

Non-Magnetic Quantum Impurities and Resultant Two-Channel Kondo Effect in $\text{ZrAs}_{1.58}\text{Se}_{0.39}$

Tomasz Cichorek¹, Lukasz Bochenek¹, Andreas Czulucki, Marcus Schmidt, Rainer Niewa², Gudrun Auffermann, Yurii Prots, Ryszard Wawryk¹, Michael Baenitz, Frank Steglich, and Rüdiger Kniep

Many intriguing problems in condensed matter physics may occur if a finite, strongly interacting quantum mechanical system couples to a weakly interacting extended one [1]. A prominent example is the single Kondo impurity in a metallic environment with internal degrees of freedom, e.g., due to an effective spin $S = \frac{1}{2}$ (in units of \hbar). Such a spin- $\frac{1}{2}$ impurity is a well-known realization of a quantum impurity often called a *two-level system* (TLS). However, two-state quantum systems can also arise from a non-magnetic origin like, e.g., interstitial hydrogen [2]. Due to their low mass, interstitial hydrogen atoms or their isotopes may exhibit a marked quantum transport over two or more interstitial sites separated by a barrier being much higher than its thermal energy. Similar physics governs tunneling centers derived from structural disorder. Here, a particle with the mass m tunnels between two metastable states separated by the spatial distance, d , in the double-well potential characterized by the barrier height, V . In the case of symmetrical TLSs (twofold degeneracy) the energy difference between the two eigenstates is equal to the coupling between the equivalent states, which *exponentially decreases* with the tunneling parameter λ . The latter can be written in terms of the potential parameters as

$$\lambda = d \sqrt{\frac{2mV}{\hbar^2}} .$$

For example, for an atom with moderate atomic weight, such as arsenic, $m = 74.92 \text{ g mol}^{-1}$ ($^{12}\text{C} = 12.00 \text{ g mol}^{-1}$), crossing a barrier $V = 1 \text{ eV}$ over a distance $d = 0.2 \text{ \AA}$ (typical parameters of structural TLS) one obtains $\lambda \approx 40$. Even for hydrogen jumping between interstitial sites separated by $d = 1 \text{ \AA}$, one still anticipates a large value of $\lambda \approx 23$ for the same barrier height of $V = 1 \text{ eV}$.

It was already proposed [3–5] that the dichotomy between extended and localized states may lead to a two-channel Kondo (2CK) effect if itinerant electrons interact with a twofold degenerate tunneling center. In this Kondo problem, only spherical har-

monics ($l = 0, m = 0$ and $l = 1, m = 0$) of the conduction electrons are relevant for the specific scattering process. As a consequence, the spin of the conduction electrons plays the role of a silent channel index and is unaffected by spin splitting in the presence of an applied magnetic field. In other words, the 2CK effect derived from structural TLSs is an intriguing, non-magnetic alternative to the spin- $\frac{1}{2}$ Kondo effect. Since this is essentially a one-impurity Kondo problem, a considerably stronger effect on the transport properties rather than on the thermodynamic ones is anticipated [6]. Nevertheless, it is still debatable whether the 2CK effect due to structural TLSs can be experimentally achieved or not [7–11]. Indeed, in its strong-coupling regime both the temperature and the level splitting cannot exceed the Kondo temperature, T_K . Since m is large for a “conventional” tunneling particle, one obtains $\lambda \gg 1$ even for relatively low barriers, a fact that implies T_K as small as $10^{-3} \text{ K} - 10^{-2} \text{ K}$. This suggests the possible realization of a strong-coupling 2CK fixed point in metals with non-magnetic TLSs whose potential parameters yield $\lambda \approx 1$.

