

# Second-order Structural Transition in (Ca<sub>0.5</sub>Sr<sub>0.5</sub>)<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub>

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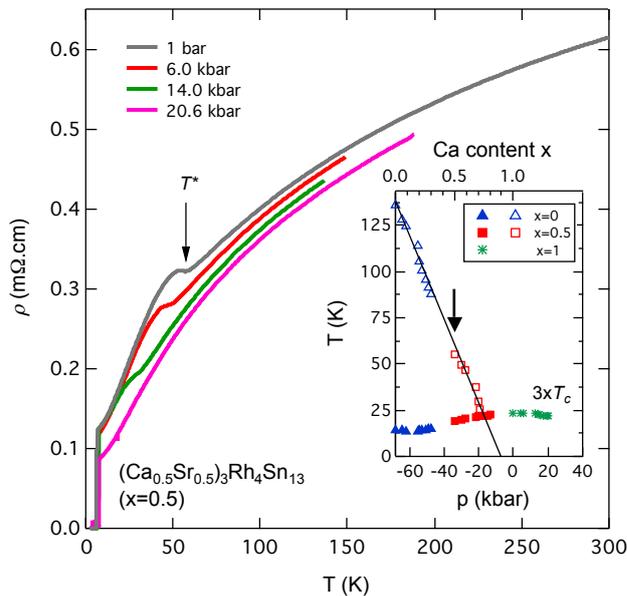
**Abstract.** (Ca<sub>0.5</sub>Sr<sub>0.5</sub>)<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub> is a member of the substitution series (Ca<sub>x</sub>Sr<sub>1-x</sub>)<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub> which has recently been argued to feature a structural quantum critical point at  $x_c = 0.9$ . In the stoichiometric compound Sr<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub>, the structural transition at  $T^* \approx 138$  K has been shown to be second-order. Moving towards  $x_c$ , we examine the character of the structural transition in (Ca<sub>0.5</sub>Sr<sub>0.5</sub>)<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub> (*i.e.*  $x = 0.5$ ,  $T^* \approx 55$  K) using electrical resistivity, heat capacity and X-ray scattering. The absence of the thermal hysteresis in specific heat around  $T^*$ , and the continuous evolution of the superlattice reflection detected by X-ray diffraction are consistent with the scenario that the structural transition associated with a modulation vector  $\mathbf{q} = (0.5 \ 0.5 \ 0)$  in (Ca<sub>0.5</sub>Sr<sub>0.5</sub>)<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub> remains second-order on approaching the quantum critical point.

## 1. Introduction

Sr<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub> is a conventional *s*-wave superconductor with a critical transition temperature ( $T_c$ ) of 4.7 K [1, 2, 3]. In addition to the superconducting transition, another second-order phase transition takes place at  $T^* = 138$  K. This high temperature transition has been established to be a structural phase transition between the  $Pm\bar{3}n$  and  $I\bar{4}3d$  space groups above and below  $T^*$ , respectively.  $T^*$  can be suppressed either by applying pressure or by calcium substitution, *i.e.* by forming a (Ca<sub>x</sub>Sr<sub>1-x</sub>)<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub> substitution series [1, 3]. If the structural transition remains second order as  $T^* \rightarrow 0$ , a structural quantum critical point can be realized [1, 4].

In the substitution series (Ca<sub>x</sub>Sr<sub>1-x</sub>)<sub>3</sub>Rh<sub>4</sub>Sn<sub>13</sub>,  $T^*$  can be completely suppressed solely by fine tuning the calcium content, and it has been established that  $T^* \rightarrow 0$  when  $x = x_c \approx 0.9$  [1]. In the vicinity of  $x_c$ , several important observations are noted: (a) Debye temperature is a minimum, (b)  $T_c$  is a maximum, and (c) strong-coupling superconductivity can be stabilized. All these features can be nicely understood in the framework of structural quantum criticality, and





**Figure 1.** Temperature dependence of the electrical resistivity measured at different pressures. The arrow indicates  $T^*$  at ambient pressure. Inset: Universal temperature-pressure phase diagram constructed using  $\text{Sr}_3\text{Rh}_4\text{Sn}_{13}$ ,  $(\text{Ca}_{0.5}\text{Sr}_{0.5})_3\text{Rh}_4\text{Sn}_{13}$ , and  $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ . For details, see reference [1].  $\text{Sr}_3\text{Rh}_4\text{Sn}_{13}$  is located at the leftmost edge of the phase diagram. The location of  $(\text{Ca}_{0.5}\text{Sr}_{0.5})_3\text{Rh}_4\text{Sn}_{13}$  is shown by the arrow.

they thus provide strong support for the identification of  $x_c$  as a quantum critical point [1, 3]. In  $\text{Sr}_3\text{Rh}_4\text{Sn}_{13}$  ( $x=0$ ), specific heat data unambiguously proved that the structural transition is second-order [1, 3]. In this article, we move closer towards  $x_c$ , and demonstrate that the  $T^*$  transition remains second-order in  $(\text{Ca}_{0.5}\text{Sr}_{0.5})_3\text{Rh}_4\text{Sn}_{13}$  ( $x = 0.5$ ) using our latest x-ray diffraction data.

