Superconductivity in the presence of disorder in skutterudite-related La$_3$Co$_4$Sn$_{13}$ and La$_3$Ru$_4$Sn$_{13}$ compounds; electrical transport and magnetic studies

A. Ślebarski*, M. M. Maška*, M. Fijalkowski*

Institute of Physics, University of Silesia, 40-007 Katowice, Poland

C. A. McElroy*, M. B. Maple*

Department of Physics, University of California, San Diego, La Jolla, California 92093, USA

Abstract

La$_3$Co$_4$Sn$_{13}$ and La$_3$Ru$_4$Sn$_{13}$ were categorized as BCS superconductors. In a plot of the critical field $H_{c2}$ vs $T$, La$_3$Ru$_4$Sn$_{13}$ displays a second superconducting phase at the higher critical temperature $T^*_c$, characteristic of inhomogeneous superconductors, while La$_3$Co$_4$Sn$_{13}$ shows bulk superconductivity below $T_c$. We observe a decrease in critical temperatures with external pressure and magnetic field for both compounds. Additionally, for La$_3$Ru$_4$Sn$_{13}$ we find that $dT^*_c/dP > dT_c/dP$. The pressure dependences of $T_c$ are interpreted according to the McMillan theory and understood to be a consequence of lattice stiffening. The investigation of the superconducting state of La$_3$Co$_x$Ru$_{4-x}$Sn$_{13}$ shows a $T^*_c$ that is larger then $T_c$ for $x < 4$. This unique and unexpected observation is discussed as a result of the local disorder and/or the effect of chemical pressure when Ru atoms are partially replaced by smaller Co atoms.

1. Introduction

The effect of atomic disorder on the electronic properties of correlated electron systems, particularly those close to a quantum critical point (QCP) [1] has been a topic of active research. In the critical regime, the system is at the threshold of an instability and even weak perturbations, e.g., disorder can cause significant effects by changing the nature of the quantum macro state. In these disordered systems, a rather large residual resistivity $\rho_0 = \rho(T \to 0)$ is often encountered, even for single crystals, which means that even weak disorder is influential. As was argued theoretically [2], such a drastic influence is possible

*Corresponding author

Email address: andrzej.slebarski@us.edu.pl (A. Ślebarski)
because the band width of a few eV and an effective Hubbard interaction $U$ of the same order of magnitude result in a much more subtle energy balance that atomic disorder can disturb more easily. Therefore, investigations of atomic scale disorder in the form of defects and vacancies, granularity, and the effective increase in disorder by doping have received renewed attention in recent times particularly because of observations of novel phenomena in strongly correlated materials.

The Kondo insulators are an example of thermoelectric materials where the defects lead to a high value of figure-of-merit $ZT = S^2\sigma T/(\kappa_e + \kappa_L)$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa_e$ is the electronic thermal conductivity, and $\kappa_L$ is the lattice contribution to the thermal conductivity [3] due to the reduction of the lattice contribution to the thermal conductivity.

The effect of disorder on superconducting properties has inspired a great deal of research, with the discovery of unconventional superconductivity in heavy fermion compounds [4] and associated quantum critical behavior. In many superconductors, the critical temperature $T_c$ decreases with increasing disorder and sufficiently strong disorder can, in fact, destroy superconductivity. As this disorder driven transition from a superconducting to a non-superconducting ground state occurs, the localization effects become so strong that often an insulating material results (at $T = 0$ this is known as a quantum phase transition). This transition is referred to as a superconductor-insulator transition [5]. There are also known strongly correlated superconductors that show evidence of nanoscale disorder, meaning that the sample exhibits electronic inhomogeneity over the length scale of the coherence length. Such substantial nanoscale electronic disorder is characteristic of Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ high-$T_c$ materials, as well as PrOs$_4$Sb$_{12}$ [6, 7], CePt$_3$Si [8, 9], and CeIrIn$_5$ [10]. Our recent investigation of the filled cage superconductors La$_3$M$_4$Sn$_{13}$ with $M =$ Rh [11] and Ru [12] have shown evidence of two superconducting phases: an inhomogeneous superconducting state below $T_c^*$ and the superconducting phase at $T_c < T_c^*$. This anomaly was interpreted in the context of the presence of an inhomogeneous superconducting phase between $T_c$ and $T_c^*$.

In this work, we present a comprehensive thermodynamic and high-pressure electrical resistivity study on La$_3$Co$_x$Ru$_{4-x}$Sn$_{13}$ to explain the superconductivity in the presence of disorder. La$_3$Co$_4$Sn$_{13}$ clearly exhibits a homogeneous superconducting phase at $T_c$, while in contrast La$_3$Ru$_4$Sn$_{13}$ and its Co-alloys show evidence of nanoscale inhomogeneity with the presence of $T_c^*$. The impact of disorder on the ground state of superconducting materials has played an important role in condensed matter physics over the years. We believe that our results contribute towards developing a broader understanding of the complex behavior in novel superconducting strongly correlated electron systems.