Previous investigations on ThAsSe (nominal composition) single crystals revealed an extra, magnetic-field-independent $-AT^{1/2}$ term in the low-temperature electrical resistivity $\rho(T)$ – a hallmark of the 2CK effect [12]. Additionally, both the thermal conductivity and the specific heat showed a glass-like temperature dependence which signifies the presence of tunneling states. Successive investigations of closely related Zr- and Hf-based compounds have demonstrated the universality of a B -independent $-AT^{1/2}$ behavior for $M\text{-As-Se}$ ($M = \text{Zr, Hf, Th}$) phases crystallizing in the PbFCl type of structure [13,14]. Additionally, for the Zr–As–Se system, it turned out that the homogeneity range is very narrow with a minimal deviation from the composition $\text{Zr}(\text{As,Se})_2$ (ZrAs_xSe_y ; $1.38(1) \leq x \leq 1.65(1)$, $0.32(1) \leq y \leq 0.61(1)$, $x + y \leq 2$). Finally, very recent neutron diffraction experiments performed on a $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ single crystal unambigu-

ously gave evidence for the As–Se distribution in the PbFCl type crystal structure: With respect to the crystallographic sites As ($2a$) and Se ($2c$), the latter one is occupied by both As and Se, and the former one is occupied by As only, *along with a significant amount of vacancies* [15].

These observations lead to questions about the nature of potential quantum defects in metallic arsenide selenides: Are the tunneling centers triggered by empty sites in the As ($2a$) layers or by mixed occupation of the $2c$ sites with arsenic and selenium? Would T_K of the order of a few K be an obvious consequence of non-local oscillations of the chemical bonds, as previously suggested in [12]. However, prior to an estimation of relevant potential parameters, one must unambiguously exclude a possible impact of enhanced electron-electron interactions (EEI). Indeed, besides the 2CK effect, three-dimensional (3D) EEI are the only known phenomena that can also result in a magnetic-field-independent $-AT^{1/2}$ correction to the resistivity in disordered conductors. This may happen if the electron screening is strongly reduced yielding the unique case of a screened Coulomb interaction parameter, F , very close or even equal to zero [16]. As a consequence, only the field-independent singlet ($l = 0, m = 0$) term would determine the low $-T \cdot \rho(T)$ behavior resulting from the EEI, even in the high-field limit $g\mu_B H > k_B T$ [17]. To resolve these problems, we performed a comparative study on the closely related phases $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ (3 at.% of vacancies within the monoatomic As layer) and $\text{ZrP}_{1.54}\text{S}_{0.46}$ ($2a$ site fully occupied with P).

Starting from microcrystalline powders, the Zr–P–S single crystals were grown by an exothermal Chemical Transport Reaction applying a temperature gradient from 875 °C (source) to 975 °C (sink) and using iodine as transport agent. The chemical composition of a selected crystal was determined by wavelength dispersive X-ray spectroscopy (WDXS, Cameca SX 100) to $\text{Zr}_{1.000(4)}\text{P}_{1.543(5)}\text{S}_{0.460(4)}$. Other crystals from the same batch were characterized by chemical analyses (ICP–OES, Vista RL, Varian) to $\text{Zr}_{1.00(2)}\text{P}_{1.56(1)}\text{S}_{0.461(4)}$ (normalized to Zr), respectively. The variation of the chemical composition within these datasets is below 0.5 wt.% for Zr, P, and S. The ternary phase crystallizes in the PbFCl structure type with similar structural features as previously reported for $\text{ZrAs}_{1.4}\text{Se}_{0.5}$, $\text{ZrAs}_{1.6}\text{Te}_{0.4}$ [18]

and $\text{HfAs}_{1.7}\text{Se}_{0.2}$. The crystal structure contains square planar phosphorus nets (Wyckhoff site $2a$) without detectable indications for vacancies.

