The effective increase in atomic scale disorder by doping and superconductivity in Ca$_3$Rh$_4$Sn$_{13}$.

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The comprehensive research of the electronic structure, thermodynamic and electrical transport properties reveals the existence of inhomogeneous superconductivity due to structural disorder in Ca$_3$Rh$_4$Sn$_{13}$ doped with La (Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$) or Ce (Ca$_{3-x}$Ce$_x$Rh$_4$Sn$_{13}$) with superconducting critical temperatures $T_c^*$ higher than those ($T_c$) observed in the parent compounds. The $T-x$ diagrams and the entropy $S(x)/T$ isotherms document the relation between degree of an atomic disorder and separation of the high-temperature $T_c^*$ and $T_c$-bulk phases. In these dirty superconductors with the mean free path much smaller than the coherence length, the Werthamer-Helfand-Hohenberg theoretical model does not well fit the $H_{c2}(T)$ data. We suggest that this can result from two-band superconductivity or from the presence of strong inhomogeneity in these systems. The multiband model very well describes the $H_{c2}(T)$ dependencies, but the present results as well as our previous studies give arguments for the scenario based on the presence of nanoscopic inhomogeneity of the superconducting state. We also revisited the nature of structural phase transition at $T^* \sim 130-170$ K and documented that there might be another precursor transition at higher temperatures. The impact of the magnetic Ce-Ce correlations on the increase of $T_c$ in respect to the critical temperatures of Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$ is also discussed.

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I. INTRODUCTION

The family of $R_3M_2$Sn$_{13}$ compounds, where $R$ is an alkali metal or rare earth and $M$ is a transition metal (Ir, Rh, Ru, or Co), was first synthesized by Remeika et al.$^{11}$ Recently, there has been a resurgence of interest among the condensed matter community due to unusual properties of these materials, characterized by strong electronic correlation effects,$^3$ structural phase transitions associated with the Fermi surface reconstruction,$^{4,5}$ and superconductivity.$^{6}$ Ca$_3$Rh$_4$Sn$_{13}$, a member of this skutterudite-related family is a good model material to study the various low-temperature and structural properties. Ca$_3$Rh$_4$Sn$_{13}$ adopts the $Pm\bar{3}n$ cubic structure and has been found to be a BCS superconductor with a superconducting transition temperature $T_c$ of about 8.4 K, which can be strongly reduced by antisite defects generated by different heat treatment.$^{10,11}$ Similarly, an atomic disorder can occur as a result of doping. Recently, we documented experimentally, that the effect of nanoscale disorder generated by doping of the Ca$_3$Rh$_4$Sn$_{13}$ and isostructural La$_3$M$_2$Sn$_{13}$ superconductors leads to appearance of an inhomogeneous superconducting state, characterized by the critical temperature $T_c^*$ higher than $T_c$ of the bulk phase. Similar interesting behavior has been observed in a number of other strongly-correlated superconductors (see, e.g.$^{13,19}$), particularly those close to a quantum critical point (QCP), where an increase of $T_c$ was documented by nanoscale electronic disorder. In the critical regime, such a system is at the threshold of an instability, and even a weak perturbation, such as disorder can cause significant macroscopic effects. This is a reason for continuing our research of the atomic scale disorder and its impact on a novel phenomena in Ca$_3$Rh$_4$Sn$_{13}$ and similar materials. Moreover, for a series of $R_3M_2$Sn$_{13}$ it was claimed that the cubic crystallographic structure $Pm\bar{3}n$ is modulated below temperature $T^* \sim 130-170$ K with a kstar of a propagation vector $q=(\frac{1}{2}, \frac{1}{2}, 0)$. The structural second order-type transition at $T^*$ converts the simple cubic high-temperature structure $Pm\bar{3}n$ into a body centered cubic structure $I4_1$ with twice the lattice parameters due to the distortion of the Sn1Sn2$_2$ icosahedra related to a charge transfer from Sn2 toward Sn1 atoms.$^{21}$ However, no signature of this anomaly associated with $T^*$ was observed for undoped Ca$_3$Rh$_4$Sn$_{13}$.
We documented, that Ca, when is partially replaced by La \((\text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13})\) or Ce \((\text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13})\) which simulates a negative chemical pressure, revealed the existence of this structural transformation at the presence of \(T_c\) and \(T^*_c\) superconducting phases. Recently, it was also shown that this phase transition remains second-order at \(T = 0\), which leads to a novel structural QCP\(^{[18]}\). In this manuscript, we discuss the impact of the magnetic correlations on the increase of \(T_c\) and \(T^*_c\) of the Ce-doped alloys with respect to superconducting temperatures of \(\text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13}\). On the basis of electrical transport, thermodynamic properties, and band structure calculations we propose a phenomenological model, which qualitatively interprets the experimental data. Finally, we revisit the effect of structural instability at \(T^*_c\) and show that there might be another, precursor transition at higher temperatures.

II. EXPERIMENTAL DETAILS

The \(\text{Ca}_3\text{Rh}_4\text{Sn}_{13}\), \(\text{La}_3\text{Rh}_4\text{Sn}_{13}\) and \(\text{Ce}_3\text{Rh}_4\text{Sn}_{13}\) polycrystalline 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 \(\text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13}\) and \(\text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}\) alloys were then prepared by diluting the parent compounds with nominal compositions of La or Ce and Ca which were then annealed at 870°C for 2 weeks. All samples were examined by x-ray diffraction (XRD) analysis and in the first approximation found to have a cubic structure (space group \(\text{Pm} \bar{3} \text{m}\)).

Variable temperature powder XRD measurements were carried out on a single crystal diffractometer Rigaku (Oxford Diffraction) Supernova in a powder mode using Cu \(K_\alpha\) microsource (50 kV, 0.80 mA). Small amounts of samples (< 1 mg) were powdered before the experiments and glued to a tip of a glass rod (0.1 mm). Data were collected on a heating ramp with stops at temperatures chosen in a 90 K to 390 K range. At each temperature 2x30 s acquisitions (30 degree rotation) were collected for 8 detector positions, effectively covering 2\(\theta\) range from 2 to 155 degrees. Synchrotron powder XRD was carried out on \(\text{La}_{2.8}\text{Ca}_{0.2}\text{Rh}_4\text{Sn}_{13}\) at the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble. The specimen was powdered and loaded into a 0.3 mm quartz capillary. The instrument was operated at wavelength 0.71446 Å and the temperature was maintained using Cryostream 700+ temperature controller. The datasets were collected on a heating ramp with 6 K/min. The 2D images were processed using CrysAlis software package and full pattern Rietveld refinements were carried out using Fullprof Suite\(^{[22]}\). Variable temperature ramps were merged, visualized and fit using the DAVE package\(^{[23]}\).