2. Experimental details

Polycrystalline La$_3$Co$_4$Sn$_{13}$ and La$_3$Ru$_4$Sn$_{13}$ samples were prepared by arc melting the constituent elements on a water cooled copper hearth in a high-purity argon atmosphere with an Al getter. The dilute La$_3$Co$_x$Ru$_{4-x}$Sn$_{13}$ alloys
were prepared by diluting nominal compositions of the parent compounds. The samples were then annealed at 870 °C for 2 weeks. All samples were carefully examined by x-ray diffraction analysis and found to have a cubic structure (space group \( Pm\overline{3}n \)) [13] and for \( x = 1 \) and 3.5, the samples were single phase while for \( x = 2 \) and 3, the alloys were a mixture of two phases.

Stoichiometry and homogeneity were verified by the microprobe technique (scanning microscope JSM-5410) and by XPS analysis. As an example, measurements of \( \text{La}_3\text{Co}_4\text{Sn}_{13} \) showed a composition close to the nominal ratio 3:4:13 (i.e., 14.87:19.93:65.20 for La:Co:Sn). For the \( \text{La}_3\text{Ru}_4\text{Sn}_{13} \) and \( \text{La}_3\text{Co}_x\text{Ru}_{4-x}\text{Sn}_{13} \) alloys, the composition of the samples were also close to the nominal ratio 3:4:13 stoichiometry, and in Table 1, we present the results from measurements of \( \text{La}_3\text{Ru}_3\text{CoSn}_{13} \) noted at different points of the surface.

Table 1: Atomic % reflecting the stoichiometric ratios for \( \text{La}_3\text{CoRu}_x\text{Sn}_{13} \) sample at different areas on the surface.

| element | assumed | stoichiometry in at. % | measured |
|---------|---------|------------------------|----------|
| La      | 15      | 15.94                  | 15.55    | 17.07    | 14.16    |
| Ru      | 15      | 13.97                  | 12.45    | 12.75    | 13.70    |
| Co      | 5       | 4.72                   | 6.62     | 3.62     | 5.07     |
| Sn      | 65      | 65.37                  | 65.38    | 66.47    | 67.07    |

Ambient pressure electrical resistivity \( \rho \) was investigated by a conventional four-point ac technique using a Quantum Design Physical Properties Measurement System (PPMS). Electrical resistivity measurements under pressure were performed in a beryllium-copper, piston-cylinder clamped cell. A 1:1 mixture of \( n \)-pentane and isoamyl alcohol in a teflon capsule served as the pressure transmitting medium to ensure hydrostatic conditions during pressurization at room temperature. The local pressure in the sample chamber was inferred from the inductively determined, pressure-dependent superconducting critical temperature of a Sn ingot [14].

Specific heat \( C \) was measured in the temperature range 0.4 – 300 K and in external magnetic fields up to 9 T using a Quantum Design PPMS platform. The dc magnetization \( M \) and magnetic susceptibility \( \chi \) results were obtained using a commercial (Quantum Design)superconducting quantum interference device magnetometer from 1.8 K to 300 K in magnetic fields up to 7 T.

3. Results and discussion

3.1. Electric transport, magnetic properties, and specific heat of \( \text{La}_3\text{Co}_x\text{Ru}_{4-x}\text{Sn}_{13} \) near the critical temperature \( T_c \) or \( T_c^* \)

