Unveiling charge density wave quantum phase transitions by x-ray diffraction

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We investigate the thermal-driven charge density wave (CDW) transition by x-ray diffraction of two cubic intermetallic systems Lu(Pt1−xPd)x2In and Sr3−xCa4Ir4S13. A detailed analysis of the CDW modulation superlattice peaks as function of temperature is performed for both systems as the CDW transition temperature TCW is suppressed to zero by an non-thermal control parameter. Our results indicate a crossover of the classical thermal-driven CDW order parameter critical exponent expected for a three-dimensional universality class to a mean-field tendency, as TCDW vanishes. Such behavior might be associated with presence of quantum fluctuations which influences the classical second-order phase transition, strongly suggesting the presence of a quantum critical point (QCP) at TCDW = 0. This also provides experimental evidence that the effective dimensionality exceeds its upper critical dimension due to a quantum phase transition.

Classical thermal-driven continuous or second-order phase transitions are well known to be defined by an order parameter which has a finite value that continuously vanishes to zero at a critical point. Though the thermodynamic average of the order parameter is zero above the critical point, its fluctuations are non-zero, giving rise to critical phenomena near the phase transition. These fluctuations cause a breakdown of the normal macroscopic laws, and as a consequence, all observables depend via power laws, which in turn define critical exponents. The set of critical exponents completely characterize the critical behavior near the phase transition, depending only on the dimensionality of the system and the symmetry of the order parameter [1]. In such a way, microscopic details of a particular phase transition becomes unimportant and, e.g. all systems with 3D order parameter in three-dimensions with the same symmetries share the same critical exponents, called universality class [2, 3].

Another set of second-order phase transitions can occur at T = 0, where a non-thermal control parameter such as magnetic field, chemical substitution or pressure may drive the system to a critical point, namely a quantum critical point (QCP) [4]. Though one cannot access experimentally T = 0, these quantum fluctuations are known to affect many thermodynamic observables well above the QCP. This phenomena has been commonly observed in materials presenting antiferromagnetic [5, 6], spin density wave [7] or superconducting [8] phase transitions, in which the ordering temperature is suppressed to zero at a QCP by a non-thermal control parameter. In these systems the presence of quantum fluctuations is evidenced by the collapse of the conventional quasi-particle excitations, giving rise to non-Fermi liquid behavior and unusual power laws of the observables near the quantum critical region [3].

As one approaches a quantum phase transition asymptotically it is possible to describe the quantum critical behavior classically, since this transition is related to a classical analog in a different spatial dimensionality [1, 4]. This is because changing the dimensionality is equivalent to change the universality class of a classical phase transition. The effective dimensionality of a quantum phase transition is given by deff = (d + z), where d is the space dimension and z is a dynamic critical exponent. If deff is equal to or exceeds the upper critical dimension d* = 4 (for most critical phenomena), fluctuations are irrelevant, and all the critical exponents reach their mean-field values [1, 5, 9], for which the order parameter critical exponent is β = 0.5 [3]. This critical behavior has been suggested to occur in the antiferromagnetic MnCl2-4H2O [10] and EuTe [11].

Charge density waves (CDW) QCP have been a subject of intense research in the recent years. Usually, systems displaying CDW also show a variety of interesting physical properties, such as a superconducting state, which can be enhanced as the charge instability is tuned to zero by pressure and/or chemical doping [12–16]. The suppression of the CDW, which sets in below TCDW, may be related with the enhancement/emergence of the superconducting state, associated with quantum fluctuations near the QCP in the limit TCDW → 0. For several CDW systems, however, the evidence that quantum fluctuations play an important role in the suppression of the CDW are not clear. The fact that the superconducting temperature transition TC is favoured as TCDW decreases may be solely related to the closing of the partially gapped CDW, which increases the density of states at the Fermi energy N(EF) benefiting the superconducting state as TC ∝ e−1/[N(EF)Veff], where Veff is an effective attractive interaction [14].
In this work, we follow directly the temperature dependence of the order parameter critical exponent $\beta$ by x-ray diffraction of two cubic intermetallic CDW systems, $\text{Sr}_3−x\text{Ca}_x\text{Ir}_4\text{Sn}_{13}$ and $\text{Lu}(\text{Pt}_{1−x}\text{Pd}_x)_2\text{In}$, as function of pressure and chemical substitution, respectively. We observe that as both systems approach the critical point, where $T_{CDW} \to 0$, $\beta$ continuously changes its value from the expected 3D dimensionality to a mean-field value, supporting the increase of $d_{eff}$ by quantum fluctuations for this thermal-driven phase transition. This can also be interpreted as a decrease (shrinking) of the classical critical region around the critical line, where Wilson exponents control the non-mean field classical critical behavior. In any case, both interpretations provide evidence for the existence of a QCP in these intermetallic CDW materials, rather than relying only on unusual power laws of thermodynamic observables and/or enhancement of superconductivity.