Variable temperature Raman spectra were collected on a Horiba Yvon Jobin LabRAM HR instrument using a 531 nm laser and Linkam Examina THMS 600 cold stage. Measurements were performed using twenty integrations with a 6 s acquisition time with x50 long working distance objective and 600 lines per mm grating (giving a spectral resolution of 0.5 cm\(^{-1}\)) over a Raman shift range between 80 cm\(^{-1}\) and 1200 cm\(^{-1}\).

The compositions of the \(\text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}\) and \(\text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13}\) samples, checked by electron micro-probe technique and by XPS analysis were very close to the assumed stoichiometry. However, local fluctuations in stoichiometry over the length of the sample were observed at the nanoscale for all \(x\) components of the both systems, the greatest one exist for Ce or La, which explain the strong disorder induced by doping (c.f. the detailed investigations of the homogeneity of the series of \(\text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}\) compounds and discussed in Ref. \[^{[12]}\] similar fluctuations in the composition are observed in the system of \(\text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13}\) alloys, which signals site disorder).

Figure 1 displays the lattice parameters \(a\) vs \(x\) obtained at room temperature for \(\text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13}\) and \(\text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}\) samples, with an error bar determined by the experimental accuracy of \(\Delta \theta = 0.005°\) for each XRD pattern. For both cases \(a\) increases linearly with the increasing concentration of the dopant, although the La and Ce atomic radii are smaller than the Ca atomic radius. This behavior can be explained by different ionic radius of \(\text{Ca}^{2+} \approx 1 \text{ Å}, \text{La}^{3+} \approx 1.15 \text{ Å},\) and \(\text{Ce}^{3+} \approx 1.11 \text{ Å},\) respectively, which suggests the localized character of \(f\)-electron bands and the localized magnetic moment of Ce. Electrical resistivity \(\rho\) at am-

![FIG. 1. The lattice parameter, \(a\), plotted against La or Ce concentration, \(x\), for the \(\text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13}\) and \(\text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}\) series of alloys. The lattice parameters follow Vegard’s law, which suggests good sample quality and stoichiometry of the components \(x\).](image)
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 (dc and ac) magnetic susceptibility $\chi$ were obtained using a commercial superconducting quantum interference device magnetometer from 1.8 K to 300 K in magnetic fields up to 7 T.

The XPS spectra were obtained with monochromatized Al $K\alpha$ radiation at room temperature using a PHI 5700 ESCA spectrometer. The sample was broken under high vacuum better than $6 \times 10^{-10}$ Torr immediately before taking a spectrum.

The refined lattice parameters shown in the Fig. 1 and corresponding atomic positions were used in our band structure calculations. The band structure calculations were accomplished using fully relativistic full potential local orbital method (FPLO9-00-34 computer code$^{26}$) within the local spin density approximation (LSDA) as well as ELK FP-LAPW/APW+lo code$^{27}$. The exchange correlation potential $V_{xc}$ was used in the form proposed by Perdew-Wang$^{28}$ in both cases. The number of k-points in the irreducible wedge of Brillouin Zone was 80. The results obtained from both methods were accomplished for the same $V_{xc}$, and as expected were essentially the same. The ELK-code was used for accurate calculations of the electron localization function (ELF), whereas the FPLO method was used to study the pressure effects on the electron density of states (DOS) of the samples.

III. RESULTS AND DISCUSSION

A. Superconductivity in the presence of disorders in Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$ doped with La and Ce: a comparative study

1. Electrical resistivity; the effect of magnetic field and pressure on superconductivity

We expect that an increase of crystallographic disorder by doping of Ca$_{3-x}$Rh$_4$Sn$_{13}$ will enhance the separation of the $T^*_c$ and $T_c$ superconducting phases. We present a comprehensive magnetic and electrical resistivity study which indeed give evidence of these two superconducting phases. Figure 2 displays temperature dependence of electrical resistivity $\rho(T)$ for Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$ with $x = 0.2, 1.5$, and $2.8$ in various magnetic fields. Similar $\rho(T)$ dependencies vs $B$ were very recently reported for the series of Ca$_{3-x}$Ce$_x$Rh$_4$Sn$_{13}$ alloys$^{29}$. The critical temperature $T^*_c$ is defined as the temperature at which the resistivity falls to 50% of its normal state value. The transitions shown in Fig. 2 are much broader than that of Ca$_3$Rh$_4$Sn$_{13}$, which signals strong inhomogeneity due to the doping. The effect is so strong that for the alloys $x = 1.5$ and $2.8$, $\rho(T)$ exhibits two distinct drops, which indicate a double resistive phase transition to the superconducting state, e.g., for the sample $x = 2.8$, the first resistivity drop is observed at $\sim 5.3$ K where isolated super-

conducting islands begin to be formed, while the second one is at lower temperature $T_c \sim 3.9$ K, where a global phase coherence develops with a limit of $\rho \to 0$. This complex transition is also seen in the ac susceptibility (see section III.2.). For Ce-substituted $x > 1$ samples, a large atomic disorder may have contributed to the formation of the only inhomogeneous superconducting phase (see the $T - H$ diagram in section A.3). Another inter-

FIG. 2. Electrical resistivity for Ca$_{1-x}$La$_x$Rh$_4$Sn$_{13}$ ($x = 0.2, 1.5$, and $2.8$) at various externally applied magnetic field. The left inset shows the details near the critical temperature. The right inset displays the value of $\rho$ measured just above $T_c$ at $T = 9$ K.
estimating phenomenon is the observation of positive magneto-resistivity \( MR = [\rho(4T) - \rho(0)]/\rho(0) \) obvious near \( T_c^\star \). At the critical temperature \( MR \) coefficient is about 20\% for La-doped and about 90\% for superconducting Ce-doped alloys. The positive magneto-resistivity can be interpreted as an effect of strong \( d \)-electron correlations,\(^\text{12,29}\) which dominate the field-dependent electronic transport in this nonmagnetic material.\(^\text{30}\) Figures 3 and 4 show

![Graph showing electrical resistivity vs. temperature for Ca\(_{2.8}\)La\(_{0.2}\)Rh\(_{4}\)Sn\(_{13}\) under applied pressure.](image)

**FIG. 3.** Electrical resistivity for Ca\(_{2.8}\)La\(_{0.2}\)Rh\(_{4}\)Sn\(_{13}\) under applied pressure. The inset shows the value of \( \rho \) measured just above \( T_c^\star \) at \( T = 8 \) K.