Our previous studies have demonstrated that \( \text{La}_3\text{Rh}_4\text{Sn}_{13} \) [11], and \( \text{La}_3\text{Ru}_4\text{Sn}_{13} \) [12] show evidence of two superconducting phases: the high temperature inhomogeneous superconducting state below \( T_c^* \) and the second superconducting phase below \( T_c \), while for \( \text{La}_3\text{Co}_4\text{Sn}_{13} \) the electrical resistivity, specific heat, and
ac and dc susceptibility data exhibit only one homogeneous superconducting state below $T_c$. We demonstrated evidence of nanoscale inhomogeneity in $T_c^*$ high temperature phase as a bulk property in the sense that the samples exhibit electronic disorder over length scale of the coherence length. To summarize these unique results we present the $H - T$ phase diagrams obtained recently for the series of the La$_3$M$_4$Sn$_{13}$ compounds ($M$ = Co, Rh, and Ru) (Fig. 1). The critical temperatures $T_c^*$ and $T_c$ are obtained from electrical resistivity and/or $C(T)$ data under magnetic fields. For La$_3$Co$_4$Sn$_{13}$ the resistivity and specific heat data in $H - T$ diagram are identical, represent the bulk superconducting $T_c$ phase (Fig. 1a), and are well approximated by the Ginzburg-Landau (GL) theory. The best fit of the equation $H_{c2}(T) = H_{c2}(0)(1 - t^2)/(1 + t^2)$, where $t = T/T_c$ gives upper critical field $H_{c2}(0) = 1.38$ T. In case of La$_3$Rh$_4$Sn$_{13}$, the $H - T$ plot shown in Fig. 1b is more complicated. The upper critical field for La$_3$Rh$_4$Sn$_{13}$ deviates from GL theory for $T > 1.4$ K and the electrical resistivity at $H = 0$ gives $T_c^* = 2.98$ K, while the superconducting homogeneous bulk phase, observed in $C(T)$ data below $T_c = 2.13$ K is well approximated by the $H_{c2}(T)$ expression with $H_{c2}(0) = 1.6$ T. In Fig. 1c, the $H - T$ diagram for La$_3$Ru$_4$Sn$_{13}$ indicates the presence of two separate superconducting phases, one ($T_c^*$) obtained from electrical resistivity and other ($T_c$) from specific heat data, the both well approximated by GL theory giving $H_{c2}(0)^* = 3.05$ T, $T_c^* = 3.78$ K and $H_{c2}(0) = 1.45$ T, $T_c = 1.55$ K, respectively for the high-$T$ and low-$T$ superconducting states. The possible explanation of more complex behavior in La$_3$Ru$_4$Sn$_{13}$ is based on the presence of an inhomogeneous superconducting phase [12] with evident impact of atomic disorder. Indeed, $T_c^*$ linearly increases within the system of La$_3$M$_4$Sn$_{13}$ when $T_c^*$ is plotted vs lattice parameter $a$ (c.f. Fig. 1d). For these La$_3$M$_4$Sn$_{13}$ compounds, the largest $a$ value was obtained for La$_3$Ru$_4$Sn$_{13}$, although the atomic radii of Rh and Ru are identical ($r_{Co} < r_{Rh} \approx r_{Ru}$). We also noted, that the magnetic susceptibility $\chi_{ac}$ exhibits the continuous increase of the diamagnetic signal in the Rh and Ru samples within the presence of inhomogeneous superconducting phase with spatial distribution of the magnitude of the superconducting energy gap $\Delta$ (will be discussed). We expect, that an increase of atomic disorder will enhance the separation of the $T_c^*$ and $T_c$ superconducting phases, in consequence large atomic disorder may have contributed to the formation of the only inhomogeneous superconducting phase. We performed a comprehensive thermodynamic and electrical resistivity study which indeed reveal a homogeneous superconducting phase for La$_3$Co$_4$Sn$_{13}$, whereas for La$_3$Ru$_4$Sn$_{13}$ and the Co-substituted La$_3$CoRu$_4$Sn$_{13}$ samples there is evidence of two superconducting phases. Fig. 2 shows results of resistivity measurements of La$_3$CoRu$_4$Sn$_{13}$ vs temperature $T$ in various magnetic fields up to 5.2 T. Here we define the critical temperature at 50 % of the normal state resistivity value. Similar $\rho(T)$ dependencies vs $B$ were presented for La$_3$Co$_4$Sn$_{13}$ and La$_3$Ru$_4$Sn$_{13}$ very recently (c.f. Refs. [11, 12]). In Fig. 3, we show the $H - T$ phase diagram obtained for several investigated compounds and alloys of the system La$_3$Co$_2$Ru$_{4-x}$Sn$_{13}$, where $T_c$ is obtained from electrical resistivity under increasing magnetic fields (curves: $a$ for La$_3$CoRu$_4$Sn$_{13}$, $d$ for La$_3$Ru$_4$Sn$_{13}$, and $g$ for La$_3$Co$_4$Sn$_{13}$). The Ginzburg-Landau (GL) theory fits
Figure 1: Temperature dependence of the upper critical fields $H_{c2}$ in the $H - T$ diagram for La$_3$Co$_4$Sn$_{13}$ (a), La$_3$Rh$_4$Sn$_{13}$ (b), and La$_3$Ru$_4$Sn$_{13}$ (c), the data are taken from Refs. [11] and [12]. $T^*_c$ are obtained from electrical resistivity (red points) the squares (blue) represents $T_c$ value obtained from $C(T)/T$ at different magnetic fields. Panel (d) displays $T^*_c$ vs lattice parameter $a$ at the magnetic field $H = 0$ (the lattice parameters are obtained at the room temperature).
Figure 2: The temperature dependence of the resistivity $\rho$ of $\text{La}_3\text{CoRu}_3\text{Sn}_{13}$ at various externally applied magnetic fields, demonstrating the smooth suppression of $T_c^*$. 

the data well as is shown in the $H - T$ plots in Fig. 3. The best fit of the equation $H_{c2}(T) = H_{c2}(0)(1 - t^2)/(1 + t^2)$ gives the value of the upper critical field $H_{c2}(0)$ presented in Table 2. Within the weak-coupling theory [15] the upper critical field through the relation $\mu_0H_{c2}(0) = \Phi_0/2\pi\xi_0^2$ can be used to estimate the coherence length (where the flux quantum $\Phi_0 = h/2e = 2.068 \times 10^{-15}$ Tm$^2$), and these values are also listed in Table 2. The table also displays the $H_{c2}(0) = 0.693T_c\frac{dH_{c2}}{dT}\bigg|_{T=T_c}$ [16, 17] based on the results presented in Fig. 3.