In the $\text{Sr}_3−x\text{Ca}_x\text{Ir}_4\text{Sn}_{13}$ cubic compounds ($Pm\overline{3}m$ space group), pressure and chemical substitution were combined to suppress the CDW phase and it was argued that a linear temperature dependence of the electrical resistivity near the point where $T_{CDW}$ vanishes would be related with a CDW QCP, which occurs at a critical pressure $P_c \approx 18$ kPa $^{12}$. The same argument was used for $\text{Sr}_3−x\text{Ca}_x\text{Rh}_x\text{Sn}_{13}$ $^{13}$ where the QCP is thought to be at a critical substitution $x_c = 0.9$ of Ca content, though more recent lattice dynamics studies also show evidence for quantum criticality $^{17}$.

In cubic Heusler $\text{Lu}(\text{Pt}_{1−x}\text{Pd}_x)_2\text{In}$ ($L2_1$ structure; $Fm\overline{3}m$ space group), the parent compound $\text{LuPt}_2\text{In}$ presents a robust partially gaped CDW transition which sets in at $T_{CDW} = 497$ K and a superconducting state at $T_c = 0.45$ K $^{14}$. Increasing the Pd content, $T_{CDW}$ is tuned to zero while $T_c$ is enhanced and reaches a sharp maximum at $x_c = 0.58$, where the CDW also vanishes. Evidence of quantum fluctuation were seen in unusual power laws of the magnetic susceptibility, electrical resistivity and specific heat, as the QCP is approached $^{14}$. Additionally, neutron diffraction experiments for $x = 0$ were carried out and the superlattice peaks intensity ($I$), related with the CDW transition, was followed as function of temperature. The order parameter critical exponent was evaluated using the scaling relation $I \propto (1 - T/T_{CDW})^{2\beta}$, in which was found $\beta = 0.31 \pm 0.09$, within the expected value for a Ising three-dimensional universality class $^{3,14}$.

Polycrystalline samples of $\text{Lu}(\text{Pt}_{1−x}\text{Pd}_x)_2\text{In}$ ($x = 0.3$, 0.4 and 0.5) were synthesized using an arc-melting furnace under argon atmosphere and pellets were annealed for 150 h at 750°C $^{14}$. An amount of each sample were grinded and the powder was subsequently annealed for another 100 h at the same temperature before x-ray diffraction characterization. Measurements of electron dispersive spectroscopy were carried out to confirm the compositions. Flux-grown single crystals of $\text{Sr}_3\text{Ir}_4\text{Sn}_{13}$ and $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$ were synthesized using Sn excess $^{18}$. Phase purity was checked by conventional powder x-ray diffraction (PXRD) on all produced samples. Temperature dependent four-probe method electrical resistivity were measured in a Quantum Design PPMS DynaCool for primarily sample characterization. Synchrotron PXRD measurements on $\text{Lu}(\text{Pt}_{1−x}\text{Pd}_x)_2\text{In}$ samples were performed at XPD beamline of the Brazilian Synchrotron Light Source (LNLS). The samples were placed in a coldfinger of a closed-cycle He cryostat. The synchrotron PXRD patterns were obtained performing $\theta - 2\theta$ scans and the intensity was collected using a linear Mythen detector with an angular window of 3.5°. The beamline energy ($E$) was set to 10 keV. High pressure single crystal x-ray diffraction (SCXRD) experiments on $\text{Sr}_3\text{Ir}_4\text{Sn}_{13}$ were performed at XDS beamline/LNLS ($E = 20$ keV) $^{19}$ and $\text{Ca}_3\text{Ir}_4\text{Sn}_{13}$ at P07 beamline ($E = 98.7$ keV) of PETRA III, DESY $^{20}$. For details of the SCXRD experiments against pressure see Ref. $^{21}$.