the electrical resistivity as a function of temperature for Ca\(_{2.8}\)La\(_{0.2}\)Rh\(_{4}\)Sn\(_{13}\) and Ca\(_{0.5}\)La\(_{2.5}\)Rh\(_{4}\)Sn\(_{13}\) under external pressure. From these data we obtained the pressure coefficients \( \frac{dT_c}{dP} \) = −0.19 K/GPa for Ca\(_{2.8}\)La\(_{0.2}\)Rh\(_{4}\)Sn\(_{13}\) and −0.21 K/GPa for Ca\(_{0.5}\)La\(_{2.5}\)Rh\(_{4}\)Sn\(_{13}\), respectively. Very similar pressure coefficients of \( T_c^\star \) are: −0.2 K/GPa for Ca\(_{3}\)Rh\(_{4}\)Sn\(_{13}\) and −0.3 K/GPa for the \( x = 0.2 \) cerium doped sample.\(^\text{12}\) These coefficients \( \frac{dT_c^\star}{dP} \) are significantly larger than the pressure coefficients of \( T_c \), found in similar isostructural La-based superconductors (e.g., \( \frac{dT_c}{dP} \) is only −0.05 K/GPa for La\(_{3}\)Rh\(_{4}\)Sn\(_{13}\)).\(^\text{13}\) The \( P \)-dependence of \( T_c \) can be interpreted according to the Eliashberg theory of superconductivity\(^\text{31,32}\) and the McMillan expression,\(^\text{32,33}\)

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

as a solution to the finite-temperature Eliashberg equations, where \( \lambda \) is the electron-phonon coupling parameter, and the Coulomb repulsion \( \mu^* \) is assumed to be \( \sim 0.1 \) which is a typical value known for \( s \) and \( p \) band superconductors. Our estimation gives \( \lambda \approx 0.62 \) for \( T_c \) phase of Ca\(_{3}\)Rh\(_{4}\)Sn\(_{13}\), and slightly higher value of \( \mu^* \approx 0.63 \) for its inhomogeneous \( T_c^\star \) phase. For La\(_{3}\)Rh\(_{4}\)Sn\(_{13}\) \( \lambda \approx 0.52 \), while \( \mu^* \approx 0.59 \). Since the coupling \( \lambda \) given by the expression\(^\text{32,33}\)

\[
\lambda = \frac{N(e_F)\langle I^2 \rangle}{M\langle \omega^2 \rangle}, \tag{2}
\]

where \( \langle I^2 \rangle \) 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 \( (\omega \sim \theta_D) \), \( N(e_F) \) is a density of states at the Fermi energy, and \( M \) is the atomic mass, is larger for the inhomogeneous superconducting \( T_c^\star \) state with respect to the bulk effect observed below \( T_c \), the primary reason for \( \frac{dT_c^\star}{dP} > \frac{dT_c}{dP} \) is the pressure dependence of \( \theta_D \), which leads to larger lattice stiffening in the \( T_c^\star \) phase with respect to the bulk effect below \( T_c \) and contributes to the \( T_c^\star > T_c \) effect. The \( P \)-dependence of \( \theta_D \) is given by the Grüneisen parameter \( \gamma_G = -\frac{d\ln\theta_D}{d\ln\nu} \), which determines the lattice stiffening. It was documented experimentally\(^\text{15}\) that \( \gamma_G \) strongly determines the magnitude and sign of \( \frac{dT_c}{dP} \). In the case of inhomogeneous superconductivity one can also suppose the dominant impact of the pressure dependence of the DOS at the Fermi level, \( \epsilon_F \), more pronounced than in bulk superconducting phases.

![Graph showing the \( H - T \) phase diagram for Ca\(_{3}\)Rh\(_{4}\)Sn\(_{13}\).](image)

**FIG. 4.** Electrical resistivity for Ca\(_{0.5}\)La\(_{2.5}\)Rh\(_{4}\)Sn\(_{13}\) under applied pressure. The inset displays the value of \( \rho \) measured just above \( T_c^\star \) at \( T = 7 \) K.

Figure 5 shows the \( H - T \) phase diagram of the Ca\(_{3}\)-Ce\(_{2}\)Rh\(_{4}\)Sn\(_{13}\) and Ca\(_{3}\)-Ce\(_{2}\)Rh\(_{4}\)Sn\(_{13}\) alloys, respectively. Temperatures \( T_c^\star \) were obtained from the resistivity data, while \( T_c \) were obtained from the specific heat measurements. The Ginzburg-Landau (GL) theory fits well the data as is shown in the \( H - T \) plots in Fig. 5. The best fit of GL equation \( H_{c2}(T) = H_{c2}(0)\frac{1}{1+t/t_c} \), where \( t = T/T_c \) gives the upper critical field
FIG. 5. Temperature dependence of the upper critical field $H_{c2}$ and/or $H'_{c2}(0)$ in the $H-T$ phase diagram, shown for Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$ in panel (a) and for Ca$_{3-x}$Ce$_x$Rh$_4$Sn$_{13}$ in panel (b). $T_c^*$ vs $H$ data are obtained from electrical resistivity under $H$, and defined as the temperature at which $\rho$ drops to 50% of its normal-state value. $T_c$ vs $H$ data for Ca$_3$Rh$_4$Sn$_{13}$ [in panel (a)] and for La$_x$Rh$_4$Sn$_{13}$ [in panel (a)] are obtained from $C(T)/T$ vs $T$ data (see Refs. [12,13]). The solid lines represent a fit using the GL model of $H_{c2}(T)$.

values of $H_{c2}(0)$ and $H'_{c2}(0)$, where $H'_{c2}(0) > H_{c2}(0)$, as shown in the Figure 5. Moreover, a significant increase of $H'_{c2}(0)$ due to chemical doping has been documented in both lanthanum (Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$) and cerium (Ca$_{3-x}$Ce$_x$Rh$_4$Sn$_{13}$) doped samples in respect to $H_{c2}(0)$ of the parent compounds, e.g., $H_{c2}(0) = H'_{c2}(0)$ is about 3.1 T for Ca$_3$Rh$_4$Sn$_{13}$, 1.6 T for La$_x$Rh$_4$Sn$_{13}$, while $H'_{c2}(0)$ is $\sim 4.3$ T or $\sim 3.8$ T in Ca$_3$Rh$_4$Sn$_{13}$ substituted with La or Ce, respectively. Indeed, magnetization $M$ vs $B$ measurements and the residual resistivity ratio suggest an increase of $H'_{c2}(0)$ associated with a progressive change of atomic disorders. Within the weak-coupling theory, the expression $\mu_B H_{c2}(0) = \frac{\Phi_0}{2\pi R}$ gives the superconducting coherence length $\xi(0)$ or $\xi^*(0)$ ($\Phi_0 = h/2e = 2.068 \times 10^{-15}$ Tm$^2$ is the flux quantum). Ca$_3$Rh$_4$Sn$_{13}$ exhibits similar values of $\xi(0)$ and $\xi^*(0)$ $\approx 10.3$ nm (c.f. [12]); for La$_x$Rh$_4$Sn$_{13}$, $\xi(0) \approx \xi^*(0) \approx 14$ nm [13], while for the series of Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$ and Ca$_{3-x}$Ce$_x$Rh$_4$Sn$_{13}$ alloys, $\xi^*(0) \approx 8.6$ nm and $\sim 9.3$ nm, respectively.