Shown in Fig. 4 is the specific heat $C$ plotted as $C$ vs $T$ at various magnetic fields (in panel a), and ac and dc magnetic susceptibility (panel b) for $\text{La}_3\text{Co}_{3.5}\text{Ru}_{0.5}\text{Sn}_{13}$. The heat capacity data for $\text{La}_3\text{Co}_{3}\text{Sn}_{13}$ (not shown in Fig. 4, c.f. Ref. [11]) indicates bulk superconductivity below $T_c = 1.95$ K in agreement with resistivity data, while $\text{La}_3\text{Co}_{3.5}\text{Ru}_{0.5}\text{Sn}_{13}$ shows a broad transition to the superconducting state with the same $T_c$ from the resistivity and susceptibility data.

For $\text{La}_3\text{CoRu}_3\text{Sn}_{13}$, the superconductivity shown in $C/T$ data (in Fig. 5a and Fig. 6) also shows broad transition with the maximum in $\Delta C/T$ at $T_c \approx 5$ K spanning the maximum in $\chi''$ in Fig. 5b. Under certain conditions, the ac losses in superconducting transition can exceed those of a normal metal, leading to a peak in $\chi''$ vs $T$ [18]. However, it was argued that a $\chi''$ maximum can occur in surface superconductors at sufficiently low frequencies, this is not the case in the ac magnetic susceptibility shown in Fig. 4\textsuperscript{1}. The perfect diamagnetism of

\textsuperscript{1}A surface superconductivity effect can be observed above the bulk critical field $H_{c2}$ for
Figure 3: Temperature dependence of the upper critical fields $H_{c2}$ in the $H - T$ diagram presented for La$_3$CoRu$_3$Sn$_{13}$ (points a, and b represent the inhomogeneous $T_s^c$ phase, points c, d, and e are obtained for the bulk $T_c$ phase), La$_3$Ru$_4$Sn$_{13}$ (points h are obtained for the inhomogeneous phase), and La$_3$Co$_4$Sn$_{13}$ (points g), respectively. The solid lines represent a Ginzburg-Landau fitting model for $H_{c2}(T)$. Detailed description: for La$_3$CoRu$_3$Sn$_{13}$, points a represent $T_s^c$ obtained from resistivity under $H$ at 50% decrease of the normal state $\rho$-value. Points b show the temperatures where anomalous behavior begins in $\Delta C/T$ at the high-temperature side of the specific heat peak. Points c are attributed to temperature of the maxima in the best fits of $f(\Delta)$ to the experimental data $\Delta C(T)/T$ [$\Delta C(T) = C(T, B = 0) - C(T, B = 5T)$], d is the temperature of maximum in $\chi''(T)$ at the magnetic field $B = 0$, while e show the temperatures where $\rho(T) \rightarrow 0$ (c.f. Fig. 2). For La$_3$Ru$_4$Sn$_{13}$: points h represent $T_s^c$ obtained from the $\rho$-data, while i are $T_s$ obtained from the specific heat data (Ref. [12]). For La$_3$Co$_4$Sn$_{13}$: g are $T_s$ obtained from $\rho(T)$ at 50% decrease of the normal state $\rho$-value (Ref. [11]). f are $T_s$ obtained from $C(T)$ vs $B$ for La$_3$Co$_{3.5}$Ru$_{0.5}$Sn$_{13}$ (c.f. Fig. 4).

Saint-James and de Gannes [19] have shown theoretically that a surface superconducting layer with a critical field $H_{c3} = 1.69H_{c2}$ can exist above $H_{c2}$ but only when the external magnetic field is parallel to the sample surface. Experimental evidence [20, 21, 22, 23, 24, 25] has confirmed the existence of the surface critical field $H_{c3}$. In case of La$_3$Ru$_4$Sn$_{13}$ the hypothetical $H_{c3}/H_{c2} = 1.8$ ratio is close to the calculated one, however, $T_c \neq T_s^c$ behavior observed for the surface and bulk superconductivity is not theoretically expected. Moreover, the high-$T_c$ superconducting state is observed under the zero magnetic field. The both arguments seem exclude the surface superconductivity effect in La$_3$Ru$_4$Sn$_{13}$ type II superconductors.
Table 2: Superconducting state quantities for La$_3$Co$_x$Ru$_{4-x}$Sn$_{13}$ near the bulk superconducting phase $T_c$ or the inhomogeneous phase below $T^*_c$.

