

Magnetic Properties of Nonstoichiometric and Substituted SrRuO₃

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SrRuO₃ has been known for half a century as a strongly-correlated ferromagnetic metal and proposed for use as an electrode material in micro- and nano-electronic circuits. We have discovered that annealing of stoichiometric SrRuO₃ perovskites in high-pressure oxygen produces SrRu_{1-v}O₃ compounds with vacancies on the Ru-sites. The creation of Ru vacancies rapidly suppresses ordered moment per Ru from 1.6 to 0.8 μ_B and the ferromagnetic ordering temperature, T_C , from 163 K to 45 K with increase of $v \approx 0.09$, whereas the resistivity increases. Subtle structural changes that accompany creation of Ru-site vacancies are different from the typical properties of transition metal perovskites, for which an increased formal oxidation state of the B-site cations normally leads to decreased B-O interatomic distances and contraction of the unit cell volume. The reduced charge screening caused by the Ru-vacancies offsets expected decrease of the average interatomic distance Ru-O and rotation of the RuO₆ octahedra as Sr atoms relax toward Ru-vacancies increases observed volume. Local probes of Ru with XANES, NMR, and EELS find no valence change while isomer shifts of ⁹⁹Ru from Mossbauer experiments reveal a small change from +4 toward +5 as the T_C decreases.

By using “design rules” of the synthesis and magnetic interactions for perovskites we have established that Cr substitution into Ru site of SrRuO₃ increases T_C to 188 K at the solubility limit of 12%. The ⁵³Cr and ^{99,101}Ru NMR studies reveal that the electronic configurations of Cr and Ru are 3d³ ($t_{2g}^{3\uparrow}$) and 4d⁴ ($t_{2g}^{3\uparrow 1\downarrow}$), respectively. Compared with SrRuO₃, the spin-down electron in Ru 4d shell is more itinerant in SrRu_{0.875}Cr_{0.125}O₃ which is consistent with a broadened conduction band and a possible minority band Cr(d³)-O²⁻-Ru(d⁴) double-exchange-like interaction. The exchange interaction involves the Cr³⁺ into the ferromagnetic ordering and enhances the ordering temperature. This picture is supported by a steady decrease of the ordered moment per Ru/Cr.

Neutron powder diffraction analysis revealed that below $T_C = 163$ K the b and c lattice parameters and the unit cell volume are virtually temperature independent for the stoichiometric material. We show that this previously reported invar-effect below the ferromagnetic ordering temperature originates from freezing of the octahedral tilting about the [001] axis. The invar-effect is much less pronounced in the Ru-deficient samples with decreased T_C 's = 135 K and 82 K. We show that the invar-effect gradually disappears also for the Cr-substituted samples with increased T_C 's.

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