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# Ti-Induced Ferromagnetism and the Specific Heat of $CaTi_x Ru_{1-x}O_3$ (x = 0, 0.005, 0.03)

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The influence of Ti substitution on the specific heat of the CaTi<sub>x</sub>Ru<sub>1-x</sub>O<sub>3</sub> system at low concentrations x = 0, 0.005, and 0.03 was studied in the temperature range of 2–300 K at magnetic fields up to 9 T. Small peak was revealed in the C/T vs.  $T^2$  dependence at around 3 K, which are field sensitive (the electronic specific heat coefficient  $\gamma$  linearly decreases with the increase in magnetic field), and might be connected to some kind of magnetic ordering. The coefficient  $\gamma$  is suppressed also by Ti substitution.

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## 1. Introduction

CaRuO<sub>3</sub> is an interesting member of the ruthenates family. Although it shows neither magnetic order nor superconductivity it offers many questions concerning its magnetic and electronic ground state. It is a narrow-band metal due to strong correlations, with occupied  $t_{2g}$  states that are considerably hybridized with the O 2p states. Susceptibility analyses have revealed relatively large negative Weiss temperature [1], neutron scattering in correspondence with theoretical calculations have revealed ferromagnetic fluctuations [2], but no long-range magnetic ordering was noted down to the lowest temperatures [3]. Thus CaRuO<sub>3</sub> is considered to be nearly ferromagnetic. Regarding the electronic properties, non-Fermi liquid features in electrical resistance and optical conductivity in two temperature

#### A. Zorkovská et al.

regions have been found [4]. The low temperature behavior of resistance follows the predictions for the systems close to the antiferromagnetic critical point, which is contradictory to the above mentioned ferromagnetic features.

Chemical substitutions proved to be very useful tools for characterizing the ground state properties of physical systems as they allow fine tuning of properties. Substitution of  $\operatorname{Ru}^{4+}$  by non-magnetic  $\operatorname{Ti}^{4+}$  was found to induce ferromagnetism in this system, the transition temperature was independent of Ti concentration for x = 0.2–0.8 [5]. In this article we focus on the influence of Ti substitution on the specific heat of the  $\operatorname{CaTi}_x \operatorname{Ru}_{1-x} O_3$  system at low concentrations (x = 0, 0.005, and 0.03), with the aim to contribute for understanding of magnetism in this system.

#### 2. Experimental results and discussion

Polycrystalline samples of  $\text{CaTi}_x \text{Ru}_{1-x} O_3$  have been prepared by mixing  $\text{CaCO}_3$ ,  $\text{RuO}_2$ , and  $\text{TiO}_2$ . The pellets were sintered at 1100–1200°C for 72 h in air. Powder X-ray diffraction confirmed the purity of the samples. Specific heat has been studied using the conventional Quantum Design PPMS-9 device in temperature range 2–300 K and magnetic field up to 9 T.



Fig. 1. Influence of magnetic field on the C/T vs.  $T^2$  dependence for CaRuO<sub>3</sub>.

Despite the abrupt increase in magnetization at 34 K indicating ferromagnetic type ordering in both substituted samples [6], no anomaly of the temperature dependence of specific heat pointing at magnetic phase transition has been noticed at this temperature. Unexpectedly, small peak has been found in C/T vs.  $T^2$  for all samples at much lower temperatures, at around 3 K. This feature is field dependent, although insensitive to weak fields (Fig. 1). The electronic specific heat



Fig. 2. The electronic specific heat coefficient  $\gamma$  vs. magnetic field. The table inset shows the Ti concentration dependence of  $\gamma$ .



Fig. 3. Influence of Ti substitution on the C/T vs.  $T^2$  dependence.

coefficient  $\gamma$  has been estimated from the dependences at the lowest temperatures: it scales linearly with magnetic field (Fig. 2).

The influence of Ti content can be seen in Fig. 3: the small peak shifts to higher temperature with substitution (for x = 0 it occurs at 2.6 K, for x = 0.005 and 0.03 at 3.2 K). Interestingly, Klein et al. [4] found that the resistivity becomes qualitatively different in a way indicative of a first-order phase transition below 3.5 K, that is almost the same temperature. It is possible that some kind of percolating ordering occurs at this temperature among the already existing short-

357

-range correlated clusters, nevertheless this point needs further investigation. The linear specific heat coefficient is suppressed by Ti substitution as it can be seen from the table inset in Fig. 2.

#### 3. Conclusion

The specific heat of the  $\operatorname{CaTi}_x \operatorname{Ru}_{1-x} O_3$  system at low concentrations (x = 0, 0.005, and 0.03) has been studied in the temperature range of 2–300 K at magnetic fields up to 9 T. Although previous magnetic measurements indicated ferromagnetic-type ordering at 34 K [6], no specific heat anomaly was observed at this temperature. On the other hand, small peak in the C/T vs.  $T^2$  dependences, both magnetic field and Ti content dependent suggest further phase transition, likely of first-order type. The nature of this transition should be investigated in more detail.

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