Replacement of As and Se by P and S (i.e., by the lightest homologue of the pnictogen and chalcogen families) does not result in distinctly different basic physical properties of $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ and $\text{ZrP}_{1.54}\text{S}_{0.46}$. In fact, differences in the metallic-like behavior of $\rho(T)$ are of minor significance only, as depicted in Figure 1. For the As-based system, the c axis residual resistivity ρ_0 amounts to about 500 $\mu\Omega\text{cm}$. For the P-based system, we found a lower value of $\rho_0 = 270 (\pm 40) \mu\Omega\text{cm}$ and a residual resistivity ratio $\text{RRR} = 1.65$, slightly larger with respect to $\text{RRR} \approx 1.1$ for $\text{ZrAs}_{1.58}\text{Se}_{0.39}$. These observations point to a somewhat smaller structural disorder in the former system, as naturally expected for a compound with full occupancy of the square-planar layer by pnictogen atoms. Additionally, for both zirconium pnictide chalcogenides, a steep drop of $\rho(T)$ at the lowest temperatures signals a superconducting phase transition at $T_c \approx 0.14$ K ($\text{ZrAs}_{1.58}\text{Se}_{0.39}$) and 3.5 K ($\text{ZrP}_{1.54}\text{S}_{0.46}$). However, a zero value of the resistivity was found only far below the onset temperature (see the inset of Fig. 1). The complex behavior of the resistivity data in the vicinity of the superconducting transition for all samples investigated can be tentatively ascribed to

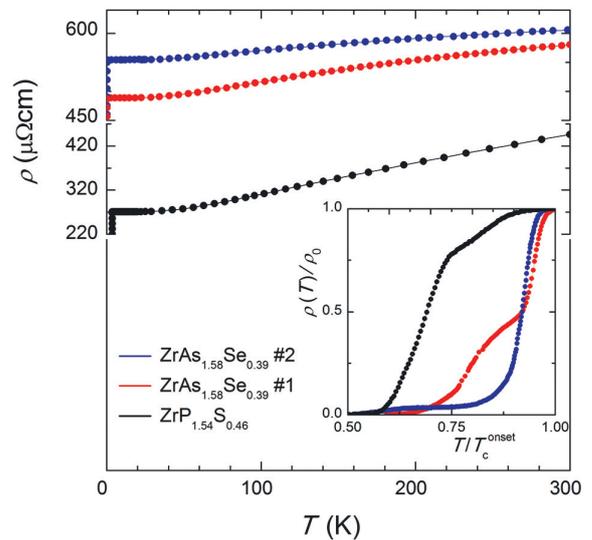


Fig. 1: Temperature dependence of the electrical resistivity along the c axis of $\text{ZrP}_{1.54}\text{S}_{0.46}$ and of $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ (for the latter, the two specimens were cut off from the same single crystal). Inset: The same results but with focus on the vicinity of the superconducting transition, plotted as $\rho(T)/\rho_0$ vs. T/T_c^{onset} . For clarity, the $\rho(T)$ data for the P-based system were multiplied by a factor of 5.

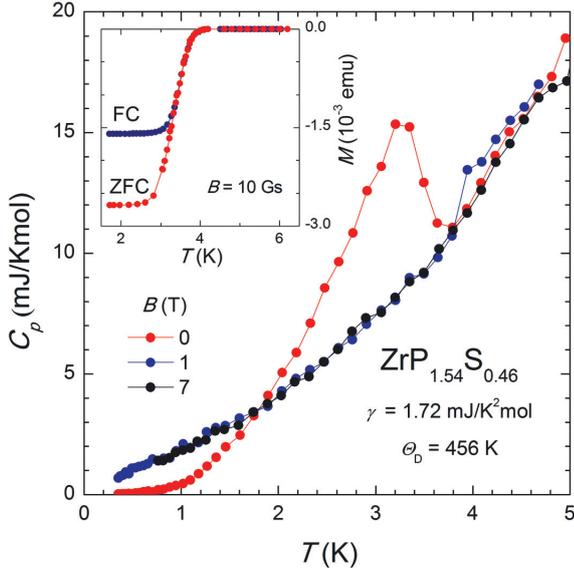


Fig. 2: Temperature dependence of the specific heat of the $\text{ZrP}_{1.54}\text{S}_{0.46}$ single crystal measured in zero and overcritical magnetic fields. Inset: Zero-field-cooled (ZFC) and field-cooled (FC) magnetization as a function of temperature for the same $\text{ZrP}_{1.54}\text{S}_{0.46}$ sample.

a delicate variation of the chemical composition, i.e., below 0.5 wt. % which is the resolution limit of our analyses. Most likely, such chemical inhomogeneities are also responsible for the slight sample dependence observed in the $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ system, for which two specimens had been cut off from the same part of a large single crystal used for neutron diffraction experiments.