From the theoretical point of view, the upper critical field in a dirty superconductor, where the free mean path $l \ll \xi$, can be described by the Werthamer-Helfand-Hohenberg (WHH) or Maki–de Gennes theories. The WHH theory gives

$$H_{c2}(0) = 0.69 \frac{dH_{c2}}{dT} T_c.$$  \hspace{1cm} (3)

It can be seen in Fig. 6 that these approaches underestimate $H_{c2}(T)$ at low temperatures. Moreover, they do not predict the positive curvature of $H_{c2}(T)$ close to $T_c$.

![Image](image_url)

FIG. 6. Examples of the upper critical field for La– (a) and Ce-doped (b) systems fitted by solutions of the WHH equations. The green dashed lines marked as “WHH” show results of the WHH model with a single gap, whereas the solid blue lines marked as “two bands” represent a two-gap model described in Ref. [41].

One possible explanation for this behavior of $H_{c2}(T)$ is multiband/multigap nature of superconductivity in these systems. With the help of the quasiclassical Us-
It was shown in Ref. 11 that the upper critical field in a two-band superconductor can be determined as a solution of the following equation:

\[
\begin{align*}
a_0 \ln t + U(U) & \ln t + U(U) \phi_h] \\
+ a_2 \ln t + U(\eta h) & + a_1 \ln t + U(h) = 0,
\end{align*}
\]

(4)

where \( U(x) \equiv \psi(x + 1/2) - \psi(1/2), \psi(\ldots) \) is the digamma function, \( t = T/T_c \), \( h \) is reduced magnetic field defined as \( h = H_{c2} D_1/2\Phi_0 T_1 \). \( D_1 \) is the band diffusivity, \( \eta = D_2/D_1 \). The parameters \( a_{0,1,2} \) can be expressed by the intra- and interband BCS superconducting coupling constants \( \lambda_{11}, \lambda_{22}, \lambda_{12} \) and \( \lambda_{21} \). The experimental data shown in Fig. 4 can be very well reproduced by fitting these parameters within the framework of the two-band/two-gap model. This, however, is not a solid proof of the multiband nature of superconductivity in \( \text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13} \) and \( \text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13} \). One reason is that there are so many fitting parameters in the model that the agreement with the experimental data is relatively easy to achieve. Other explanations for the deviation from the WHH theory are also possible. It is known that a positive curvature of \( H_{c2}(T) \) can result from microscopic segregation in the superconducting material, where an array of Josephson junctions is formed. In Refs. 12, 13 and 14 we demonstrated the presence of two superconducting transitions due to the existence of inhomogeneous phase with \( T^* \) that is different from the \( T_c \) of the bulk sample. The first one corresponds to the onsets of inhomogeneous phase where superconductivity is present only in a fraction of the volume and the second one that signals the onset of bulk superconductivity. Arguments for this scenario can also be seen in Fig. 2, where a double transition, characteristic for inhomogeneous superconductors,13 and suggesting the presence of microscopic segregation, can be seen. Other explanations of the shape of \( H_{c2}(T) \) are related to the presence of magnetic impurities,22,23,45 strong quantization of Landau orbitals,10,52 inhomogeneity-induced reduction of the diamagnetic pair-breaking22 or singularities in the density of states,53.

2. Magnetic properties, evidence of short range magnetic order in Ce-doped alloys and the superconducting state

The superconducting state of \( \text{Ca}_3\text{Rh}_4\text{Sn}_{13} \) is strongly dependent on the atomic disorder, which, upon quenching, leads to a significant decrease in \( T_c \).13,11,13 Our simple model explains this observation based on the assumption that the atomic disorder leads to local stress.13 We have calculated the systematic decrease of the density of states (DOS) at the Fermi energy with pressure12 and documented for \( \text{Ca}_3\text{Rh}_4\text{Sn}_{13} \) obtained under various technological treatment, that the DOS change well correlates with this decrease of \( T_c \). According to this model, even a slight change in the DOS at \( E_F \) may cause a significant change in \( T_c \). With this motivation, we present a magnetic study of \( \text{Ca}_3\text{Rh}_4\text{Sn}_{13} \) substituted with La and Ce to demonstrate evidence of nanoscale disorder as a bulk property, leading to an inhomogeneous superconducting state with an enhanced critical temperature \( T^*_c > T_c \). Here, \( T^*_c \) represents a drop of resistivity due to formation of percolation paths, while \( T_c \) determined from magnetic susceptibility and specific heat, indicates the onset of bulk superconductivity. A comparative study has shown that, the effect of short-range magnetic correlations has a significant effect on \( T_c \). Figures 6 and 8 compare frequency dependence of the real \( (\chi'') \) and imaginary \( (\chi'''\) parts of ac magnetic susceptibility \( \chi_{ac} \), and show derivative \( d\chi'/dT \) and \( d\chi''/dT \) for the selected \( \text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13} \) samples and for \( \text{Ca}_{0.5}\text{La}_{2.5}\text{Rh}_4\text{Sn}_{13} \), characteristic of the \( \text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13} \) series.

Frequency \( \nu \) dependencies in \( \chi' \) and \( \chi'' \), depicted in Fig. 4 with characteristic Vogel-Fulcher-like behavior,14,15 shown in the inset of panel (b), become apparent of spin-glass-like magnetic correlations in Ce doped alloys, while the \( \nu \) effect is not observed for \( \text{Ca}_3\text{Rh}_4\text{Sn}_{13} \) doped with La. The maxima in derivative \( d\chi'/dT \) and \( d\chi''/dT \) we assigned, respectively to critical temperatures \( T'_c \) and \( T''_c \). Figures 9 and 10 display the magnetization \( M \) vs \( B \) isotherms for \( \text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13} \) and \( \text{Ca}_{2}\text{La}\text{Rh}_4\text{Sn}_{13} \) (a representative of the \( \text{Ca}_2\text{La}\text{Rh}_4\text{Sn}_{13} \) family). \( \text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13} \) alloys are diamagnetic in the wide temperature region with hysteresis loops representing the effect of vortex pinning, while the \( M(B) \) isotherms for \( \text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13} \) are well approximated by Langevin function \( L(\xi) = \cosh(\xi) - 1 \), with total magnetic moment \( \mu \approx 0.8 - 0.9 \mu_B \) per Ce atom obtained for the isotherms at 2 K. The hysteresis loop effect completely disappears for Ce content \( x > 1 \).