| La$_3$Co$_x$Ru$_{4-x}$Sn$_{13}$ | $x = 4$ | $x = 3.5$ | $x = 1$ | $x = 0$ |
|--------------------------------|--------|--------|--------|--------|
| $T_c$ (K)                     | 1.95   | 2.41   | $\approx 5$ | 1.58   |
| $T^*_c$ (K)                   | 5.58   | 3.76   |        |        |
| $\frac{dH_{c2}}{dT} |_{T=T_c}$ (T/K) | -0.904 | -1.34  | $-1.3 (T \rightarrow T^*_c)$ | $-1.33 (T \rightarrow T_c)$, $-1 (T \rightarrow T^*_c)$ |
| $H_{c2}(0) = 0.693T_c \frac{dH_{c2}}{dT} |_{T=T_c}$ (T) | 1.22   | 2.24   | 4.97 $(T \rightarrow T^*_c)$ | 1.45 $(T \rightarrow T_c)$, 2.61$(T \rightarrow T^*_c)$ |
| $\xi(0)$ (nm)                | 16     | 11     | $\xi^*(0) = 8$ | 18, $\xi^*(0) = 9$ |
| $\frac{\Delta C}{\gamma T_c}$ | 1.5(5) | 1.7    | undefined | 1.6(1) |
| $\frac{dT_c}{dP}$ (K/GPa)    | 0.05   | -0.12  | -0.32  | -0.24  |
| $\frac{dT^*_c}{dP}$ (K/GPa)  |        |        |        |        |

the full Meissner state $\chi' = -1/(4\pi d) = 9.55 \times 10^{-3}$ emu/g for mass density $d = 8.3$ g/cm$^3$ (Refs. [26, 27]) is reached below the temperature of the maximum in $\chi''$, it should also be noted that $\chi''$ depends on the frequency of the magnetic field, and that is characteristic of magnetically inhomogeneous materials. We believe that the superconductivity in La$_3$Co$_3$Ru$_3$Sn$_{13}$ is completely inhomogeneous superconductivity to explain the anomalies in the specific heat and $\chi''$. Namely, we believe that the resistivity drop marks the onset of an inhomogeneous superconducting phase with spatial distribution of the magnitude of the superconducting gap, as a bulk property of the sample. Since the drop of the resistivity at $T^*_c$ is not accompanied by a maximum of $\chi''$ (c.f. Fig. 5), the volume occupied by the inhomogeneous phase is too small to cancel out normal-state paramagnetic contributions. On the other hand, the superconducting regions must be arranged as to form the necessary continuous paths reflected in the resistivity measurements.

The main argument for the inhomogeneous superconducting phase is the broadness of the thermodynamic phase transition seen in Fig. 5a, that is characteristic for systems mesoscopic size pair disorder. It has been shown in Ref. [28] that potential disorder smooth on a scale comparable to the coherence length leads, in contradistinction to conventional impurity potential scatterers, to large modulation of the superconducting gap and large transition width.

and La$_3$CoRu$_3$Sn$_{13}$. 
Figure 4: (a) The temperature dependence of the specific heat $C(T)$ of La$_3$Co$_{3.5}$Ru$_{0.5}$Sn$_{13}$ at different magnetic fields $B$. (b) The ac magnetic susceptibility $\chi_{ac}$ at $B = 12$ Gs divided by theoretical value of the full Meissner state $\chi' = 1/(4\pi d)$, and zero-field-cooled (ZFC) and field-cooled (FC) dc magnetic susceptibility in an applied field of $B = 500$ Gs.

Following Ref. [29] we assume a simple Gaussian gap distribution

$$f(\tilde{\Delta}) \propto \exp \left[ -\frac{(\tilde{\Delta} - \tilde{\Delta}_0)^2}{2D} \right],$$

where $\tilde{\Delta}_0$ and $D$ are treated as fitting parameters. The best fit of $f(\tilde{\Delta})$ to the experimental data $\Delta C(T)/T$ gives the points $c$ in Fig. 3, in good agreement with the points $e$ in Fig. 3. Points $d$ represents the temperature of the maximum in $\chi''$. The behavior observed in this strongly disordered alloy is qualitatively different than that in La$_3$Ru$_4$Sn$_{13}$ [12], or La$_3$Rh$_4$Sn$_{13}$ [11] with clear evidence for two superconducting phases: the high temperature inhomogeneous superconducting state below $T^*_c$ and the second (bulk) superconducting phase below $T_c$, where $T^*_c > T_c$. We also note that the $C(T)/T$ data for La$_3$CoRu$_4$Sn$_{13}$ is not
Figure 5: (a) The temperature dependence of the specific heat $\Delta C(T)/T$ with a Gaussian gap distribution fit $f(\tilde{\Delta})$ and resistivity $\rho(T)$, both at $B = 0$ for La$_3$CoRu$_3$Sn$_{13}$. For the sample under $B = 0$, $\Delta C(T)/T = C(T, B = 0)/T - C(T, B = 5T)/T$, see Fig. 6. (b) The ac magnetic susceptibility ($B = 12$ Gs) $\chi'$ and $\chi''$ at different frequencies, and ZFC and FC dc magnetic susceptibility ($B = 500$ Gs).