In order to determine the Meissner volume in $\text{ZrP}_{1.54}\text{S}_{0.46}$, magnetization experiments were performed. The inset of Figure 2 displays the zero-field-cooled (ZFC) and field-cooled (FC) magnetization data. If we assume that the ZFC data show the complete diamagnetic shielding below $T_c \approx 3.5$ K, we conclude from the FC results a volume of about 60% of the sample was in the Meissner-Ochsenfeld state at these temperatures. Further evidence for bulk superconductivity in $\text{ZrP}_{1.54}\text{S}_{0.46}$ is provided by the sizeable specific heat jump at $T_c \approx 3.5$ K in $B = 0$ (Fig. 2). The small mass of 0.2 mg and the low value of T_c have yet prevented such detailed low-temperature volume-sensitive experiments on $\text{ZrAs}_{1.58}\text{Se}_{0.39}$. Nevertheless, their thermodynamic properties are very similar, as highlighted by the same value of the Sommerfeld coefficient of the electronic specific heat $\gamma = 1.7 (\pm 0.1) \text{ mJ K}^{-2} \text{ mol}^{-1}$. This is further corroborated by similar Debye temperatures $\Theta_D = 355$ K and 456 K for

$\text{ZrAs}_{1.58}\text{Se}_{0.39}$ and $\text{ZrP}_{1.54}\text{S}_{0.46}$, respectively, in accord with the mass difference of the two systems.

For structurally disordered materials such as $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ and $\text{ZrP}_{1.54}\text{S}_{0.46}$, the disorder parameter can be calculated from the free-electron formula $(k_F l_e)^{-1} = \hbar 3 m_e D^{-1}$, where D is the electron diffusion constant. Along the c axis direction, we estimated $D \approx 1.0$ and $1.9 \text{ cm}^2 \text{ s}^{-1}$ for the As- and P-based systems, respectively. Here, we used the Einstein relation,

$$D = \frac{1}{e^2 N(E_F) \rho_0} = \frac{1}{3} \left(\frac{\pi k_B}{e} \right)^2 \frac{1}{\gamma \rho_0}$$

where $N(E_F)$ is the density of states at the Fermi level calculated from the electronic specific heat and ρ_0 is the residual resistivity. Within this formalism we obtained $(k_F l_e)^{-1} \approx 0.37$ ($\text{ZrAs}_{1.58}\text{Se}_{0.39}$) and 0.21 ($\text{ZrP}_{1.54}\text{S}_{0.46}$) which again points to a similar, but somewhat less pronounced structural disorder in the free-of-vacancies phase.

Having established a far-reaching similarity of the main physical properties of $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ and $\text{ZrP}_{1.54}\text{S}_{0.46}$, we now turn to a discussion of their normal-state electronic transport properties at low temperatures at which an additional contribution to $\rho(T)$ emerges. Details are shown in Figure 3: Here, we plotted the relative change of the resistivity normalized to the minimum value, $(\rho - \rho_{\min})/\rho_{\min}$ as a function of $T^{1/2}$. The zero-field $\rho(T)$ data for $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ (#2) and the resistivity of $\text{ZrP}_{1.54}\text{S}_{0.46}$ (obtained at an overcritical magnetic field, $B = 1$ T [19]) exhibit a very similar temperature dependence. Below a broad minimum at $T_{\min} \approx 15.0$ K [$\text{ZrAs}_{1.58}\text{Se}_{0.39}$ (#2)] and 8.5 K ($\text{ZrP}_{1.54}\text{S}_{0.46}$), the resistivity depends strictly linearly on $T^{1/2}$ in a wide temperature range, i.e., down to the vicinity of the superconducting transition temperature. The A coefficient in the extra $-AT^{1/2}$ term amounts to $0.167 \mu\Omega \text{ cm/K}^{1/2}$ and $0.038 \mu\Omega \text{ cm/K}^{1/2}$ for the As- and P-based samples, respectively. We emphasize that a magnetic field of $B = 14$ T, which is the largest field accessible in our experiment, does not alter the square-root temperature dependence of the resistivity for the phase with vacancies in the mono-atomic pnictide layer. The same behavior of the low- T electrical resistivity, i.e., the magnetic-field-independent $-AT^{1/2}$ term, was found in all M -As-Se single crystals. Moreover, this behavior is independent of both the crystallographic orientation and the superconducting properties. In striking contrast are the resistivity data of the free-of-vacancies phase $\text{ZrP}_{1.54}\text{S}_{0.46}$.