Figure 11 displays the specific heat data \( C(T)/T \) and \( \Delta C(T)/T \) for selected \( \text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13} \) compounds, the \( \Delta C(T)/T \) is defined as a difference between the \( C/T \) data measured at the zero magnetic field and at the field of 5 T. There is no sharp transition at \( T_c \) in the specific heat data of the sample with \( x = 0.2 \); instead, the specific heat displays a broad peak below \( T_c \), which is strongly reduced by field. This \( C(T) \) effect was attributed to the inhomogeneous high temperature superconducting \( T'_c \) phase due to atomic disorder.14,15 It has been shown in Ref. 55 that potential disorder smooth on a scale comparable to the coherence length leads to large modulation of the superconducting gap and large transition width15.

A simple Gaussian gap \( \Delta \) distribution15

\[
f(\Delta) \propto \exp\left[ -\frac{(\Delta - \Delta_0)^2}{2D} \right],
\]

(5)

where \( \Delta_0 \) and \( D \) are treated as fitting parameters, well fits the \( \Delta C(T)/T \) data for strongly disordered \( \text{Ca}_{2.8}\text{La}_{0.2}\text{Rh}_4\text{Sn}_{13} \) alloy. The maximum of \( f(\Delta) \) distribution well agrees with the temperature of the \( \chi'' \) maximum (3) in Fig. 8. The \( C(T)/T \) behavior in this strongly disordered alloy is qualitatively different than that in
FIG. 7. The real and imaginary components of the ac magnetic susceptibility, $\chi'$ and $\chi''$, for $\text{Ca}_{2-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}$, as a function of temperature measured at different frequencies in a field $B = 2$ Oe. The derivative $d\chi'/dT$ and $d\chi''/dT$ are also presented. The inset to panel (b) and (c) shows how $\chi''$ depends on frequency with evidence of the spin-glass state. The minimum (2) of $d\chi''/dT$ exhibits the temperature at which the inhomogeneous superconducting phase is formed, while the maxima (3) and (5) defines temperature $T_c^*$ and $T_c$, respectively.

reach in $\text{La}_{4-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}$ compounds with clear evidence for two superconducting phases: the high temperature inhomogeneous superconducting $T_c^*$ phase and the bulk superconducting state below $T_c$, where $T_c^* > T_c$. Recently we noted that the $C(T)$ data for $\text{La}_3\text{Rh}_4\text{Sn}_{13}$ [13] and $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ [12] are well estimated by $C(T) \sim \exp[-\Delta(0)/k_BT]$ which indicates that these parent compounds are $s$-wave superconductors and follows the behavior described by the BCS theory in the weak-coupling limit ($\Delta(0)$ is the energy gap of $T_c$ phase at zero temperature). The $C(T)$ data of cerium doped ($\text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}$) samples were recently reported in Ref. [12]. It was documented [12] that the broad maximum observed at $T < T_c$ in the specific heat data of the samples $0 < x < 1.2$ represents an inhomogeneous superconducting phase in presence of spin-glass-like state, with evident contribution of the short-range magnetic correlations to entropy. Figure [12] compares the entropy of $\text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}$ alloys with that of nonmagnetic La-doped alloys. Panel (b) displays the magnetic entropy $S$ which for $x \geq 0.6$ has a linear scaling with $x$, and is $R\ln 2$ per Ce atom at about 6 – 7 K, indicating that the entropy represents the behavior of the ground state doublet. Figure [13] displays $S$ vs $x$ isotherms for Ce [panel (a)] and La [panel (b)] alloys. The $S(x)$ isotherms of $\text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}$ are plotted at different temperatures $T$ larger than the temperature of spin-glass-like ordering. In Fig. [13] a $S(x)_{T=\text{const}}$ increases with Ce substitution, which can easily be explained as a result of the $x$ dependent paramagnetic spin-disorder effect (c.f. Fig. [9]). This behavior was not observed for the nonmagnetic La-doped series of alloys, as is shown in Fig. [13]. In addition, for $x = 0.3$ and 0.8 when $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ is substituted by Ce, and for $x = 0.6$ and $\sim 2$ for La doping, the isotherms $S(x)_{T=\text{const}}$ show a clear maxima that correspond to the largest separation between the superconducting phases $T_c^*$ and $T_c$ due to atomic disorder, as is displayed in $T-x$ diagram (will be discussed in section A.3.).
3. $T_c - x$ phase diagrams for $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ doped with La and Ce

In summary, we present in Fig. 14 a $T - x$ diagram of the superconducting $T_c^*$ and $T_c$ phases for $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ doped with La (panel a) and Ce (panel b). The comprehensive magnetic, electrical resistivity, and specific heat study suggest coexistence of short-range magnetic correlations with superconductivity in the Ce-doping regime $x < 1.2$ and, however, not a case of $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ doped with La. In Fig. 14 points (1) are obtained at 50% of the normal state resistivity value (c.f. Fig. 2). The temperatures of the respective maxima in $d\chi /dT$ shown in Fig. 7 are presented as the points (2), (3) and (5). The $\chi$ versus $T$ dc magnetic susceptibility data obtained at 500 Oe in zero field (ZFC) and field cooling (FC) modes reveals the onset of diamagnetism and thermal hysteresis associated with the superconducting state below $T_c^*$ [points (4)]. Points (6) represent temperature of the maximum in $d\chi_{dc}/dT$, which is $T$ of about 1/2 of the diamagnetic dc susceptibility drop. Finally, points (7) and (8) represent $T_c^*$ and $T_c$ obtained from specific heat $C(T)/T$ data, respectively (c.f. Fig. 11). The $T - x$ diagram clearly indicates the presence of two separate superconducting phases, $T_c^*$ and $T_c$. An increase of atomic disorder enhances the separation between them and the largest one is obtained for the La substituted samples with $x \sim 0.6$ and for the Ce substituted $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$ alloys with $x \sim 0.3$. We also documented that spin-glass-like magnetic correlations increases $T_c^*$ and $T_c$ for the $\text{Ca}_3-x\text{Ce}_x\text{Rh}_4\text{Sn}_{13}$ compounds with respect to $\text{Ca}_3-x\text{La}_x\text{Rh}_4\text{Sn}_{13}$. This observation is interesting, and previously was motivated by theory [57,58]. It was theoretically documented that the superconducting transition temperature is higher in the presence of the...
spin-spin interactions of the magnetic impurities, which form a spin-glass state.