In x-ray diffraction, the CDW/superlattice modulation gives rise to satellites peaks around the reciprocal lattice points for $T < T_{CDW}$, which intensities increase as the temperature decreases. For $\text{Sr}_3−x\text{Ca}_x(\text{Rh},\text{Ir})_4\text{Sn}_{13}$ and other related compounds, it is well established that the CDW transition doubles the cubic lattice parameter in respect to the higher temperature phase, with a commensurate propagation vector of $q_{CDW} = (0.5,0.5,0)$ $^{21,22}$. By analysing the positions of the superlattice satellites peaks of our PXRD data for $\text{Lu}(\text{Pt}_{1−x}\text{Pd}_x)_2\text{In}$ (see Fig. 1), we are able to index these peaks with the same $q_{CDW} = (0.5,0.5,0)$ of $\text{Sr}_3−x\text{Ca}_x(\text{Rh,Ir})_4\text{Sn}_{13}$, as also indicated by inelastic neutron scattering experiments $^{24}$. The data also suggests that the modulation vector re-
mains constant in the whole inspected temperature range (not shown). An impurity peak was detected very close to the same PXRD pattern range previously reported in Ref. 14.

The intensities of the (4,5, 1.5, 2) superlattice peak at 2θ ≈ 57.4° (Q_{CDW} ≈ 4.864 Å⁻¹), studied by synchrotron PXRD, for Lu(Pt₁₋ᵡPdₓ)₂In (ᵡ = 0.3, 0.4 and 0.5) are followed as a function of temperature (at ambient pressure) [Figs. 2(a)-(c)]. There is a clear temperature dependence of the superlattice peaks intensities, which disappears at around T_{CDW}. The same behavior, measured by SCXRD, is seen for the superlattice peaks of Sr₃Ir₃Sn₁₃ (3, 2.5, 0.5) and Ca₃Ir₃Sn₁₃ (3, 1.5, 0.5), at P = 2.9 [Fig. 2(d)] and P = 0.54 GPa [Fig. 2(e)], respectively. Figs. 2(d)-(f) are representative of the behavior at all pressure range measured for the (Sr,Ca)₃Ir₃Sn₁₃ materials. As a comparison, we show that the temperature dependence of the Bragg (1, 1, 0) reflection for Ca₃Ir₃Sn₁₃ at P = 0.54 GPa [Fig. 2(f)], where no perceivable changes occur as the compound goes through the CDW transition.

The temperature dependence of the integrated intensity of the superlattice reflection is proportional to the temperature dependence of the CDW order parameter. In this way, one may use the power law I ≈ (1 − T/T_{CDW})^{2β} to obtain the CDW order parameter critical exponent β. This analysis is depicted in Fig. 3 for Lu(Pt₁₋ᵡPdₓ)₂In as a function of chemical substitution [Fig. 3(a)], and for Sr₃Ir₃Sn₁₃ [Fig. 3(b)] and Ca₃Ir₃Sn₁₃ [Fig. 3(c)] against pressure. One can observe that in Sr₃Ir₃Sn₁₃ the curve shape does not change by increasing pressure. In contrast, for Lu(Pt₁₋ᵡPdₓ)₂In and Ca₃Ir₃Sn₁₃ a clear modification of the temperature dependence of the integrated intensity occurs as a function of chemical doping and pressure, respectively, thus affecting β as it will be discussed later. These results were obtained on warming the samples through the CDW/superlattice transition. We have, in addition, performed measurements on cooling for all samples and no appreciable thermal hysteresis, within the instrument resolution, was observed, implying that the CDW phase transition remains second-order as T_{CDW} → 0.