well approximated by $C/T \sim \exp(-\tilde{\Delta}(0)/k_BT)$, while the bulk superconducting phases in both La$_3$Ru$_4$Sn$_{13}$ and La$_3$Co$_4$Sn$_{13}$ are well fit by this expression (c.f., Fig. 6). Excluding the case of La$_3$CoRu$_3$Sn$_{13}$, we found $C(T)$ follows the behavior described by the BCS theory in the weak-coupling limit, which indicates $s$-wave superconductivity. The BCS theory for $s$-wave superconductors provides a relation $\Delta C/(\gamma T_c) = 1.43$ between the jump of the specific heat $\Delta C$ at the critical temperature $T_c$ and the normal metallic state contribution $\gamma$; the theoretical value $\Delta C/(\gamma T_c) = 1.43$ is very close to the values presented in Table 2.

In Fig. 7, we show that the hysteresis loop in the superconducting state of La$_3$CoRu$_3$Sn$_{13}$ is about 3 T, while in the case of the remaining compounds, it is nearly an order of magnitude smaller. The broad hysteresis loop suggests strongly inhomogeneous material.

We expect that external pressure applied to strongly disordered materials
Figure 6: The specific heat $\Delta C(T)/T$ under various magnetic fields for La$_3$CoRu$_3$Sn$_{13}$. The arrow indicates the beginning of the superconductivity at $B = 0$, the transitions under magnetic fields $B \neq 0$ are similarly broad. The insets display the $C/T$ data near $T_c$ for La$_3$Ru$_4$Sn$_{13}$ and La$_3$Co$_4$Sn$_{13}$. In case of La$_3$Ru$_4$Sn$_{13}$ the bulk effect at $T_c$ and inhomogeneous superconducting phase between $T_c^*$ and $T_c$ are both shown. The dotted line is the best fit to the data for the expression $C(T)/T = \gamma + \beta T^2 + A \exp(-\Delta(0)/k_BT)$.

may drive lattice instabilities from the compounds by varying the dominant parameters of the superconducting state, e.g., electronic density of states at the Fermi level. Most of the known superconductors show a decrease of $T_c$ with increasing applied pressure [30]; however, increasing pressure should also partially mitigate the inhomogeneity and stabilize the structural properties of the disordered system, and as a consequence, $T_c^*$ is also expected to decrease with pressure. The evidence of this is shown in Figs. 8 - 10 and summarized in Fig. 11. The observed increase of $T_c$ with pressure shown in Fig. 11 for La$_3$Co$_4$Sn$_{13}$ was recently discussed as a possible result of a subtle structural distortion below $T = 140$ K [11].

The pressure coefficients $dT_c/dP$ and $dT_c^*/dP$ obtained from the respective $T_c$ vs $P$ data shown in Fig. 11 are listed in Table 2. The pressure coefficients of $T_c^*$ are almost twice large as those of $T_c$, while for La$_3$Co$_4$Sn$_{13}$, the $dT_c/dP = 0.05$ K/GPa is positive. The $P$-dependence of $T_c$ has been discussed according to the Eliashberg theory of strong-coupling superconductivity [31]. We employ the McMillan expression [32, 33]

$$T_c = \frac{\theta_D}{1.45} \exp \left\{ \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right\},$$

where $\theta_D$ is the Debye temperature, $\lambda = \mu^*/\lambda^*$, and $\mu^*$ is the effective mass.

$$
\text{Fig. 6: The specific heat } \Delta C(T)/T \text{ under various magnetic fields for } \text{La}_3\text{CoRu}_3\text{Sn}_{13}. \text{ The arrow indicates the beginning of the superconductivity at } B = 0, \text{ the transitions under magnetic fields } B \neq 0 \text{ are similarly broad. The insets display the } C/T \text{ data near } T_c \text{ for } \text{La}_3\text{Ru}_4\text{Sn}_{13} \text{ and } \text{La}_3\text{Co}_4\text{Sn}_{13}. \text{ In case of } \text{La}_3\text{Ru}_4\text{Sn}_{13} \text{ the bulk effect at } T_c \text{ and inhomogeneous superconducting phase between } T_c^* \text{ and } T_c \text{ are both shown. The dotted line is the best fit to the data for the expression } C(T)/T = \gamma + \beta T^2 + A \exp(-\Delta(0)/k_BT).