The $T - x$ diagram also shows the minimum for $T_c$ versus $x$ dependence at $x_{\text{min}} \sim 1.2$ for Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$, and at $x \sim 0.4$ for Ca$_{3-x}$Ce$_x$Rh$_4$Sn$_{13}$, however, in the both cases $x_{\text{min}}$ is about 40% of the whole superconducting $x$-region.

B. Electronic structure of Ca$_3$Rh$_4$Sn$_{13}$ doped with La and Ce; experiment and calculations

In order to explain the alloying effect on the band structure of Ca$_3$Rh$_4$Sn$_{13}$ superconductor, we
investigated valence-band (VB) XPS spectra of the Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$ and Ca$_{3-x}$Ce$_x$Rh$_4$Sn$_{13}$ samples. We also analyze the Sn 4d XPS core-level spectra to demonstrate the nature of the covalent bonding between Sn1 and Sn2 atoms in Sn1Sn$_2$12 cages. Figure 15 shows the VB XPS spectra for the series of Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$ alloys. The XPS bands for the components $x = 0, 0.5, 2.5$, and 3 are compared with calculated total DOSs. Panel (c) displays also the VB XPS spectra obtained for intermediate components $0.5 < x < 2.5$. The valence band XPS spectra of Ca$_{3-x}$Ce$_x$Rh$_4$Sn$_{13}$ alloys were recently presented in Ref. [12], therefore are not shown here. All
and by Sn 5s states with the broad maximum centered at \( \sim 7 \) eV. With increasing concentration of La or Ce, the shape of the VB XPS spectra are almost the same, excluding the narrow energy range near \( \epsilon_F \), which strongly relates to the electric transport properties of these alloys. Recently, we have demonstrated that, for metallic state of the \( \text{Ca}_{3-x}\text{La/Ce}_x\text{Rh}_4\text{Sn}_{13} \) alloys, the subtle change of DOS at \( \epsilon_F \) correlates well with the observed resistivity behavior \( \frac{d\rho}{dP} \) giving \( \frac{dN(\epsilon_F)}{dP} \propto \frac{d\rho}{dP} \). A similar effect was observed for \( \text{Ca}_3\text{Rh}_4\text{Sn}_{13} \) with Ca atoms partially replaced by La. Figure 16 demonstrates the change of calculated DOS at \( \epsilon_F \) with pressure \( P \). Figure 16 also shows the energy shift of the DOS maxima with \( P \) in the vicinity of \( \epsilon_F \) to higher binding energy \( |E| \) in respect to \( \epsilon_F \). This response for heavy Fermi metals to the applied pressure is characteristic of electron-type conductivity at high pressure.

**FIG. 16.** The total DOS near the Fermi energy calculated for \( \text{Ca}_{2.5}\text{La}_{0.5}\text{Rh}_4\text{Sn}_{13} \) at the pressure 0 and 2.1 GPa.

DOS at \( P = 0 \) and 2.1 GPa for \( \text{Ca}_{2.5}\text{La}_{0.5}\text{Rh}_4\text{Sn}_{13} \). Calculations documented the increase of the total DOS at \( \epsilon_F \) with \( P \), giving \( \frac{dN(\epsilon_F)}{dP} \cong -0.5 \) eV\(^{-1}\) GPa\(^{-1}\), which correlates well with the observed negative \( \frac{d\rho}{dP} \) in normal metallic state at \( T = 8 \) K, as shown in Fig. 16. This simple explanation assumes the relation \( \rho \sim 1/n \) between the resistivity and the number of carriers \( n \), that naïvely reflects the DOS at \( \epsilon_F \). For the skutterudite-related \( \text{Ce}_3\text{M}_4\text{Sn}_{13} \) and \( \text{La}_3\text{M}_4\text{Sn}_{13} \) compounds, where \( M \) is a \( d \)-electron metal, the charge density analysis revealed a strong charge accumulation between Sn1 atom and Sn2 atoms of the Sn2\(_{12} \) cage, and between metal \( M \) or rare earth element and Sn2 atoms, which implies a strong covalent bonding interaction and leads to a subtle structural transition. The Sn 4d XPS lines confirm the charge accumulation between Sn2 and Sn1, obtained from the calculated difference charge density for \( \text{La}_3\text{Rh}_4\text{Sn}_{13} \).

1. **Bonding properties investigated by electron localization function**

For the skutterudite-related \( \text{Ce}_3\text{M}_4\text{Sn}_{13} \) and \( \text{La}_3\text{M}_4\text{Sn}_{13} \) compounds, where \( M \) is a \( d \)-electron metal, the charge density analysis revealed a strong charge accumulation between Sn1 atom and Sn2 atoms of the Sn2\(_{12} \) cage, and between metal \( M \) or rare earth element and Sn2 atoms, which implies a strong covalent bonding interaction and leads to a subtle structural transition. The structural deformation observed in this class of materials at \( T^* \sim 170 \) K, is usually accompanied by formation of a charge density wave (CDW) phase transition, and under external pressure \( T^* \rightarrow 0 \) defines a novel structural quantum critical point. Based on the present structural data, which documented the second order structural phase transition at much higher temperature of about 310 K, we revise the previous understanding of the nature of \( T^* \sim 170 \) K...
(section III.C.). The structural deformation, however, has not been documented for Ca$_3$Rh$_4$Sn$_{13}$. To determine the subtle bonding properties of the charge distribution in La substituted Ca$_3$Rh$_4$Sn$_{13}$, a full-potential chemical-bonding analysis via calculation of the electron localization function (ELF) within the density functional theory was used [similar band structure ELF calculations were presented for cerium doped (Ca$_{1-x}$Ce$_x$Rh$_4$Sn$_{13}$) compounds recently in Ref. 12]. Figures 18 and 19 exhibit the ELF distribution in planes $z = \frac{3}{4}$ and $z = \frac{1}{4}$ for Ca$_{2.5}$La$_{0.5}$Rh$_4$Sn$_{13}$ and Ca$_{0.5}$La$_{2.5}$Rh$_4$Sn$_{13}$, respectively, while Fig. 20 compares the ELF isosurfaces $z = 1$ sections for parent and doped compounds.

