four-point-probe) electrical resistivity (ρ) were measured using a Physical Property Measurement System (Quantum Design PPMS, San Diego, CA) at various magnetic fields (H) up to 9 T over the temperature (T) range from 10 to 300 K. Other experimental details were similar to those used in our previous work described elsewhere [5, 6].

3. Results and discussion

The XRD patterns of $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$ shown in figure 1(a) can be indexed using an orthorhombic unit cell (figure 1(b)) with cell dimensions that increase with x. All the samples are metallic ($d\rho/dT > 0$) at higher temperature, see figure 2; for x up to 0.35

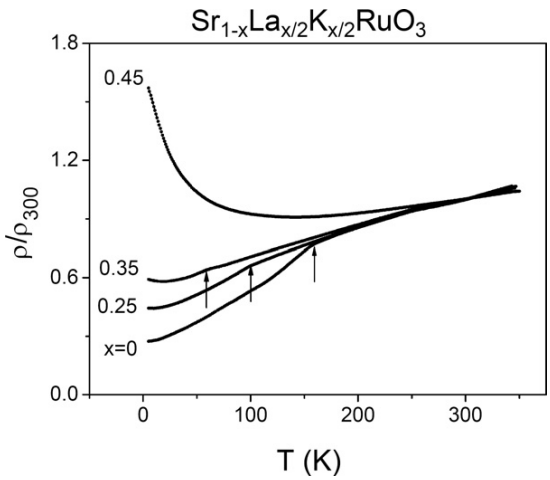

Figure 2. Resistivity, normalized by its 300 K value, for several compositions ($x = 0, 0.25, 0.35, 0.45$) of $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$. Arrows indicate kinks at the ferromagnetic transition.

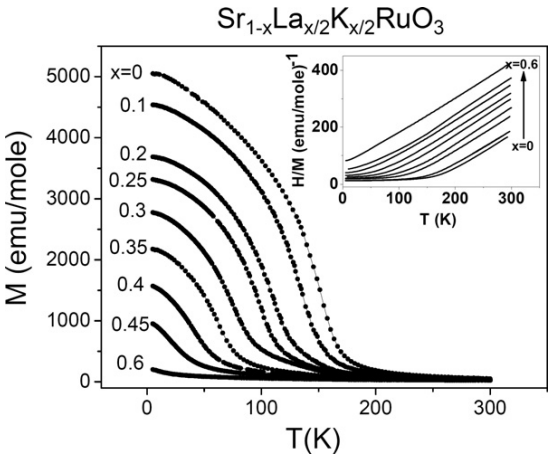

Figure 3. DC magnetization (M) of $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$ at $H = 1$ T. Inset: H/M versus temperature (T) showing Curie–Weiss behaviour at high temperature.

they also exhibit a characteristic kink at a progressively lower temperature (T_{kink}) caused by the scattering of itinerant electrons by enhanced critical spin fluctuations at T_c [12]. This is supported by the magnetic measurements indicating the suppression of FM properties, such as M at 1 T (shown in figure 3) and T_c from the peak of $\chi(T)$ (shown as T_{peak} in figure 4), with increasing substitution. For a quantitative comparison, we plot the reciprocal DC susceptibility at 1 T, M/H, in the inset of figure 3 and fit its high temperature portion with the Curie–Weiss equation, $M/H = \chi_T + C/(T - \theta_p)$. Here χ_T is a temperature-independent constant, $C = N\ (\mu_B \mu_{\text{eff}})^2/3k$ and θ_p is the Curie–Weiss temperature, with N = Avogadro's constant, μ_B = Bohr magneton, μ_{eff} = effective moment in units of Bohr magneton, and k = Boltzmann's constant. The fitted θ_p also shown in figure 4 is in good agreement with the T_c

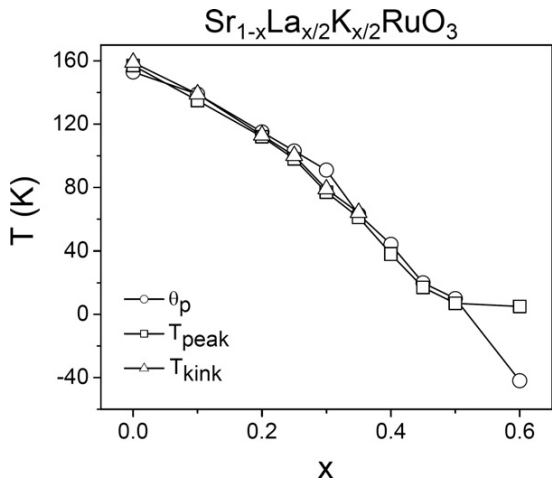

Figure 4. Curie–Weiss temperature (θ_p) and T_c determined from the resistivity kink (T_{kink}) and AC susceptibility peak (T_{peak}) versus x of $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$.

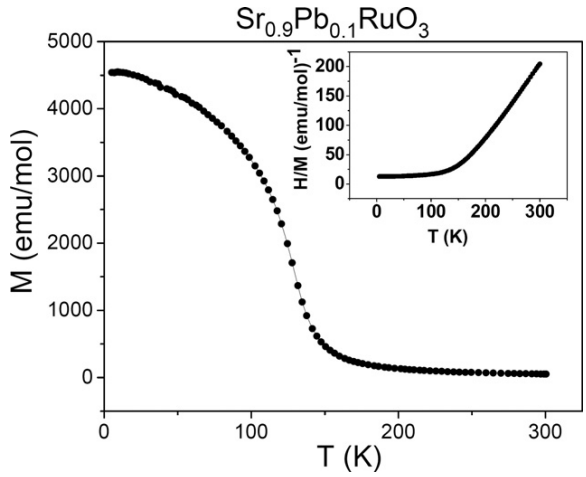

Figure 5. DC magnetization (M) of $Sr_{0.9}Pb_{0.1}RuO_3$ at $H = 1$ T. Inset: H/M versus temperature (T) showing Curie–Weiss behaviour at high temperature.

determined from the resistivity kink and AC susceptibility, confirming that FM is progressively suppressed by La/K substitution despite its larger orthorhombic cells.