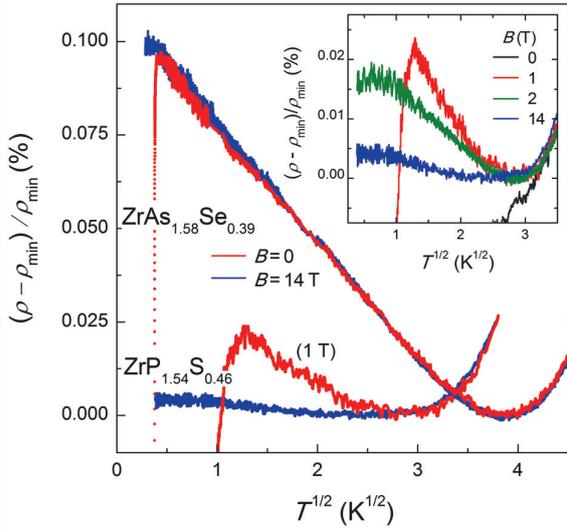


Fig. 3: Qualitatively different effects of magnetic fields on the low-temperature electrical resistivities as $(\rho - \rho_{\min})/\rho_{\min}$ vs. $T^{1/2}$ for $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ and $\text{ZrP}_{1.54}\text{S}_{0.46}$, i.e., for systems with and without vacancies in the pnictogen layers. Inset: Suppression of the square-root temperature dependence of the resistivity for $\text{ZrP}_{1.54}\text{S}_{0.46}$ in varying magnetic fields applied along the a axis direction.

Clearly, the $-AT^{1/2}$ term displays a completely different response to an applied field. For $B = 14$ T, the low- T upturn is strongly suppressed, as evidenced by an order-of-magnitude smaller value, $A \approx 0.005 \mu\Omega\text{cm} (\text{K}^{1/2})^{-1}$. The inset of Figure 3 provides more insight into the resistivity vs. temperature curves measured in various fields $B \leq 14$ T. These observations yield striking evidence for *entirely* different phenomena occurring in the material without ($\text{ZrAs}_{1.58}\text{Se}_{0.39}$) and with ($\text{ZrP}_{1.54}\text{S}_{0.46}$) a full occupancy of the square-planar pnictogen layers. While the B -independent $-AT^{1/2}$ term, formed for the former material, is expected for a 2CK problem derived from isolated doubly degenerate non-magnetic quantum impurities, the very strong field dependence of $\rho(T)$ for the latter system points to considerable 3D quantum interference effects and superconducting fluctuations. Most importantly, however, electron-electron interactions in the spin-singlet channel are apparently negligible in the M - Pn - Q ($Pn = \text{P, As}$; $Q = \text{S, Se}$) single crystals investigated. This can be concluded from the $B = 14$ T upturn in $\text{ZrP}_{1.54}\text{S}_{0.46}$ with it about 18 times smaller than the expected $(\rho - \rho_{\min})/\rho_{\min}$ correction due to the EEI in magnetic fields. Apparently, the latter are sufficiently large, such that the field-induced spin splitting becomes comparable to $k_B T$.