The ELF maxima are essentially located on the atoms in the plane, the charge density analysis also reveals the covalent bondings between the nearest-bounding atoms: Sn1-Sn2, Rh-Sn2 and La-Sn2 due to charge accumulation between them. These bondings are the strongest between Rh-Sn2 and Sn1 and Sn2, which can be a reason of structural distortion. XRD analysis confirms the charge modulation on the Rh atoms. As a result of this charge modulation, some of the Sn2 atoms are located closer to Rh than the remaining one, which leads to distortion of the Sn2 cages. Moreover, when Ca in Ca$_3$Rh$_4$Sn$_{13}$ is fractionally replaced by larger La or Ce atom, the Sn$_{12}$ cage can easily be deformed due to strong chemical stresses, as is shown in Fig. 20 (c.f. Fig. [1]). The superlattice transition that is connected with Sn2 cage instability is, however, not observed in Ca$_3$Rh$_4$Sn$_{13}$.

C. New insights into structural properties of Ca$_{3-x}$La$_x$Rh$_4$Sn$_{13}$ and Ca$_{3-x}$Ce$_x$Rh$_4$Sn$_{13}$ at high temperatures

There has been only one type of structure related transition reported in the 3:4:13 system, related to the appearance of the modulation with a single arm or a whole k-star of the propagation vector $k = (\frac{1}{2}, \frac{1}{2}, 0)$. 
Transition temperatures associated with an appearance of the superstructure, commonly called $T^*$, were usually lower than 150 K and could be suppressed to QCP by doping.\(^{22}\)

The first round of temperature dependent XRD aimed for screening any similar effects in both series. As a starting crystallographic model, a simple cubic cell (SG $Pm\bar{3}n$ No. 223, without the superstructure) was selected and atom occupancies were constrained to the nominal values. Atom positions were chosen as $La/Ca/Ce$ (6d) ($\frac{1}{4}$, $\frac{1}{4}$, 0), Rh (8e) ($\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{4}$), Sn1 (2a) (0, 0, 0), Sn2 (24k) (0, $ySn2$, $zSn2$). All sites were refined with individual isotropic atomic displacement parameters (ADP) $B_{iso}$.\(^{22}\)

1. Ca-Ce series

In the $Ca_{1-x}Ce_xRh_4Sn_{13}$ system we have studied two compositions with $x = 1$ and $x = 2$. Figure 21 presents middle sections of the diffraction patterns, which clearly shows presence of a possible transition for the Ce rich side (a) $x = 2$ and uniform patterns in the other case (b) $x = 1$. The experimental setup did not allow to observe any superstructure reflections. In all cases, the variations in the intensities of reflections were accompanied by a prominent changes in ADPs (Fig. 22(a) and (b)). Other parameters varied smoothly with the temperature (see Supplemental Information).

An evidence of a possible transition is clearly seen for $CaCe_2Rh_4Sn_{13}$, where a gradual loss on intensity occurs in the 250 K to 300 K range (Fig. 21(a)). At the same time, the intensities for $Ca_2CeRh_4Sn_{13}$ monotonically decrease over the whole temperature range (Fig. 21(b)). The transition for the Ce rich material is clearly seen in Rietveld refinement as a gradual increase of ADPs (Fig. 22(a)), which is not present on a Ca rich side (b). It is impossible to determine only from the diffraction data, if the origin of the increase of ADPs is static (phase transition) or dynamic (rattling of the central Sn1) and complementary studies are under way. There are also no signatures of the low temperature transition $T_D$ seen in resistance and susceptibility data. At this moment, it suggests that transition at $T_D$ is rather confined to electronic and not the crystal structure. On the other hand, the high temperature transition (with onset around 250 K and completed around $T_{HT} = 310$ K), is most likely connected to an appearance of 2a x 2a x 2a superstructure observed in similar materials\(^{20,65–67,69}\) but is below the detection limit for the Supernova setup. We can estimate that for $CaCe_2Rh_4Sn_{13}$ the $T_{HT}$ lies between 310 K and 320 K.

2. Ca-La series

In the Ca-La series a possible high temperature transition was observed around 250 K for $Ca_{2.8}La_{0.2}Rh_4Sn_{13}$ (Fig. 21(d)) but not for $CaLa_2Rh_4Sn_{13}$ (Fig. 21(c)). The refinement of the temperature dependence of ADPs for $Ca_{2.8}La_{0.2}Rh_4Sn_{13}$ (Fig. 22(d)) revealed 4 characteristic regions: (1) up to 140 K where ADPs anomalously decrease, (2) between 140 K and 250 K where they increase as expected from increased thermal fluctuations, (3) a sharp decrease around 250 K, which points towards sharp decrease of the disorder and (4) again a small step around 300 K. At this moment the increase of ADPs between 140 K and 250 K can be attributed to an increase of a static disorder which contributes to atomic displacements equally with the thermal noise. This disorder is eliminated by an onset of a possible transition at 250 K,
which is completed at around 300 K. Similarly to the CaCeRh$_4$Sn$_{13}$, this increase is most likely caused by a structural transition which is below the detection limit of the current Supernova setup.

In order to justify the result, we present preliminary analysis of synchrotron PXRD carried out on Ca$_{0.2}$La$_{2.8}$Rh$_4$Sn$_{13}$ (Fig. 23), which lies on the La rich side of the Ca-La series and is expected to undergo the $T^*$ transition.

![Image](55x444 to 298x627)

**FIG. 23.** Low section of synchrotron PXRD diffractograms for Ca$_{0.2}$La$_{2.8}$Rh$_4$Sn$_{13}$ (a) shows gradual variation of intensities and (b) appearance of very low overlapping $2a \times 2a \times 2a$ superstructure peaks (532)(611). The variation of intensities is correlated with a sudden jump in $B_{iso}$ at $T_{HT} = 310$ K (c), which does not affect Raman spectra (inset). On the other hand the superstructure reflections display critical behavior with $T^* \approx 250$ K (d).