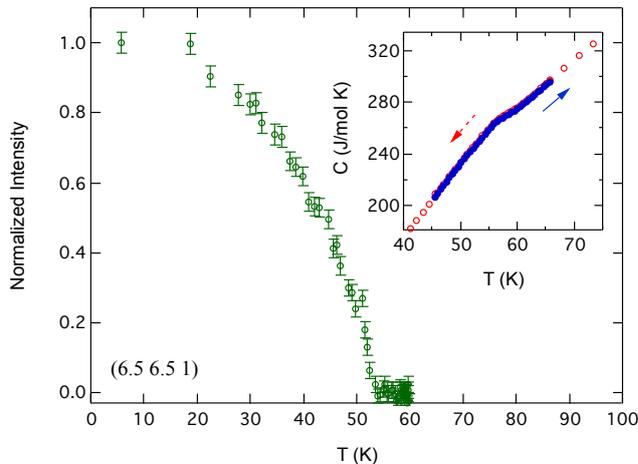
## 2. Experimental Details

Single crystals of  $(\text{Ca}_{0.5}\text{Sr}_{0.5})_3\text{Rh}_4\text{Sn}_{13}$  were grown using the Sn-flux method as described elsewhere [5]. Electrical resistivity and heat capacity were measured using Quantum Design's Physical Properties Measurement System. High pressure electrical resistivity was measured using a piston-cylinder pressure cell with Daphne 7373 as the pressure transmitting medium. Superlattice reflection was measured at BL35XU of SPring-8, Japan with a Si(11 11 11) backscattering analyzer on the two-theta arm, which helps to reduce the background. The X-ray energy is 21.747 keV.

## 3. Results and Discussion

The inset to Figure 1 displays the universal temperature-pressure phase diagram constructed earlier [1], with the arrow marking the position of  $(\text{Ca}_{0.5}\text{Sr}_{0.5})_3\text{Rh}_4\text{Sn}_{13}$ . It is therefore more than halfway between  $x = 0$  and  $x_c$ . The main panel of Figure 1 shows the temperature dependence of the electrical resistivity for  $(\text{Ca}_{0.5}\text{Sr}_{0.5})_3\text{Rh}_4\text{Sn}_{13}$  at ambient pressure, 6.0 kbar, 14.0 kbar and 20.6 kbar. In addition to the superconducting transition at low temperature, the structural transition at  $T^* \sim 55$  K can be identified as the hump in the electrical resistivity. When pressure is applied,  $T^*$  decreases rapidly, reaching 46.9 K and 29.7 K at 6.0 kbar and 14.0 kbar, respectively. At 20.6 kbar, the  $T^*$  feature is no longer visible in the electrical resistivity. This confirms the trend that pressure moves the system towards the right hand side of the phase diagram.

In  $\text{Sr}_3\text{Rh}_4\text{Sn}_{13}$ , a pronounced lambda-like jump was detected at  $T^*$  [1, 6], without any thermal hysteresis [1]. In the inset to Figure 2, we display the specific heat data of  $(\text{Ca}_{0.5}\text{Sr}_{0.5})_3\text{Rh}_4\text{Sn}_{13}$  around  $T^*$  collected on warming and on cooling. The specific heat anomaly is significantly weaker here compared with the case of  $\text{Sr}_3\text{Rh}_4\text{Sn}_{13}$ . However, the absence of thermal hysteresis



**Figure 2.** Temperature evolution of the X-ray diffraction intensity associated with the superlattice reflection with  $\mathbf{q} = (0.5 \ 0.5 \ 0)$ . (Inset) Temperature dependence of the specific heat in  $(\text{Ca}_{0.5}\text{Sr}_{0.5})_3\text{Rh}_4\text{Sn}_{13}$  around  $T^*$ , collected on cooling (open symbols) and on warming (closed symbols).

is still clear. In the main panel of Figure 2, we present the temperature evolution of the elastic X-ray scattering intensity for  $\mathbf{Q} = (6.5 \ 6.5 \ 1.0)$ . The additional reflection at  $\mathbf{Q} = \mathbf{k} + \mathbf{q}$  below  $T^*$ , where  $\mathbf{k} = (6.0 \ 6.0 \ 1.0)$  corresponds to the Bragg spots in the high temperature ( $T > T^*$ ) phase, is consistent with a modulation vector with  $\mathbf{q} = (0.5 \ 0.5 \ 0)$  (or the  $\mathbf{M}$  point).  $T^*$  determined from the onset of the superlattice reflection is slightly below that obtained from the specific heat data. This difference can be attributed to a slight variation in the calcium content between different samples. From the slope  $dT^*/dx$  (*c.f.* Figure 1 and Ref. [1]), a variation of 0.03 in  $x$  can cause a variation of up to 5 K in  $T^*$ . Finally, the gradual and continuous increase of the diffraction intensities on cooling below  $T^*$  is consistent with the scenario of a second-order phase transition.

#### 4. Conclusion

In summary, we have studied single crystals of  $(\text{Ca}_{0.5}\text{Sr}_{0.5})_3\text{Rh}_4\text{Sn}_{13}$  using electrical resistivity, heat capacity and X-ray diffraction. From the absence of the thermal hysteresis around  $T^*$  in the heat capacity data and the continuous evolution of the superlattice peak intensity at  $(6.5 \ 6.5 \ 1)$ , we conclude that the structural transition in  $(\text{Ca}_{0.5}\text{Sr}_{0.5})_3\text{Rh}_4\text{Sn}_{13}$  is a second-order phase transition with  $\mathbf{q} = (0.5 \ 0.5 \ 0)$ . Similar conclusion has recently been reached in related compounds  $\text{La}_3\text{Co}_4\text{Sn}_{13}$  [7],  $\text{Sr}_3\text{Ir}_4\text{Sn}_{13}$  [6],  $\text{Sr}_3\text{Rh}_4\text{Sn}_{13}$  [6] and  $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$  [8] from x-ray/neutron diffraction. These data highlights the similarity across different 3-4-13 families in which the notion of structural quantum criticality has been discussed [1, 4, 9].

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