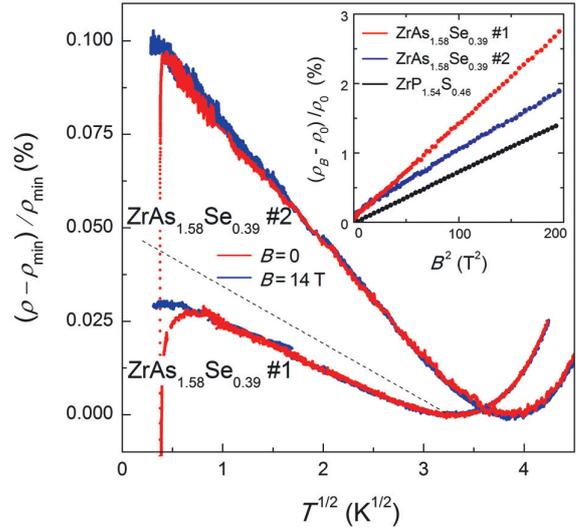


Fig. 4: Remarkable differences of the low-temperature electrical resistivity plotted as $(\rho - \rho_{\min})/\rho_{\min}$ vs. $T^{1/2}$ for two single-crystalline $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ specimens with similar residual resistivity. The dashed line shows the magnitude of a hypothetical correction to $\rho(T)$ for the sample #2, as discussed in the text. Inset: Transverse magnetic field dependencies of the electrical resistivities for $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ and $\text{ZrP}_{1.54}\text{S}_{0.46}$ at liquid-helium temperature. For clarity, the magnetoresistivity of $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ was multiplied by a factor of 10.

Independent arguments which additionally rule out any significant impact of the EEI on the low-temperature charge transport in M - As - Se are provided by a comparison of the $(\rho - \rho_{\min})/\rho_{\min}$ dependencies obtained for two $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ specimens. As inferred from $\rho_0 = 490(\pm 40) \mu\Omega\text{cm}$ for the sample #1 and $550(\pm 40) \mu\Omega\text{cm}$ for the sample #2 (see Fig. 1), similar elastic relaxation times can be assumed for the two samples. In spite of this, the magnitude of the magnetic-field-insensitive $-AT^{1/2}$ term differs by more than a factor of 3. These experimental observations, displayed in Figure 4, are at strong variance to the expectation of enhanced EEI in specimens of the same disordered metal [16]. Indeed, since the chemical composition of the two samples does not vary by more than 0.5 wt.%, one expects a very similar electronic structure. In other words, an anticipated correction to the resistivity due to the EEI has to be calculated under the assumption of a nearly identical interaction parameter F [16,20,21]. In such a case of a sample-independent F , the magnitude of a hypothetical $(\rho - \rho_{\min})/\rho_{\min}$ anomaly would only vary with $\rho_0 D^{-1/2} \propto \rho_0^{3/2}$ in any disordered metal. This, however, is in a striking contrast to our exper-

imental observation on $\text{ZrAs}_{1.58}\text{Se}_{0.39}$. In fact, a supposed $-AT^{1/2}$ term, estimated for sample #2 on the basis of the value of the A-coefficient of sample #1 would be substantially smaller than what is experimentally found for sample #2, see dashed line in Fig. 4. (We note that $F = 0$ was assumed in our calculations.) Finally, to provide further support to the accuracy of our estimates of the residual resistivity are accurate, the isothermal response of the resistivity to a magnetic field was studied by taking advantage of the fact that the magnetoresistivity [$\text{MR} = (\rho - \rho_0)/\rho_0$] is a dimensionless relaxation-time-dependent quantity. The MR data, obtained at $T = 4.2$ K, are depicted in the inset of Figure 4. Neither any temperature dependence nor any deviation from the B^2 behavior was observed in the temperature range 0.15 K – 15 K and for $B \geq 1$ T. From the differences in the $\text{MR} \propto (1/\rho_0)^2$, e.g., 40% at $B = 14$ T, one can estimate ρ_0 of sample #2 to exceed ρ_0 of sample #1 by about 18% [22]. This estimate, being in satisfactory agreement with the 12% difference between the measured ρ_0 values, leads to minor changes in the hypothetical $(\rho - \rho_{\min})/\rho_{\min}$ anomaly and, hence, provides further support to a novel scattering mechanism which we relate to a random distribution of non-magnetic quantum impurities in the $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ single crystal.