The $Sr_{0.9}Pb_{0.1}RuO_3$ samples are also orthorhombic and metallic at high temperatures. Its magnetic properties are similarly depressed, as evidenced by the lower saturation magnetism and T_c (figure 5 and inset) compared to those of SRO. This is despite the fact that Pb^{2+} has a larger ionic radius (0.149 nm) than Sr^{2+} (0.144 nm) in 12-fold coordination according to Shannon [13].

To compare $Sr_{0.9}Pb_{0.1}RuO_3$ with $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$, we first choose $x = 0.1$, i.e., the same degree of substitution. At this composition, magnetic properties (e.g., saturation magnetism ∼4500 emu mol^{-1}, $\theta_p \sim 138$ K and peak-χ temperature ∼130 K) are similar

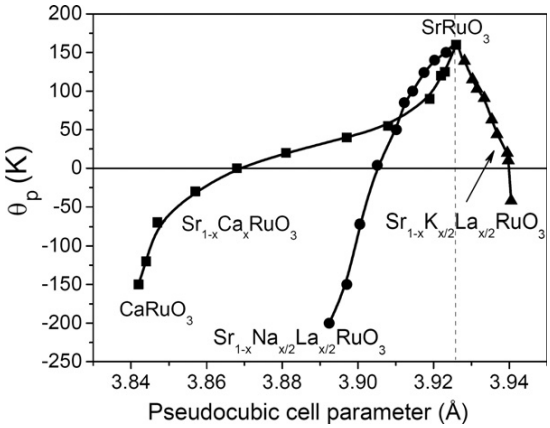

Figure 6. Curie–Weiss temperature (θ_p) of $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$, $Sr_{1-x}La_{x/2}Na_{x/2}RuO_3$ from [4] and $Sr_{1-x}Ca_xRuO_3$ from [14] versus average perovskite (pseudocubic) subcell size.

in both samples. We next choose $x = 0.25$ since the average radius for A-site cations (r^{3+}_{La} (0.132 nm) $< r^{2+}_{Sr}$ (0.144 nm) $< r^{2+}_{Pb}$ (0.149 nm) $< r^{+}_{K}$ (0.160 nm)) is 0.1445 nm for both $Sr_{0.75}La_{0.125}K_{0.125}RuO_3$ and $Sr_{0.9}Pb_{0.1}RuO_3$. It is then clear that the FM is substantially weaker in $Sr_{0.75}La_{0.125}K_{0.125}RuO_3$ ($\theta_p = 103$ K) than $Sr_{0.9}Pb_{0.1}RuO_3$ ($\theta_p = 137$ K). If the average lattice distortion is indeed an important factor [2], this finding would be consistent with the notion of A-site disorder being an FM-suppressing factor [4]. This is because, compared to (undersized) La^{3+} along with (oversized) K^+ substitution, Pb^{2+} substitution for Sr^{2+} causes only a relatively smaller size disorder and no charge disorder. Lastly, to illustrate the unique position of SRO, we summarize in figure 6 the θ_p data of $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$ and $Sr_{1-x}Ca_xRuO_3$ [14] versus the average perovskite (pseudocubic) subcell size, which was calculated from lattice parameters of the orthorhombic cell using $[(b/2)(a/2^{1/2})(c/2^{1/2})]^{1/3}$. Also included in the plot are data of $Sr_{1-x}La_{x/2}Na_{x/2}RuO_3$ [4]. Because of its dependence on the A-site disorder, this plot is clearly not unique, as is evident from the two distinct branches on the left. Nevertheless, it does point to the strong possibility that SRO would maintain the strongest FM regardless of the unit cell volume achievable by A-site substitution. Moreover, since this volume change is likely to be accompanied by a systematic change in the degree of tilting of the RuO_6 octahedra, we can likewise speculate that SRO would maintain the strongest FM regardless of the octahedra tilting achievable by A-site substitution.

Lastly, although we noted in the introduction that nearly all alloying attempts on SRO severely suppress the FM [4–11], one notable exception was reported by Cao *et al*, who found that Pb addition to SRO polycrystals increased the T_c to about 200 K in a nearly composition-independent manner within the $SrPb_{1-x}Ru_xO_3$ formulation. This formulation would likely result in the Pb substitution on the B site, which is possible under a highly oxidative environment that stabilizes Pb^{4+}. We believe our study of the Pb effect clearly rules out the possibility of A-site Pb^{2+} being a T_c enhancer. However, the mechanism of the concentration-independent B-site Pb effect on FM and T_c remains an open question.

4. Conclusions

We have demonstrated that, despite a larger average size of the A-site cations, $Sr_{1-x}La_{x/2}K_{x/2}RuO_3$ and $Sr_{1-x}Pb_xRuO_3$ manifest a gradual loss of ferromagnetism. There

is also further evidence for a magnetism-suppressing disorder effect due to the charge and size disorder introduced by A-site substitution, suggesting that the unique Stoner ferromagnetism in $SrRuO_3$ cannot be enhanced by tuning the lattice distortion.

Acknowledgments

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