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$$T_c = \frac{\theta_D}{1.45} \exp \left\{ \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right\},$$

\text{where } \theta_D \text{ is the Debye temperature, } \lambda = \mu^*/\lambda^*, \text{ and } \mu^* \text{ is the effective mass.}
Figure 7: Magnetization $M$ per formula unit vs magnetic field at various temperatures. The inset shows a symmetric hysteresis loop at $T = 1.8$ K for the superconducting state in La$_3$Co$_4$Sn$_{13}$. Panel (a) shows the data for La$_3$Co$_3$Ru$_{0.5}$Sn$_{13}$, panel (b) displays $M$ for La$_3$CoRu$_3$Sn$_{13}$, which is a solution of the finite-temperature Eliashberg equations, to connect the value of $T_c$ with the electron-phonon coupling parameter $\lambda$, Debye temperature $\theta_D$ and the Coulomb repulsion $\mu^*$ (the value of $\mu^*$ was chosen to be 0.1 as is typical for $s$ and $p$ band superconductors). This yields $\lambda \approx 0.4$ for $T_c$s and a larger $\lambda$ value $\sim 0.5$ for $T_c^{*}$s. However, in the both superconducting states, relatively small $\lambda$ negates the strong coupling superconductivity. The coupling $\lambda$ is given by

$$\lambda = \frac{N(E_F)\langle I^2 \rangle}{M\langle \omega^2 \rangle},$$

(3)
where $\langle \langle I^2 \rangle \rangle$ is the square of the electronic matrix element of electron–phonon interactions averaged over the Fermi surface, $\langle \omega^2 \rangle$ is an average of the square of the phonon frequency, and $M$ is the atomic mass. Usually, $\mu^*$ and $\langle I^2 \rangle$ are very weakly pressure dependent\(^2\), so that the main pressure effect on the transition temperature comes from $\theta_D$ and $N(E_F)$ ($\langle \omega^2 \rangle$ depends on $\theta_D$). The pressure dependence of $\theta_D$ is given by the Gr"uneisen parameter $\gamma_G = -\frac{d \ln \theta_D}{d \ln V}$, which represents the lattice stiffening. Using the McMillan expression it was found [34] that $\gamma_G$ strongly determines the magnitude and sign of $dT_c/dP$. Our data suggest a larger $\gamma_G$ for the inhomogeneous superconducting state with respect to the bulk effect observed below $T_c$; in case of La$_3$Co$_4$Sn$_{13}$, the Gr"uneisen parameter is expected to be smaller. It is also possible that in the case of inhomogeneous superconductivity, the pressure dependence of the density of states at the Fermi level is more pronounced than in bulk superconductors, and may lead to a larger value of $dT_*^*/dP$ than $dT_c/dP$.

Since the Co radius is smaller than that of Ru, increasing the amount of Co in the La$_3$Co$_x$Ru$_{4-x}$Sn$_{13}$ system leads to an effective internal pressure. With $x$ increasing from 0 to 1, $T_c$ increases as well, but further, for $x$ going from 1 to 4, $T_c$ decreases almost linearly from 5 K to 1.95 K (see Fig. 12). For $x \geq 1$ the dependence of $T^*_c$ on the chemical pressure is consistent with the effects of external pressure. With $x$ increasing from 1 to 4, i.e., with increasing chemical pressure, $T^*_c$ decreases from about 5.58 K to 1.95 K. In this case $T^*_c$ is slightly more sensitive to the chemical pressure than $T_c$, what resembles the situation presented in Fig. 11.

It is difficult to understand the abnormally large critical temperature for La$_3$CoRu$_3$Sn$_{13}$, that is much larger than the $T^*_c$ characterizing the inhomogeneous superconducting phase in of La$_3$Ru$_4$Sn$_{13}$. Typically, disorder strongly reduces the critical temperature due to the elevated impurity scattering; therefore, large value of $T^*_c$ is surprising. It is, however, also possible to enhance superconductivity by local disorder [40]. In this case, the superconductor may be inhomogeneous with lower and higher $T_c$ regions. Above $T^*_c$, superconducting clusters appear, which at $T^*_c$ form a network of continuous paths through the entire sample. The random character of the Co substitution leads to a statistical (chaotic) distribution of these clusters. Despite the drop in the electrical resistivity, the fraction of the volume occupied by the superconducting state can still be small. This is a typical percolation scenario [41]. Such a double}