The results presented in this contribution are obviously associated with the occurrence of non-magnetic quantum impurities within those layers in $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ that are exclusively formed by As, since the absence of a significant number of such defects in the closely related $\text{ZrP}_{1.54}\text{S}_{0.46}$ phase leads to a fundamentally different physical behavior. We, therefore, propose that the formation of tunneling centers in the pnictogen layer with vacancies is triggered by non-local oscillations of the As-As chemical bonds. This suggests that an electron rather than an atom (as usually assumed) plays the role of the tunneling particle. Taking advantage of the theoretical calculations of the atomization energy per atom, AE , for As_n clusters, i.e., the energy required to break the As_n molecule completely into its component atoms [23], one can estimate the tunneling exponent λ for $M\text{-As-Se}$ phase: For example, in the case of an As_4 tetramer, characterized by $AE = 2.68$ eV and the bond length $d_0 = 2.46$ Å, one obtains λ as small as 1.5, providing an opportunity to approach a strong-coupling 2CK fixed point at experimentally accessible temperature. (Here we

assumed $V = AE$ and $d = \frac{1}{2}d_0$.) Obviously, a substantially smaller value of the tunneling exponent compared to the one for “conventional” potential parameters ($\lambda \gg 1$), is a natural consequence of the electron mass being smaller than atomic masses by about 4 orders of magnitude. In other words, we suppose that a non-magnetic 2CK effect in $\text{ZrAs}_{1.58}\text{Se}_{0.39}$ and other $M\text{-As-Se}$ phases originates from a two-state quantum system formed by non-local oscillations of the As-As chemical bonds.

References

- [1] Q. Si and F. Steglich, *Science* **329** (2010) 1161.
- [2] P. Esquinazi and R. König, „Tunneling Systems in Amorphous and Crystalline Solids“, Springer Verlag, Berlin (1998).
- [3] R. W. Cochrane et al., *Phys. Rev. Lett.* **35** (1975) 677.
- [4] J. Kondo, *Physica (Utrecht)* **84B** (1976) 40.
- [5] A. Zawadowski, *Phys. Rev. Lett.* **45** (1980) 211.
- [6] See, for a review, D. L. Cox and A. Zawadowski, *Adv. Phys.* **47** (1998) 599.
- [7] I. L. Aleiner et al., *Phys. Rev. Lett.* **86** (2001) 2629.
- [8] I. L. Aleiner and D. Controzzi, *Phys. Rev. B* **66** (2002) 045107.
- [9] G. Zarand, *Phys. Rev. B* **75** (2007) 045129.
- [10] M. Arnold et al., *Phys. Rev. Lett.* **99** (2007) 186601.
- [11] Ch. Kolf and J. Kroha, *Phys. Rev. B* **75** (2007) 045129.
- [12] T. Cichorek et al., *Phys. Rev. Lett.* **94** (2005) 236603.
- [13] M. Schmidt et al., *J. Phys.: Condens. Matter* **17** (2005) 5481.
- [14] A. Czulucki et al., *ChemPhysChem* **11** (2010) 2639.
- [15] R. Niewa et al., *J. Solid. State Chem.* **183** (2010) 1309.
- [16] P. A. Lee and T. V. Ramakrishnan, *Rev. Mod. Phys.* **57** (1985) 287.
- [17] Note that even in the case of $F \approx 0.1$, application of $B = 14$ T will lead to a detectable resistivity change due to an additional contribution of the field-dependent triplet ($l = 1, m = \pm 1$) terms.
- [18] A. Schlechte et al., *Sci. Techn. Adv. Mater.* **8** (2007) 341.
- [19] In $B = 1$ T, a total drop of the resistivity does not exceed 1 % and is obviously caused by surface effects.
- [20] W. B. Jian et al. *Phys. Rev. B* **54** (1996) 4289.
- [21] S. M. Huang et al. *Phys. Rev. Lett.* **99** (2007) 046601.
- [22] Also for $\text{ZrP}_{1.54}\text{S}_{0.46}$, we observed the “classical” B^2 dependence of the MR which is two orders of magnitude larger than an anticipated MR due to the EEI (see the inset of Fig. 4).
- [23] J. Zhao et al. *Phys. Rev. B* **73** (2006) 115418.

¹ Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland

² Institute for Inorganic Chemistry, University of Stuttgart, Germany