With T_{CDW} and CDW order parameter critical exponent extracted from the analysis presented in Fig. 3 we construct the phase diagram shown in Fig. 4. Here we present our x-ray diffraction investigation on both Lu(Pt₁₋ᵡPdₓ)₂In and (Sr,Ca)₃Ir₃Sn₁₃ cubic compounds. For Lu(Pt₁₋ᵡPdₓ)₂In, T_{CDW} is driven to zero by chemical substitution, by changing the Pd content. While for (Sr,Ca)₃Ir₃Sn₁₃, the non-thermal control parameter r is pressure. In this sense, we have normalized r of both systems by its value when T_{CDW} = 0, which were extracted from the linear fittings of the phase diagram in Fig. 4(a). The quantum critical points were estimated as being, respectively, x_c ≈ 0.61 (Pd content) and P_c ≈ 1.55 GPa. At P = 0 the Sr₃Ir₃Sn₁₃ parent compound represents a negative pressure of P = −5.2 GPa

Thus, the ratio r/r_c measures the distance to where T_{CDW} = 0 for both systems. Within the studied pressure range of Sr₃Ir₃Sn₁₃, T_{CDW} is still very far from where it vanishes, so that the CDW order parameter critical expo-
The question whether the suppression of $T_{\text{CDW}}$ in Lu(Pt$_{1-x}$Pd$_x$)$_2$In by chemical doping and Sr$_{3-x}$Ca$_x$Ir$_4$Sn$_{13}$ under pressure is in fact driving these systems to QCP can now be addressed. As both systems approach $T_{\text{CDW}} \to 0$ the CDW modulation order parameter critical exponent systematically increases to its the mean-field result $\beta \sim 0.3$ to the mean field result $\beta \sim 0.5$ for $d_{eff} = (d + z) \geq 4$ is clearly observed in Fig. 4. This indicates the presence of quantum fluctuations due to a quantum phase transition at the QCP ($r_c$), which are effectively increasing the spatial dimensionality. While we were not able to follow $T_{\text{CDW}}$ down to very low temperatures, the increase in the effective dimensionality promotes a quantum-to-classical crossover in the vicinity of the QCP that already sets in at appreciable temperatures [23]. By mapping the CDW order parameter critical exponent through a quantum phase transition, one has a more reliable thermodynamic parameter to attest the dominance of quantum fluctuations. It is yet to be studied the role of these quantum fluctuations on the superconducting state in these compounds and if indeed the presence of a QCP enhances $T_c$. Nevertheless, we clearly show compelling evidence that a quantum phase transition is present in Lu(Pt$_{1-x}$Pd$_x$)$_2$In and Sr$_{3-x}$Ca$_x$Ir$_4$Sn$_{13}$ systems.

In summary, we have studied two cubic superconducting intermetallic systems Lu(Pt$_{1-x}$Pd$_x$)$_2$In and Sr$_{3-x}$Ca$_x$Ir$_4$Sn$_{13}$, which present a vanishing CDW transition, under chemical doping and pressure, respectively. For both systems we were able to determine the presence of quantum fluctuations due to a QCP at $T_{\text{CDW}} = 0$, by following the CDW order parameter critical exponent as function of the control parameter. This approach can be used to explore other CDW/superconducting compounds, such as Sr$_{3-x}$Ca$_x$Rh$_4$Sn$_{13}$ [13] and R$_2$T$_3$X$_5$ (R = rare-earth elements; T = transition metal, and X = s-p metal) [20], and test whether the suppression of $T_{\text{CDW}}$ leads to a quantum phase transition. The experimental study of quantum criticality would be strengthened by probing directly the order parameter in order to gain insights if quantum fluctuations are truly playing some role to the physical observables/phenomena being seen.

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