\(^2\)Recently [11], we demonstrated the $s$-wave superconductivity in La$_3$M$_4$Sn$_{13}$ (M=Co, Rh) compounds. For traditional $sp$ metal superconductor the pressure dependence of the effective electron-electron Coulomb repulsion $\mu^*$ appearing in the McMillan expression was usually neglected due to the small change of $\mu^*$ compared with that of the electron-phonon coupling parameter $\lambda$ [35]. Recently [36], it also has been shown that the contribution from $\mu^*(P)$ to the variation of $T_c$ with pressure is much more important than that of $\lambda(P)$ for MgB$_2$ superconductor with high value of $T_c = 40$ K. It was, however, argued that the pressure dependence of $\mu^*$ makes a significant contribution to the change of $T_c$ under very high pressures [37]. We used much smaller pressure in our experiment, therefore this is not a case. The pressure dependence of the mean-square electron-ion matrix element $I$ is assumed pressure independent [38, 39].
transition at $T^*_c$ and $T_c$ can not be the result of the sample being two-phase. A large shielding effect in the $\chi_{ac}$ susceptibility within the inhomogeneous phase and the $\chi'_{ac}$ maximum at $T^*_c$ (c.f. Figs. 4 and Fig. 5, and also Ref. [11]) strongly confirm the absence of minority phase at the few volume % level. At a lower temperature $T_c$, the previously normal regions becomes superconducting and a macroscopic (bulk) superconducting state is formed. This is the transition that is seen in the specific heat and susceptibility measurements.

4. Concluding remarks

In most of the known superconductors, the transition temperature $T_c$ decreases as a consequence of increased disorder. However, there are known examples of strongly correlated superconductors which show evidence of nanoscale disorder leading to an inhomogeneous superconducting state and, as a consequence, the critical temperature $T^*_c > T_c$. Both superconducting phases: the $T_c$-bulk phase and the $T^*_c$ high-temperature inhomogeneous phase whose onset is observed between $T^*_c$ and $T_c$ are present in the skutterudite-related La$_3$Rh$_4$Sn$_{13}$ and La$_3$Ru$_4$Sn$_{13}$ compounds. In these compounds, we observed a decrease of the critical temperature with the application of external pressure, however, the pressure coefficients $dT^*_c/dP$ are nearly twice as large as their respective $dT_c/dP$ values. In the case of La$_3$Co$_4$Sn$_{13}$, $dT_c/dP$ is positive. The $P$-variations of $T_c$ were interpreted in the context of the Eliasberg theory and discussed as a consequence
Figure 9: Resistivity of La$_3$Co$_{3.5}$Ru$_{0.5}$Sn$_{13}$ at different applied pressure. The inset displays the details.

Figure 10: Resistivity of La$_3$Co$_{3.5}$Ru$_{0.5}$Sn$_{13}$ at different applied pressure. The inset displays the details.
Figure 11: Critical temperatures \( T_c \) and \( T^*_c \) vs pressure \( P \). The critical temperatures are obtained from resistivity under applied pressure at 50% of the normal state value. For \( \text{La}_3\text{Ru}_4\text{Sn}_{13} \), \( T_c \) is estimated as a very weak change in \( \rho(T) \) below \( T^*_c \) (the inset exhibits the low temperature details in \( \rho(T) \) of \( \text{La}_3\text{Ru}_4\text{Sn}_{13} \) at \( P=0.11 \) GPa, an arrow indicates the temperature \( T_c \)).

of the lattice stiffening. The results shown in this work should be of interest for understanding the \( x \)-dependent superconducting state of \( \text{La}_3\text{Co}_x\text{Ru}_{4-x}\text{Sn}_{13} \) where \( T^*_c \) is larger than \( T^*_c \) for \( \text{La}_3\text{Ru}_4\text{Sn}_{13} \), (e.g., for \( \text{La}_3\text{CoRu}_3\text{Sn}_{13} \) it is almost twice as large). This unique observation is not predicted by the BCS theory and not observed in other chemically substituted superconductors. We suggest that local disorder is responsible for the increase in \( T_c \) in strongly inhomogeneous regions in the sample and/or the effect of chemical pressure when \( \text{La}_3\text{Ru}_4\text{Sn}_{13} \) is substituted with by Co. This scenario should be verified theoretically.

**Acknowledgments**

The research was supported by National Science Centre (NCN) on the basis of Decision No. DEC-2012/07/B/ST3/03027. M.M.M. acknowledges support by NCN under grant DEC-2013/11/B/ST3/00824. High-pressure research at
Increasing chemical pressure T$_c$, T$_c^*$ as a function of x for La$_3$Co$_x$Ru$_{4-x}$Sn$_{13}$. Dashed lines are a guide to the eye. The blue area represents the inhomogeneous superconducting phase (IS), whereas the red area represents bulk superconductivity (BS).

Figure 12: Ambient pressure $T_c$ and $T_c^*$ as a function of x for La$_3$Co$_x$Ru$_{4-x}$Sn$_{13}$. Dashed lines are a guide to the eye. The blue area represents the inhomogeneous superconducting phase (IS), whereas the red area represents bulk superconductivity (BS).

the University of California, San Diego, was supported by the National Nuclear Security Administration under the Stewardship Science Academic Alliance program through the U. S. Department of Energy under Grant Number DE-NA0001841. One of us (A.Š.) is grateful for the hospitality at the University of California, San Diego (UCSD).

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