The low angle section of the pattern (Fig. 23 (a)) reveals three important features: (1) a sudden drop of the background around 310 K, which is accompanied by an increase of peak intensity, which we attributed to a transfer of scattering intensity from a long range order represented by Bragg reflections to a short range component visible as diffuse scattering. (2) an appearance of $2a \times 2a \times 2a$ superstructure reflections (overlapping (532) and (611) in 22 (b)), which decrease gradually with the temperature having a critical-like behavior below 250 K. An order parameter-like curve fitted for the stronger pair of reflections (Fig. 23 (d)) gave better estimates of parameters: the $T^* = 247 \pm 19$ K and the critical exponent $\beta = 0.71 \pm 0.06$. We do not imply here that this transition is necessarily continuous but the quality of the fit and earlier reports on similar materials strongly support this conclusion. It must be noted that the intensity of the reflection is proportional to the $\left| F_{22} \right|^2$, which in the first approximation is proportional to the square of the deviation from the ideal symmetry. This means that the critical exponent calculated from intensities is twice as large as the one potentially calculated from the displacements (in a similar way intensities of magnetic peaks are proportional to the square of magnetic moment). Therefore the actual critical exponent of the order parameter will be equal to $\beta^* = 0.35 \pm 0.03$.

At the end, a quick look at representative ADPs (Fig. 23 (c)) shows that the change in intensities of the main reflections and the jump of the background at $T_{HT} = 310$ K is connected to displacive disorder. An attempt was done to differentiate between static and dynamic (increased rattling) origins of the transition by carrying out Raman measurements, in the energy range suitable for phonon excitations, at room temperature (below $T_{HT}$ but above $T^*$) and 350 K (above $T_{HT}$) (Fig. 23 (c) inset). For better comparison a baseline was subtracted from both spectra and their respective maxima were normalized to 1. No significant difference in intensities is observed while crossing the 310 K boundary, therefore there is no evidence of sudden changes in vibrational/phonon modes. More plausible explanation of this transition is an appearance of a static disorder, which leads to static long range ordered superstructure at lower temperatures. The possible presence of an additional high temperature transition $T_{HT}$, which is associated with a sudden jump in ADPs and a decrease in a background seems to be a precursor to the long range order developed at $T^*$ has not been previously reported in similar systems. Our data shows that it is present in samples with $x_{La} = 0.2$ (Fig. 22 (d)), $x_{La} = 2.8$ (Fig. 23 (c)) and $x_{Ce} = 2.0$ (Fig. 22 (a)) and is most likely connected with the appearance of short range correlations between atomic displacements. A striking feature for the Ca-La series is that it is visible for the border compositions $x_{La} = 0.2$ and $x_{La} = 2.8$ but not for $x_{La} = 2.0$.

One can ask if the transition $T_D$ is somehow reflected in the structural properties. Due to limited angular resolution of Supernova scans, no subtle transitions could be detected in slopes of thermal expansion of lattice parameters (see the Supplementary Information) and detailed studies are under way. For the purpose of this paper we have repeated temperature scans with higher angular resolution over the angular range of (622) reflection. Interplanar d-spacing calculated in this way was plotted on a $\log - \log$ scale in a way similar to the resistance data (see Supplementary Information). The plot revealed two possible inflection points with temperatures equivalent to $T_D$ and $T^*$. At present we can only associate the lower transition with the $T_D$ since it perfectly correlates with temperatures observed in resistance and susceptibility data in both La and Ce dopes series (Fig. 24).

**IV. CONCLUSIONS**

The comprehensive research on La and Ce substituted Ca$_3$Rh$_4$Sn$_{13}$ leads to several important observations, which are helpful for a better understanding of the nature of its superconductivity. The basic problem of our studies is an atomic disorder, which plays a crucial role in the strongly correlated materials. It was documented
To distinguish two behaviors. First, the atomic disorder due to doping, i.e., located in $T - x$ diagram near the parent compounds $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$, $\text{La}_3\text{Rh}_4\text{Sn}_{13}$, or $\text{Ce}_3\text{Rh}_4\text{Sn}_{13}$, while for $x$-range, where the isothersms $S(x)_T$ show a maxima that correspond to the largest separation between the superconducting phases $T_c^*$ and $T_c$ the superstructure effect is missing. This means that strong atomic disorder generated by doping is not significant enough so that structural changes can be observed at $T_{HT}$ within an experimental detection limit.

In such dirty $\text{Ca}_{3-x}\text{La}_x\text{Rh}_4\text{Sn}_{13}$ and $\text{Ca}_{3-x}\text{Ce}_x\text{Rh}_4\text{Sn}_{13}$ superconductors, where the mean free path is much smaller than the coherence length, the upper critical field $H_{c2}(T)$ is usually interpreted within the Werthamer-Helfand-Hohenberg or Maki–de Gennes theoretical model. This model, however, does not well fit the $H_{c2}$ vs. $T_c$ data, and does not interpret the observed positive curvature of $H_{c2}$ close to $T_c$. One of the possible scenarios of the observed $H_{c2}(T)$ dependencies could be a two-band nature of superconductivity in these systems. Previously, intriguing evidence for multiband effects was also documented in structurally similar filled skutterudite $\text{LaRu}_4\text{As}_1$ and $\text{LaOs}_4\text{As}_1$ compounds. However, it is also possible that the shape of $H_{c2}(T)$ stems from the presence of nanoscopic inhomogeneities of the superconducting state.

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As in reference to Ref. [77], a double superconducting transition, which appears in the good PrOs$_4$Sb$_{12}$ single crystals, with the best residual resistivity ratio $\text{RRR}_{2K} = 24$ and high jump at the superconducting transition, shows that its occurrence is phenomenon related to inhomogeneity within the size smaller than the size of investigated sample (100 $\mu$m). The PrOs$_4$Sb$_{12}$ samples that exhibit a double transition are most likely divided into macroscopically segregated parts: one with a large distribution of $T_c^*$ and the other one with a single sharp superconducting transition at $T_c$, which seems to be intrinsic one.

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Supplementary information for
The effective increase in atomic scale disorder by doping and superconductivity in Ca$_3$Rh$_4$Sn$_{13}$

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1. Variations of lattice parameters refined from Supernova experiments.

(A) CaCe$_2$Rh$_4$Sn$_{13}$

(B) Ca$_2$CeRh$_4$Sn$_{13}$

(C) CaLa$_2$Rh$_4$Sn$_{13}$

(D) Ca$_{2.8}$La$_{0.2}$Rh$_4$Sn$_{13}$
2. Variations of Sn2 positional parameters.

| CaCe$_2$Rh$_4$Sn$_{13}$ | Ca$_{1.8}$La$_{0.2}$Rh$_4$Sn$_{13}$ |
|-------------------------|-----------------------------------|

(C) CaLa$_2$Rh$_4$Sn$_{13}$

(D) Ca$_{2.8}$La$_{0.2}$Rh$_4$Sn$_{13}$
3. For the d-spacing data log-log plot method (similar to resistivity) was applied to investigate changes in curvature in selected compound. For example Ca$_{0.2}$La$_{2.8}$Rh$_4$Sn$_{13}$.